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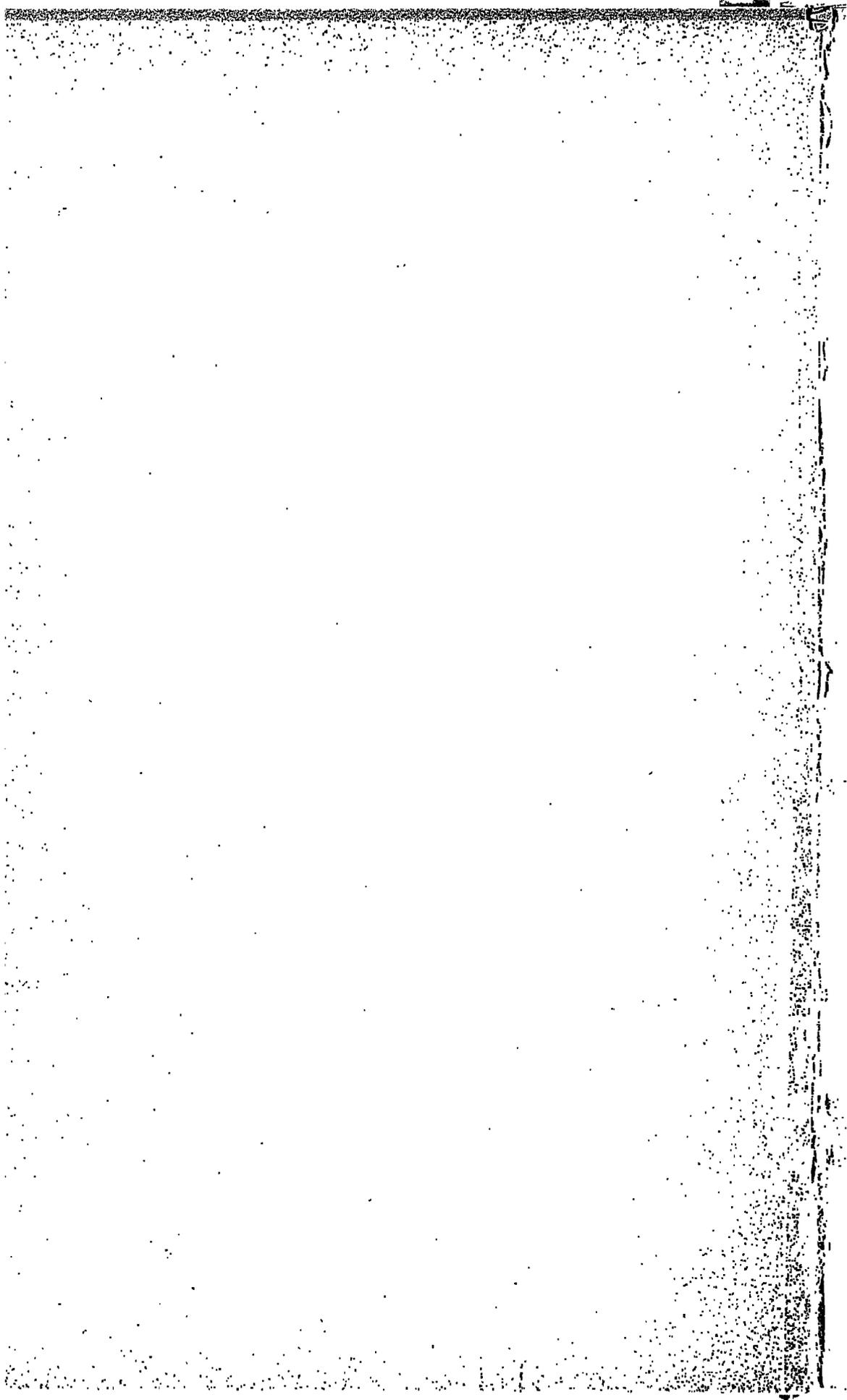
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KONINKLIJKE AKADEMIE
VAN WETENSCHAPPEN
-- TE AMSTERDAM --

PROCEEDINGS OF THE
SECTION OF SCIENCES

VOLUME XX
— (1ST PART) —
— (N^o. 1—5) —

JOHANNES MÜLLER :—: AMSTERDAM
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Natuurkundige Afdeling Dl. XXIV, XXV and XXVI).

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

VOLUME XX

N^o. 1.

President: Prof. H. A. LORENTZ.
Secretary: Prof. P. ZEEMAN.

(Translated from: "Verslag van de gewone vergaderingen der Wis- en
Natuurkundige Afdeling," Vol. XXIV, XXV and XXVI).

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Proceedings Royal Acad. Amsterdam. Vol. XX.

Physics. — “On EINSTEIN’S *Theory of gravitation*”. III. By Prof.
H. A. LORENTZ.

(Communicated in the meeting of April 1916.)¹⁾

§ 32. In the two preceding papers²⁾ we have tried so far as possible to present the fundamental principles of the new gravitation theory in a simple form.

We shall now show how EINSTEIN’S differential equations for the gravitation field can be derived from HAMILTON’S principle. In this connexion we shall also have to consider the energy, the stresses, momenta and energy-currents in that field.

We shall again introduce the quantities g_{ab} formerly used and we shall also use the “inverse” system of quantities for which we shall now write g^{ab} . It is found useful to introduce besides these the quantities

$$g^{ab} = \sqrt{-g} g^{ab}.$$

Differential coefficients of all these variables with respect to the coordinates will be represented by the indices belonging to these latter, e.g.

$$g_{ab,p} = \frac{\partial g_{ab}}{\partial x_p}, \quad g_{ab,pq} = \frac{\partial^2 g_{ab}}{\partial x_q \partial x_p}.$$

We shall use CHRISTOFFEL’S symbols

$$\left[\begin{array}{cc} a & b \\ & c \end{array} \right] = \frac{1}{2} (g_{ac,b} + g_{bc,a} - g_{ab,c})$$

and RIEMANN’S symbol

$$(ik, lm) = \frac{1}{2} (g_{im,kl} + g_{kl,im} - g_{il,km} - g_{km,il}) + \\ + \sum (ab) g^{ab} \left\{ \left[\begin{array}{cc} i & m \\ a & b \end{array} \right] \left[\begin{array}{cc} k & l \\ & b \end{array} \right] - \left[\begin{array}{cc} i & l \\ a & b \end{array} \right] \left[\begin{array}{cc} k & m \\ & b \end{array} \right] \right\}.$$

Further we put

$$G_{im} = \sum (kl) g^{kl} (ik, lm). \quad \dots \dots \dots (40)$$

$$G = \sum (im) g^{im} G_{im} \quad \dots \dots \dots (41)$$

This latter quantity is a measure for the curvature of the field-figure. The principal function of the gravitation field is

¹⁾ Published September 1916, a revision having been found desirable.

²⁾ See Proceedings Vol. XIX, p. 1341 and 1354.

$$\frac{1}{2\kappa} \int Q dS,$$

where

$$Q = \sqrt{-g} G.$$

In the integral dS , the element of the field-figure, is expressed in x -units. The integration has to be extended over the domain within a certain closed surface σ ; κ is a positive constant.

§ 33. When we pass from the system of coordinates x_1, \dots, x_4 to another, the value of G proves to remain unaltered, it is a scalar quantity. This may be verified by first proving that the quantities (ik, lm) form a covariant tensor of the fourth order¹⁾. Next, (g^{kl}) being a contravariant tensor of the second order²⁾, we can deduce from (40) that (G_{im}) is a covariant tensor of the same order³⁾. According to (41) G is then a scalar. The same is true⁴⁾ for $Q dS$.

We remark that $g_{ba} = g_{ab}$ ⁵⁾ and $g_{ab,fe} = g_{ab,ef}$. We shall suppose Q to be written in such a way that its form is not altered by interchanging g_{ba} and g_{ab} or $g_{ab,fe}$ and $g_{ab,ef}$. If originally this condition is not fulfilled it is easy to pass to a "symmetrical" form of this kind.

It is clear that Q may also be expressed in the quantities g^{ab} and their first and second derivatives and in the same way in the g^{ab} 's and first and second derivatives of these quantities.

If the necessary substitutions are executed with due care, these new forms of Q will also be symmetrical.

§ 34. We shall first express the quantity Q in the g_{ab} 's and their

¹⁾ This means that the transformation formulae for these quantities have the form

$$(ik, lm)' = \sum (abce) p_{ai} p_{bk} p_{cl} p_{em} (ab, ce)$$

See for the notations used here and for some others to be used later on my communication in Zittingsverslag Akad. Amsterdam **23** (1915), p. 1073 (translated in Proceedings Amsterdam **19** (1916), p. 751). In referring to the equations and the articles of this paper I shall add the indication 1915.

²⁾ Namely:

$$g'^{kl} = \sum (ab) \pi_{ak} \pi_{bl} g^{ab}.$$

The symbol (g^{kl}) denotes the complex of all the quantities g^{kl} .

³⁾ Namely:

$$G'_{im} = \sum (ab) p_{ai} p_{bm} G_{ab}.$$

⁴⁾ On account of the relation

$$\sqrt{-g'} dS' = \sqrt{-g} dS.$$

⁵⁾ Similarly:

$$g^{ba} = g^{ab}, g^{ba} = g^{ab}$$

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derivatives and we shall determine the variation it undergoes by arbitrarily chosen variations δg_{ab} , these latter being continuous functions of the coordinates. We have evidently

$$\delta Q = \Sigma(ab) \frac{\partial Q}{\partial g_{ab}} \delta g_{ab} + \Sigma(abe) \frac{\partial Q}{\partial g_{ab,e}} \delta g_{ab,e} + \Sigma(abef) \frac{\partial Q}{\partial g_{ab,ef}} \delta g_{ab,ef}.$$

By means of the equations

$$\delta g_{ab,ef} = \frac{\partial}{\partial x_f} \delta g_{ab,e} \quad \text{and} \quad \delta g_{ab,e} = \frac{\partial}{\partial x_e} \delta g_{ab}$$

this may be decomposed into two parts

$$\delta Q = \sigma_1 Q + \sigma_2 Q, \quad \dots \dots \dots (42)$$

namely

$$\sigma_1 Q = \Sigma(ab) \left\{ \frac{\partial Q}{\partial g_{ab}} - \Sigma(e) \frac{\partial}{\partial x_e} \frac{\partial Q}{\partial g_{ab,e}} + \Sigma(ef) \frac{\partial^2}{\partial x_e \partial x_f} \frac{\partial Q}{\partial g_{ab,ef}} \right\} \delta g_{ab}. \quad (43)$$

$$\begin{aligned} \sigma_2 Q = & \Sigma(abe) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,e}} \delta g_{ab} \right) + \Sigma(abef) \frac{\partial}{\partial x_f} \left(\frac{\partial Q}{\partial g_{ab,ef}} \delta g_{ab,e} \right) - \\ & - \Sigma(abef) \frac{\partial}{\partial x_e} \left\{ \frac{\partial}{\partial x_f} \left(\frac{\partial Q}{\partial g_{ab,ef}} \right) \delta g_{ab} \right\} \dots \dots \dots (44) \end{aligned}$$

The last equation shows that

$$\int \sigma_2 Q dS = 0 \quad \dots \dots \dots (45)$$

if the variations δg_{ab} and their first derivatives vanish at the boundary of the domain of integration.

§ 35. Equations of the same form may also be found if Q is expressed in one of the two other ways mentioned in § 33. If e.g. we work with the quantities g^{ab} we shall find

$$(\delta Q) = (\sigma_1 Q) + (\sigma_2 Q),$$

where $(\sigma_1 Q)$ and $(\sigma_2 Q)$ are directly found from (43) and (44) by replacing g_{ab} , $g_{ab,e}$, $g_{ab,ef}$, δg_{ab} and $\delta g_{ab,e}$ etc. by g^{ab} , $g^{ab,e}$, etc. If the variations chosen in the two cases correspond to each other we shall have of course

$$(\delta Q) = \delta Q.$$

Moreover we can show that the equalities

$$(\sigma_1 Q) = \sigma_1 Q, \quad (\sigma_2 Q) = \sigma_2 Q,$$

exist separately.¹⁾

¹⁾ Suppose that at the boundary of the domain of integration $\delta g_{ab} = 0$ and $\delta g_{ab,e} = 0$. Then we have also $\delta g^{ab} = 0$ and $\delta g^{ab,e} = 0$, so that

$$\int (\sigma_1 Q) dS = 0, \quad \int \sigma_1 Q dS = 0$$

and from

The decomposition of δQ into two parts is therefore the same, whether we use g_{ab} , g^{ab} or $g^a{}_b$.

It is further of importance that when the system of coordinates is changed, not only $\delta Q dS$ is an invariant, but that this is also the case with $\sigma_1 Q dS$ and $\sigma_2 Q dS$ separately.²⁾

We have therefore

$$\frac{\sigma_1 Q'}{\sqrt{-g'}} = \frac{\sigma_1 Q}{\sqrt{-g}} \dots \dots \dots (46)$$

§ 36. For the calculation of $\sigma_1 Q$ we shall suppose Q to be expressed in the quantities g^{ab} and their derivatives. Therefore (comp. (43))

$$\sigma_1 Q = \Sigma (ab) M_{ab} \delta g^{ab}, \dots \dots \dots (47)$$

if we put

$$M_{ab} = \frac{\partial Q}{\partial g^{ab}} - \Sigma (e) \frac{\partial}{\partial x_e} \frac{\partial Q}{\partial g^{ab,e}} + \Sigma (ef) \frac{\partial^2}{\partial x_e \partial x_f} \frac{\partial Q}{\partial g^{ab,ef}}$$

Now we can show that the quantities M_{ab} are exactly the quantities G_{ab} defined by (40). To this effect we may use the following considerations.

We know that $\left(\frac{1}{\sqrt{-g}} g^{ab}\right)$ is a contravariant tensor of the second

$$\int (\delta Q) dS = \int \delta Q dS$$

we infer

$$\int (\sigma_1 Q) dS = \int \sigma_1 Q dS.$$

As this must hold for every choice of the variations δg_{ab} (by which choice the variations δg^{ab} are determined too) we must have at each point of the field-figure $(\sigma_1 Q) = \sigma_1 Q$

²⁾ This may be made clear by a reasoning similar to that used in the preceding note. We again suppose δg_{ab} and $\delta g_{ab,e}$ to be zero at the boundary of the domain of integration. Then $\delta g'^{ab}$ and $\delta g'^{ab,e}$ vanish too at the boundary, so that

$$\int \sigma_2 Q' dS' = 0, \quad \int \sigma_2 Q dS = 0.$$

From

$$\int \sigma Q' dS' = \int \sigma Q dS$$

we may therefore conclude that

$$\int \sigma_1 Q' dS' = \int \sigma_1 Q dS.$$

As this must hold for arbitrarily chosen variations δg_{ab} we have the equation $\sigma_1 Q' dS' = \sigma_1 Q dS$.

order. From this we can deduce that $\left(\frac{1}{\sqrt{-g}}\delta g^{ab}\right)$ is also such a tensor.

Writing for it ε^{ab} we find according to (46) and (47) that

$$\Sigma (ab) M_{ab} \varepsilon^{ab}$$

is a scalar for every choice of (ε^{ab}) .

This involves that (M_{ab}) is a covariant tensor of the second order and as the same is true for (G_{ab}) we must prove the equation

$$M_{ab} = G_{ab}$$

only for one special choice of coordinates.

§ 37. Now this choice can be made in such a way that at the point P of the field-figure $g_{11} = g_{22} = g_{33} = -1, g_{44} = +1, g_{ab} = 0$ for $a \neq b$ and that moreover all first derivatives $g_{ab,e}$ vanish. If then the values g_{ab} at a point Q near P are developed in series of ascending powers of the differences of coordinates $x_a(Q) - x_a(P)$ the terms directly following the constant ones will be of the second order. It is with these terms that we are concerned in the calculation both of M_{ab} and of G_{ab} for the point P . As in the results the coefficients of these terms occur to the first power only, it is sufficient to show that each of the above mentioned terms separately contributes the same value to M_{ab} and to G_{ab} .

From these considerations we may conclude that

$$\delta_1 Q = \Sigma (ab) G_{ab} \delta g^{ab} \dots \dots \dots (48)$$

Expressions containing instead of δg^{ab} either the variations δg^{ab} or δg_{ab} might be derived from this by using the relations between the different variations. Of these we shall only mention the formula

$$\delta g^{ab} = \frac{1}{\sqrt{-g}} \delta g^{ab} - \frac{g^{ab}}{2\sqrt{-g}} \Sigma (cd) g_{cd} \delta g^{cd} \dots \dots \dots (49)$$

§ 38. In connexion with what precedes we here insert a consideration the purpose of which will be evident later on. Let the infinitely small quantity ξ be an arbitrarily chosen continuous function of the coordinates and let the variations δg_{ab} be defined by the condition that at some point P the quantities g_{ab} have after the change the values which existed before the change at the point Q , to which P is shifted when x_h is diminished by ξ , while the three other coordinates are left constant. Then we have

$$\delta g_{ab} = -g_{ab,h} \xi$$

and similar formulae for the variations δg^{ab} .

If for $\delta_1 Q$ and $\delta_2 Q$ the expressions (48) and (44) are taken, the equation

$$\delta Q - \delta_2 Q = \delta_1 Q \dots \dots \dots (50)$$

is an identity for every choice of the variations.

It will likewise be so in the special case considered and we shall also come to an identity if in (50) the terms with the derivatives of ξ are omitted while those with ξ itself are preserved.

When this is done δQ reduces to

$$-\frac{\partial Q}{\partial x_h} \xi$$

and, taking into consideration (44) and (48), we find after division by ξ

$$-\frac{\partial Q}{\partial x_h} + \sum(ab e) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,e}} g_{ab,h} \right) + \sum(ab e f) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,fe}} g_{ab,fh} \right) - \sum(ab e f) \frac{\partial}{\partial x_e} \left\{ \frac{\partial}{\partial x_f} \left(\frac{\partial Q}{\partial g_{ab,ef}} \right) g_{ab,h} \right\} = -\sum(ab) G_{ab} g^{ab,h} \dots (51)$$

In the second term of (44) we have interchanged here the indices e and f .

If for shortness' sake we put, for $e \neq h$

$$s_h^e = \sum(ab) \frac{\partial Q}{\partial g_{ab,e}} g_{ab,h} + \sum(ab f) \frac{\partial Q}{\partial g_{ab,fe}} g_{ab,fh} - \sum(ab f) \frac{\partial}{\partial x_f} \left(\frac{\partial Q}{\partial g_{ab,ef}} \right) g_{ab,h} \dots (52)$$

and for $e = h$

$$s_h^h = -Q + \sum(ab) \frac{\partial Q}{\partial g_{ab,h}} g_{ab,h} + \sum(ab f) \frac{\partial Q}{\partial g_{ab,fh}} g_{ab,fh} - \sum(ab f) \frac{\partial}{\partial x_f} \left(\frac{\partial Q}{\partial g_{ab,hf}} \right) g_{ab,h} \dots \dots \dots (53)$$

we may write

$$\sum(e) \frac{\partial s_h^e}{\partial x_e} = -\sum(ab) G_{ab} g^{ab,h} \dots \dots \dots (54)$$

The set of quantities s_h^e will be called the *complex s* and the set of the four quantities which stand on the left hand side of (54) in the cases $h = 1, 2, 3, 4$, the *divergency* of the complex.¹⁾ It will be denoted by *div s* and each of the four quantities separately by *div_h s*.

The equation therefore becomes

$$div_h s = -\sum(ab) G_{ab} g^{ab,h} \dots \dots \dots (55)$$

¹⁾ EINSTEIN uses the word "divergency" in a somewhat different sense. It seemed desirable however to have a name for the left hand side of (54) and it was difficult to find a better one.

If we take other coordinates the right hand side of this equation is transformed according to a formula which can be found easily. Hence we can also write down the transformation formula for the left hand side. It is as follows

$$\text{div}'_h \mathfrak{s}' = p \Sigma(m) p_{mh} \text{div}_m \mathfrak{s} - Q \Sigma(a) p_{ah} \frac{\partial p}{\partial x_a} + 2p \Sigma(abc) p_{ahc} g^{bc} G_{ab}. \quad (56)$$

§ 39. We shall now consider a second complex \mathfrak{s}_0 , the components of which are defined by

$$\mathfrak{s}'_{0h} = -G \Sigma(a) g^{ae} g_{ah} + 2 \Sigma(a) g^{ae} G_{ah} \quad . \quad . \quad . \quad (57)$$

Taking also the divergency of this complex we find that the difference

$$\text{div}'_h \mathfrak{s}'_0 - p \Sigma(m) p_{mh} \text{div}_m \mathfrak{s}_0$$

has just the value which we can deduce from (56) for the corresponding difference

$$\text{div}'_h \mathfrak{s}' - p \Sigma(m) p_{mh} \text{div}_m \mathfrak{s}$$

It is thus seen that

$$\text{div}'_h \mathfrak{s}' - \text{div}'_h \mathfrak{s}'_0 = p \Sigma(m) p_{mh} (\text{div}_m \mathfrak{s} - \text{div}_m \mathfrak{s}_0)$$

and that we have therefore

$$\text{div} \mathfrak{s} = \text{div} \mathfrak{s}_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

for all systems of coordinates as soon as this is the case for one system.

Now a direct calculation starting from (52), (53) and (57) teaches us that the terms with the highest derivatives of the quantities g_{ab} , (viz. those of the third order) are the same in $\text{div}_h \mathfrak{s}$ and $\text{div}_h \mathfrak{s}_0$. Further it is evident that in the system of coordinates introduced in § 37 these terms with the third derivatives are the only ones. This proves the general validity of equation (58) It is especially to be noticed that if \mathfrak{s} and \mathfrak{s}_0 are determined by (52), (53) and (57) and if the function defined in § 32 is taken for G , the relation is an identity.

§ 40. We shall now derive the differential equations for the gravitation field, first for the case of an electromagnetic system.¹⁾ For the part of the principal function belonging to it we write

$$\int L dS,$$

where L is defined by (35) (1915). From L we can derive the stresses, the momenta, the energy-current and the energy of the

¹⁾ This has also been done by DE DONDER, Zittingsverslag Akad. Amsterdam, 25 (1916), p. 153.

electromagnetic system; for this purpose we must use the equations (45) and (46) (1915) or in EINSTEIN'S notation, which we shall follow here, ¹⁾

$$\mathfrak{T}_c^c = -L + \sum_{a \neq c} (a) \psi_{ac}^* \psi_{a'c'} \dots \dots \dots (59)$$

and for $b \neq c$

$$\mathfrak{T}_c^b = \sum_{a \neq c} (a) \psi_{ab}^* \psi_{a'c'} \dots \dots \dots (60)$$

The set of quantities \mathfrak{T}_c^b might be called the stress-energy-complex (comp. § 38). As for a change of the system of coordinates the transformation formulae for \mathfrak{T} are similar to those by which tensors are defined, we can also speak of the stress-energy-tensor. We have namely

$$\frac{1}{\sqrt{-g'}} \mathfrak{T}'^b_c = \frac{1}{\sqrt{-g}} \sum (kl) p_{kc} \pi_{lb} \mathfrak{T}_k^l.$$

§ 41. The equations for the gravitation field are now obtained (comp. §§ 13 and 14, 1915) from the condition that

$$\delta_\psi \int L dS + \frac{1}{2\kappa} \delta \int Q dS = 0 \dots \dots (61)$$

for all variations δg_{ab} which vanish at the boundary of the field of integration together with their first derivatives. The index ψ in the first term indicates that in the variation of L the quantities ψ_{ab} must be kept constant.

If we suppose L to be expressed in the quantities g^{ab} and if (42), (45) and (48) are taken into consideration, we find from (61) that at each point of the field-figure

$$\sum (ab) \left(\frac{\partial L}{\partial g^{ab}} \right)_\psi \delta g^{ab} + \frac{1}{2\kappa} \sum (ab) G_{ab} \delta g^{ab} = 0 \dots (62)$$

If now in the first term we put

¹⁾ The notations ψ_{ab} , $\bar{\psi}_{ab}$ and ψ_{ab}^* (see (27), (29) and § 11, 1915), will however be preserved though they do not correspond to those of EINSTEIN. As to formulae (59) and (60) it is to be understood that if p and q are two of the numbers 1, 2, 3, 4, p' and q' denote the other two in such a way that the order $p q p' q'$ is obtained from 1 2 3 4 by an even number of permutations of two ciphers.

If x_1, x_2, x_3, x_4 are replaced by x, y, z, t and if for the stresses the usual notations X_x, X_y , etc., are used (so that e.g. for a surface element $d\sigma$ perpendicular to the axis of x, X_x is the first component of the force per unit of surface which the part of the system situated on the positive side of $d\sigma$ exerts on the opposite part) then $\mathfrak{T}_1^1 = X_x, \mathfrak{T}_1^2 = X_y$, etc. Further $-\mathfrak{T}_1^4, -\mathfrak{T}_2^4, -\mathfrak{T}_3^4$ are the components of the momentum per unit of volume and $\mathfrak{T}_4^1, \mathfrak{T}_4^2, \mathfrak{T}_4^3$ the components of the energy-current. Finally \mathfrak{T}_4^4 is the energy per unit of volume.

$$\left(\frac{\partial L}{\partial g^{ab}}\right)_\psi = \frac{1}{2} \sqrt{-g} T_{ab}, \dots \dots \dots (63)$$

and if for δg^{ab} the value (49) is substituted, this term becomes

$$\frac{1}{2} \sum (ab) T_{ab} \delta g^{ab} - \frac{1}{4} \sum (abcd) g^{ab} g_{cd} T_{ab} \delta g^{cd},$$

or if in the latter summation a, b is interchanged with c, d and if the quantity

$$T = \sum (cd) g^{cd} T_{cd} \dots \dots \dots (64)$$

is introduced,

$$\frac{1}{2} \sum (ab) (T_{ab} - \frac{1}{2} g_{ab} T) \delta g^{ab}.$$

Finally, putting equal to zero the coefficient of each δg^{ab} we find from (62) the differential equation required

$$G_{ab} = -\kappa (T_{ab} - \frac{1}{2} g_{ab} T) \dots \dots \dots (65)$$

This is of the same form as EINSTEIN'S field equations, but to see that the formulae really correspond to each other it remains to show that the quantities T_{ab} and \mathfrak{T}_c^b defined by (63), (59) and (60) are connected by EINSTEIN'S formulae

$$\mathfrak{T}_c^b = \sqrt{-g} \sum (a) g^{ab} T_{ac} \dots \dots \dots (66)$$

We must have therefore

$$2 \sum (a) g^{ac} \left(\frac{\partial L}{\partial g^{ac}}\right)_\psi = -L + \sum_{a \neq c} (a) \psi_{ac}^* \psi_{a'c'} \dots \dots (67)$$

and for $b = c$

$$2 \sum (a) g^{ab} \left(\frac{\partial L}{\partial g^{ac}}\right)_\psi = \sum_{a \neq c} (a) \psi_{ab}^* \psi_{a'c'} \dots \dots (68)$$

§ 42. This can be tested in the following way. The function L (comp. § 9, 1915) is a homogeneous quadratic function of the ψ_{ab} 's and when differentiated with respect to these variables it gives the quantities $\bar{\psi}_{ab}$. It may therefore also be regarded as a homogeneous quadratic function of the $\bar{\psi}_{ab}$. From (35), (29) and (32)¹⁾, 1915 we find therefore

$$L = \frac{1}{8} \sqrt{-g} \sum (pqrs) (g^{pr} g^{qs} - g^{qr} g^{ps}) \bar{\psi}_{pq} \bar{\psi}_{rs} \dots \dots (69)$$

Now we can also differentiate with respect to the g^{ab} 's, while not the ψ_{ab} 's but the quantities $\bar{\psi}_{ab}$ are kept constant, and we have e.g.

$$\left(\frac{\partial L}{\partial g^{ac}}\right)_\psi = - \left(\frac{\partial L}{\partial g^{ac}}\right)_{\bar{\psi}}$$

According to (69) one part of the latter differential coefficient is

¹⁾ The quantities γ_{ab} in that equation are the same as those which are now denoted by g^{ab} .

obtained by differentiating the factor $\sqrt{-g}$ only and the other part by keeping this factor constant.

For the calculation of the first of these parts we can use the relation

$$\frac{\partial \log(\sqrt{-g})}{\partial g^{ac}} = -\frac{1}{2} g_{ac} \dots \dots \dots (70)$$

and for the second part we find

$$\frac{1}{2} \sqrt{-g} \sum (pq) g^{pq} \bar{\psi}_{ap} \bar{\psi}_{cq}.$$

If (32) 1915 is used (67) and (68) finally become

$$\sum (q) \psi_{cq} \bar{\psi}_{cq} + \sum_{a \neq c} (a) \psi_{ac}^* \psi_{a'c'} = 2L,$$

$$\sum (q) \bar{\psi}_{cq} \psi_{bq} + \sum_{a \neq c} (a) \bar{\psi}_{ab}^* \psi_{a'c'} = 0.$$

These equations are really fulfilled. This is evident from : $\psi_{aa} = 0$, $\bar{\psi}_{aa} = 0$, $\psi_{ba} = -\psi_{ab}$ and $\bar{\psi}_{ba} = -\bar{\psi}_{ab}$; besides, the meaning of ψ_{ab}^* (§ 11, 1915) and equation (35) 1915 must be taken into consideration.

§ 43. In nearly the same way we can treat the gravitation field of a system of incoherent material points; here the quantities w_a and u_a (§§ 4 and 5, 1915) play a similar part as ψ_{ab} and $\bar{\psi}_{ab}$ in what precedes. To consider a more general case we can suppose "molecular forces" to act between the material points (which we assume to be equal to each other); in such a way that in ordinary mechanics we should ascribe to the system a potential energy depending on the density only. Conforming to this we shall add to the Lagrangian function L (§ 4, 1915) a term which is some function of the density of the matter at the point P of the field-figure, such as that density is when by a transformation the matter at that point has been brought to rest. This can also be expressed as follows. Let $d\sigma$ be an infinitely small three-dimensional extension expressed in natural units, which at the point P is perpendicular to the world-line passing through that point, and $\bar{\rho} d\sigma$ the number of points where $d\sigma$ intersects world-lines. The contribution of an element of the field-figure to the principal function will then be found by multiplying the magnitude of that element expressed in natural units by a function of $\bar{\rho}$. Further calculation teaches us that the term to be added to L must have the form

$$\sqrt{-g} \varphi \left(\frac{P}{\sqrt{-g}} \right) \dots \dots \dots (71)$$

where P is given by (15) 1915. As the Lagrangian function defined by (11) 1915 equally falls under this form and also the sum of this function and the new term, the expression (71) may be regarded as the *total* function L . The function φ may be left indeterminate. If now with this function the calculations of §§ 5 and 6, 1915 are repeated, we find the components of the stress-energy-tensor of the matter.

The equations for the gravitation field again take the form (65). T_{ab} is defined by an equation of the form (63), where on the left hand side we must differentiate while the w_a 's are kept constant. Relation (66) can again be verified without difficulty.

We shall not, however, dwell upon this, as the following considerations are more general and apply e.g. also to systems of material points that are anisotropic as regards the configuration and the molecular actions.

§ 44. At any point P of the field-figure the Lagrangian function L will evidently be determined by the course and the mutual situation of the world-lines of the material points in the neighbourhood of P . This leads to the assumption that for constant g_{ab} 's the variation δL is a homogeneous linear function of the virtual displacements δx_a of the material points and of the differential coefficients

$$\frac{\partial \delta x_a}{\partial x_b},$$

these last quantities evidently determining the deformation of an infinitesimal part of the figure formed by the world-lines¹⁾.

The calculation becomes most simple if we put

$$L = \sqrt{-g} H \dots \dots \dots (72)$$

and for constant g_{ab} 's

$$\delta H = \sum (a) U_a \delta x_a + \sum (ab) V_a^b \frac{\partial \delta x_a}{\partial x_b} \dots \dots \dots (73)$$

Considerations corresponding exactly to those mentioned in §§ 4—6, 1915, now lead to the equations of motion and to the following expressions for the components of the stress-energy-tensor

$$\mathfrak{E}_c^c = -L - \sqrt{-g} V_c^c \dots \dots \dots (74)$$

and for $b \neq c$

$$\mathfrak{E}_c^b = -\sqrt{-g} V_c^b \dots \dots \dots (75)$$

The differential equations again take the form (65) if the quantities T_{ab} are defined by

¹⁾ In the cases considered in § 43, δL can indeed be represented in this way.

$$\left(\frac{\partial L}{\partial g^{ab}}\right)_x = \frac{1}{2} \sqrt{-g} T_{ab};$$

in the differentiation on the left hand side the coordinates of the material points are kept constant. To show that T_{ab} and \mathfrak{T}_c^b satisfy equation (66) we must now show that

$$-L - \sqrt{-g} V_c^c = 2 \sum (a) g^{ac} \left(\frac{\partial L}{\partial g^{ac}}\right)_x$$

and for $b \neq c$

$$- \sqrt{-g} V_c^b = 2 \sum (a) g^{ab} \left(\frac{\partial L}{\partial g^{ac}}\right)_x$$

If here the value (72) is substituted for L and if (70) is taken into account, these equations say that for all values of b and c we must have

$$2 \sum (a) g^{ab} \left(\frac{\partial H}{\partial g^{ac}}\right)_x + V_c^b = 0 \quad \dots \quad (76)$$

Now this relation immediately follows from a condition, to which L must be subjected at any rate, viz. that LdS is a scalar quantity. This involves that in a definite case we must find for H always the same value whatever be the choice of coordinates.

§ 45. Let us suppose that instead of only one coordinate x_c a new one x'_c has been introduced, which differs infinitely little from x_c , with the restriction that if

$$x'_c = x_c + \xi_c$$

the term ξ_c depends on the coordinate x_b only and is zero at the point in question of the field-figure. The quantities g^{ab} then take other values and in the new system of coordinates the world-lines of the material points will have a slightly changed course.

By each of these circumstances separately H would change, but all together must leave it unaltered. As to the first change we remark that, according to the transformation formula for g^{ab} , the variation δg^{ab} vanishes when the two indices are different from c , while

$$\delta g^{cc} = 2g^{cb} \frac{\partial \xi_c}{\partial x_b}$$

and for $a \neq c$

$$\delta g^{ac} = \delta g^{ca} = g^{ab} \frac{\partial \xi_c}{\partial x_b}$$

The change of H due to these variations is

$$2 \frac{\partial \xi_c}{\partial x_b} \sum (a) g^{ab} \left(\frac{\partial H}{\partial g^{ac}}\right)_x$$

Further, in the new system of coordinates the figure formed by the world-lines differs from that figure in the old system by the variation $\delta x_c = \xi_c$ which is a function of x_b only. Therefore according to (73) the second variation of H is

$$V_c^b \frac{\partial \xi_c}{\partial x_b}$$

By putting equal to zero the sum of this expression and the preceding one we obtain (76).

§ 46. We have thus deduced for some cases the equations of the gravitation field from the variation theorem. Probably this can also be done for thermodynamic systems, if the Lagrangian function is properly chosen in connexion with the thermodynamic functions, entropy and free energy. But as soon as we are concerned with irreversible phenomena, when e.g. the energy-current consists in a conduction of heat, the variation principle cannot be applied. We shall then be obliged to take EINSTEIN'S field-equations as our point of departure, unless, considering the motions of the individual atoms or molecules, we succeed in treating these by means of the generalized principle of HAMILTON.

§ 47. Finally we shall consider the stresses, the energy etc. which belong to the gravitation field itself. The results will be the same for all the systems treated above, but we shall confine ourselves to the case of §§ 44 and 45. We suppose certain external forces K_a to act on the material points, though we shall see that strictly speaking this is not allowed.

For any displacements δx_a of the matter and variations of the gravitation field we first have the equation which summarizes what we found above

$$\begin{aligned} \delta L + \frac{1}{2\kappa} \delta Q + \Sigma(a) K_a \delta x_a = \sqrt{-g} \Sigma(a) U_a \delta x_a + \\ + \Sigma(ab) \frac{\partial}{\partial x_b} (\sqrt{-g} V_a^b \delta x_a) - \Sigma(ab) \frac{\partial}{\partial x_b} (\sqrt{-g} V_a^b) \delta x_a + \\ + \Sigma(ab) \left(\frac{\partial L}{\partial g^{ab}} \right)_x \delta g^{ab} + \frac{1}{2\kappa} \delta_1 Q + \frac{1}{2\kappa} \delta_2 Q + \Sigma(a) K_a \delta x_a. \end{aligned}$$

In virtue of the equations of motion of the matter, the terms with δx_a cancel each other on the right hand side and similarly, on account of the equations of the gravitation field, the terms with δg^{ab} and $\delta_1 Q$. Thus we can write ¹⁾

¹⁾ To make the notation agree with that of § 38 b has been replaced by e .

$$\Sigma(a)K_a\delta x_a = -\delta L + \Sigma(ae)\frac{\partial}{\partial x_e}(\sqrt{-g}V_a^e\delta x_a) - \frac{1}{2\kappa}(\delta Q - \delta_2 Q). \quad (77)$$

Let us now suppose that only the coordinate x_h undergoes an infinitely small change, which has the same value at all points of the field-figure. Let at the same time the system of values g_{ab} be shifted everywhere in the direction of x_h over the distance δx_h . The left hand side of the equation then becomes $K_h\delta x_h$ and we have on the right hand side

$$\delta L = -\frac{\partial L}{\partial x_h}\delta x_h, \quad \delta Q = -\frac{\partial Q}{\partial x_h}\delta x_h.$$

After dividing the equation by δx_h we may thus, according to (74) and (75), write.

$$-\Sigma(e)\frac{\partial \mathfrak{E}_h^e}{\partial x_e} = -\text{div}_h \mathfrak{E}.$$

By the same division we obtain from $\delta Q - \delta_2 Q$ the expression occurring on the left hand side of (51), which we have represented by

$$\Sigma(e)\frac{\partial \mathfrak{s}_h^e}{\partial x_e} = \text{div}_h \mathfrak{s},$$

where the complex \mathfrak{s} is defined by (52) and (53). If therefore we introduce a new complex \mathfrak{t} which differs from \mathfrak{s} only by the factor $\frac{1}{2\kappa}$, so that

$$\mathfrak{t}_e = \frac{1}{2\kappa}\mathfrak{s}_h^e, \quad \dots \dots \dots (78)$$

we find

$$K_h = -\text{div}_h \mathfrak{E} - \text{div}_h \mathfrak{t}. \quad \dots \dots \dots (79)$$

The form of this equation leads us to consider \mathfrak{t} as the stress-energy-complex of the gravitation field, just as \mathfrak{E} is the stress-energy-tensor for the matter. We need not further explain that for the case $K_h = 0$ the four equations contained in (79) express the conservation of momentum and of energy for the total system, matter and gravitation field taken together.

§ 48. To learn something about the nature of the stress-energy-complex \mathfrak{t} we shall consider the stationary gravitation field caused by a quantity of matter without motion and distributed symmetrically around a point O . In this problem it is convenient to introduce for the three space coordinates x_1, x_2, x_3 , (x_4 will represent the time) "polar" coordinates. By x_3 we shall therefore denote a quantity r

which is a measure for the "distance" to the centre. As to x_1 and x_2 , we shall put $x_1 = \cos \vartheta$, $x_2 = \varphi$, after first having introduced polar coordinates ϑ , φ (in such a way that the rectangular coordinates are $r \cos \vartheta$, $r \sin \vartheta \cos \varphi$, $r \sin \vartheta \sin \varphi$). It can be proved that, because of the symmetry about the centre, $g_{ab} = 0$ for $a \neq b$, while we may put for the quantities \bar{g}_{aa}

$$g_{11} = -\frac{u}{1-x_1^2}, \quad g_{22} = -u(1-x_1^2), \quad g_{33} = -v, \quad g_{44} = w. \quad (80)$$

where u , v , w are certain functions of r . Differentiations of these functions will be represented by accents. We now find that of the complex t only the components t_1^1 , t_3^3 and t_4^4 are different from zero. The expressions found for them may be further simplified by properly choosing r . If the distance to the centre O is measured by the time the light requires to be propagated from O to the point in question, we have $w = v$. One then finds

$$\left. \begin{aligned} t_1^1 &= \frac{1}{2\kappa} \left(-\frac{u'}{2u} + 2u'' - \frac{uv'}{v^2} + \frac{uv''}{v} \right), \\ t_3^3 &= \frac{1}{2\kappa} \left(-2v + \frac{u'}{2u} + \frac{u'v'}{v} \right), \\ t_4^4 &= \frac{1}{2\kappa} \left(-2v - \frac{u'}{2u} + 2u'' + \frac{uv''}{v} \right). \end{aligned} \right\} \dots \quad (81)$$

§ 49. We must assume that in the gravitation fields really existing the quantities g_{ab} have values differing very little from those which belong to a field without gravitation. In this latter we should have

$$u = r^2, \quad v = w = 1,$$

and thus we put now

$$u = r^2(1 + \mu), \quad v = w = 1 + \nu,$$

where the quantities μ and ν which depend on r are infinitely small, say of the first order, and their derivatives too. Neglecting quantities of the second order we find from (81)

$$t_1^1 = \frac{1}{2\kappa} (2 + 2\mu + 6r\mu' + 2r^2\mu'' + r^2\nu''),$$

$$t_3^3 = \frac{1}{\kappa} (\mu - \nu + r\mu' + r\nu'),$$

$$t_4^4 = \frac{1}{2\kappa} (2\mu - 2\nu + 6r\mu' + 2r^2\mu'' + r^2\nu'').$$

For our degree of approximation we may suppose that of the quantities T_{ab} only T_{44} differs from 0. If we put

$$T_{44} = \rho, \dots \dots \dots (82)$$

a quantity which depends on r and which we shall assume to be zero outside a certain sphere, we find from the field equations

$$u = \kappa \left\{ -\frac{2}{r} \int_0^r \frac{dr}{r} \int_0^r r^2 \rho dr - \frac{1}{r} \int_0^r r^2 \rho dr + \int_{\infty}^r r \rho dr \right\},$$

$$v = \kappa \left\{ -\frac{1}{r} \int_0^r r^2 \rho dr + \int_{\infty}^r r \rho dr \right\}.$$

We thus obtain

$$t_1^1 = \frac{1}{\kappa} + \int_{\infty}^r r \rho dr - \frac{1}{r} \int_0^r r^2 \rho dr - \frac{1}{2} r^2 \rho, \dots \dots \dots (83)$$

$$t_3^3 = 0, \quad t_4^4 = -\frac{1}{2} r^2 \rho. \dots \dots \dots (84)$$

§ 50. If first we leave aside the first term of t_1^1 , which would also exist if no attracting matter were present, it is remarkable that the gravitation constant κ does not occur in the stress t_1^1 , nor in the energy t_4^4 , the same would have been found if we had used other coordinates. This constitutes an important difference between EINSTEIN'S theory and other theories in which attracting or repulsing forces are reduced to "field actions". The pulsating spheres of BJERKNES e.g. are subjected to forces which, for a given motion, are proportional to the density of the fluid in which they are imbedded; and the changes of pressure and the energy in that fluid are likewise proportional to this density. In this case we shall therefore ascribe to the stress-energy-complex values proportional to the intensity of the actions which we want to explain. In EINSTEIN'S theory such a proportionality does not exist. The value of t_4^4 is of the same order of magnitude as \mathfrak{T}_4^4 in the matter. To our degree of approximation we find namely from (82) $\mathfrak{T}_4^4 = r^2 \rho$.

§ 51. If we had not worked with polar coordinates but with rectangular coordinates we should have had to put for the field without gravitation $g_{11} = g_{22} = g_{33} = -1, g_{44} = 1, g_{ab} = 0$ for $a \neq b$. Then we should have found zero for all the components of the complex. In the system of coordinates used above we found for the field without gravitation $t_1^1 = \frac{1}{\kappa}$; this is due to the complex t being no tensor. If it were, the quantities t_a^b would be zero in every system of coordinates if they had that value in one system.

It is also remarkable that in real cases the first term in (83) can be much larger than the following ones. If we consider e.g. a point P outside the attracting sphere, we can prove that the ratio of the first term to the third is of the same order as the ratio of the square of the velocity of light to the square of the velocity with which a material point can describe a circular orbit passing through P .

The following must also be noticed. In the system of polar coordinates used above there will exist in the field without gravitation the stress $t_1^1 = \frac{1}{\kappa}$. If a stress of this magnitude were produced by means of actions which give rise to a stress-energy-tensor, the passage to rectangular coordinates would give us a stress which becomes infinite at the point O . In those coordinates we should namely have

$$t_1^1 = \frac{\sin^2 \vartheta}{r^2} \cdot \frac{1}{\kappa}$$

§ 52. Evidently it would be more satisfactory if we could ascribe a stress-energy-tensor to the gravitation field. Now this can really be done. Indeed, the quantities \mathfrak{E}_{0h}^e determined by (57) form a tensor and according to (58), (79) may be replaced by

$$K_h = - \operatorname{div}_h \mathfrak{E} - \operatorname{div}_h t_0, \dots \dots \dots (85)$$

if t_0 is defined by a relation similar to (78), viz.

$$t_{0h}^e = \frac{1}{2\kappa} \mathfrak{E}_{0h}^e \dots \dots \dots (86)$$

Equation (85) shows that, just as well as t_{0h}^e , we may consider the quantities t_{0h}^e as the stresses etc. in the gravitation field. This way of interpretation is very simple. With a view to (41) we can namely derive from the equations for the gravitation field (65)

$$G = \kappa T$$

and

$$T_{ab} = - \frac{1}{\kappa} (G_{ab} - \frac{1}{2} g_{ab} G).$$

Further we find from (66)

$$\mathfrak{E}_h^e = \frac{1}{2\kappa} G \Sigma(a) \delta^{ae} g_{ah} - \frac{1}{\kappa} \Sigma(a) \delta^{ae} G_{ah}$$

and from (57) and (86)

$$t_{0h}^e = - \mathfrak{E}_h^e \dots \dots \dots (87)$$

At every point of the field-figure the components of the stress-energy-tensor of the gravitation field would therefore be equal to

the corresponding quantities for the matter or the electro-magnetic system with the opposite sign. It is obvious that by this the condition of the conservation of momentum and energy for the *whole* system would be immediately fulfilled. It was in fact this circumstance that made me think of the tensor $t_0 = -\mathfrak{E}$. The way in which \mathfrak{g}_0 was introduced in §§ 38 and 39 has only been chosen in order to lay stress on (58) being an identity, so that equation (85) is but another form of (79).

At first sight the relations (87) and the conception to which they have led, may look somewhat startling. According to it we should have to imagine that behind the directly observable world with its stresses, energy etc. there is hidden the gravitation field with stresses, energy etc. that are everywhere equal and opposite to the former; evidently this is in agreement with the interchange of momentum and energy which accompanies the action of gravitation. On the way of a light-beam e.g. there would be everywhere in the gravitation field an energy current equal and opposite to the one existing in the beam. If we remember that this hidden energy-current can be fully described mathematically by the quantities g_{ab} and that only the interchange just mentioned makes it perceptible to us, this mode of viewing the phenomena does not seem unacceptable. At all events we are forcibly led to it if we want to preserve the advantage of a stress-energy-*tensor* also for the gravitation field. It can namely be shown that a tensor which is transformed in the same way as the tensor t_0 defined by (57) and (86) and which in every system of coordinates has the same divergency as the latter, must coincide with t_0 .

Finally we may remark that (78), (86), (58), (87) give

$$\operatorname{div} \mathfrak{t} = \operatorname{div} t_0 = -\operatorname{div} \mathfrak{E},$$

so that we have, both from (79) and from (85), $K_h = 0$.

The question is this, that, so long as the gravitation field is considered as given, we may introduce "external" forces, but that in the equations for the gravitation field itself we must also take into consideration the stress-energy-tensor of the system by which those forces are exerted.

Physics. — “On EINSTEIN’s *Theory of gravitation.*” IV. By Prof. H. A. LORENTZ.

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§ 53. The expressions for the stress-energy-components of the gravitation field found in the preceding paper call for some further remarks. If by δ_h^e we denote a quantity having the value 1 for $e = h$ and being 0 for $e \neq h$, those expressions can be written in the form (comp. equations (52) and (78))

$$t_h^e = \frac{1}{2\kappa} \left\{ -\delta_h^e Q + \sum (ab) \frac{\partial Q}{\partial g_{ab,e}} g_{ab,h} + \sum (abf) \frac{\partial Q}{\partial g_{ab,fe}} g_{ab,fh} - \sum (abf) \frac{\partial}{\partial x_f} \left(\frac{\partial Q}{\partial g_{ab,ef}} \right) g_{ab,h} \right\} \dots \dots \dots (88)$$

They contain the first and second derivatives of the quantities g_{ab} . EINSTEIN on the contrary has given values for the stress-energy-components which contain the first derivatives only and which therefore are in many respects much more fit for application.

It will now be shown how we can also find formulae without second derivatives, if we start from (88).

§ 54. For this purpose we shall consider the complex u defined by

$$u_h^e = \frac{1}{2\kappa} \left\{ \delta_h^e Q - \sum (abf) \frac{\partial}{\partial x_h} \left(\frac{\partial Q}{\partial g_{ab,fe}} g_{ab,f} \right) \right\} \dots \dots (89)$$

and we shall seek its divergency.

We have

$$(div u)_h = \sum (e) \frac{\partial u_h^e}{\partial x_e} = \frac{1}{2\kappa} \left\{ \frac{\partial Q}{\partial x_h} - \sum (abfe) \frac{\partial^2}{\partial x_e \partial x_h} \left(\frac{\partial Q}{\partial g_{ab,fe}} g_{ab,f} \right) \right\}$$

or

$$(div u)_h = \frac{1}{2\kappa} \frac{\partial R}{\partial x_h} \dots \dots \dots (90)$$

if we put

$$R = Q - \sum (abfe) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,fe}} g_{ab,f} \right) \dots \dots \dots (91)$$

Now $Q = \sqrt{-g} G$ can be divided into two parts, the first of which Q_1 contains differential coefficients of the quantities $g_{\alpha\beta}$ of the first order only, while the second Q_2 is a homogeneous linear function

of the second derivatives of those quantities. This latter involves that, if we replace (91) by

$$R = Q_1 + Q_2 - \Sigma(abfe) \left(\frac{\partial Q}{\partial g_{ab,fe}} g_{ab,fe} \right) - \Sigma(abfe) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,fe}} \right) g_{ab,f},$$

the second and the third term annul each other. Thus

$$R = Q_1 - \Sigma(abfe) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,fe}} \right) g_{ab,f} \dots \dots (92)$$

If now we define a complex v by the equation

$$v_{he} = - \frac{1}{2\kappa} \delta_{he} R, \dots \dots \dots (93)$$

we have

$$(\text{div } v)_h = - \frac{1}{2\kappa} \frac{\partial R}{\partial x_h} \dots \dots \dots (94)$$

If finally we put

$$t' = t + u + v,$$

we infer from (90) and (94)

$$\text{div } t' = \text{div } t. \dots \dots \dots (95)$$

and from (88), (89), (93) and (92)

$$t'_{h^h} = \frac{1}{2\kappa} \left\{ - Q_1 + \Sigma(ab) \frac{\partial Q}{\partial g_{ab,h}} g_{ab,h} - \Sigma(abf) \frac{\partial}{\partial x_h} \left(\frac{\partial Q}{\partial g_{ab,fh}} \right) g_{ab,f} - \Sigma(abf) \frac{\partial}{\partial x_f} \left(\frac{\partial Q}{\partial g_{ab,hf}} \right) g_{ab,h} + \Sigma(abfe) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,fe}} \right) g_{ab,f} \right\} (96)$$

and for $e \neq h$

$$t'_{h^e} = \frac{1}{2\kappa} \left\{ \Sigma(ab) \frac{\partial Q}{\partial g_{ab,e}} g_{ab,h} - \Sigma(abf) \frac{\partial}{\partial x_h} \left(\frac{\partial Q}{\partial g_{ab,fe}} \right) g_{ab,f} - \Sigma(abf) \frac{\partial}{\partial x_f} \left(\frac{\partial Q}{\partial g_{ab,ef}} \right) g_{ab,h} \right\} \dots \dots \dots (97)$$

Formula (95) shows that the quantities t'_{h^e} can be taken just as well as the expressions (88) for the stress-energy-components and we see from (96) and (97) that these new expressions contain only the first derivatives of the coefficients g_{ab} ; they are homogeneous quadratic functions of these differential coefficients.

This becomes clear when we remember that Q_1 is a function of this kind and that only Q_1 contributes something to the second term of (96) and the first of (97); further that the derivatives of Q occurring in the following terms contain only the quantities g_{ab} and not their derivatives.

§ 55. EINSTEIN'S stress-energy-components have a form widely different from that of the above mentioned ones. They are

$$t'^{(E)h} = \frac{1}{2\kappa} \delta_{h^e} \Sigma (abcf) g^{ab} \Gamma_{ac}^f \Gamma_{bf}^c - \frac{1}{\kappa} \Sigma (abc) g^{ab} \Gamma_{ac}^e \Gamma_{bh}^c,$$

where for the sake of simplicity it has been assumed that $\sqrt{-g}=1$.

Further we have

$$\Gamma_{ab}^c = - \left\{ \begin{matrix} ab \\ c \end{matrix} \right\} = - \Sigma (e) g^{ce} \left[\begin{matrix} ab \\ e \end{matrix} \right].$$

If now our formulae (96) and (97) are likewise simplified by the assumption $\sqrt{-g}=1$ (so that Q becomes equal to $-G$), we may expect that t' will become identical with $t_{(E)}$. This is really so in the case $g_{ab} = 0$ for $a \neq b$; by which it seems very probable that the agreement will exist in general.

In the preceding paper it was shown already that the stress-energy-components t_{h^e} do not form a "tensor", but what was called a "complex". The same may be said of the quantities t'^{h^e} defined by (96) and (97) and of the expressions given by EINSTEIN. If we want a stress-energy-tensor, there are only left the quantities t_{0h}^e defined by (86) and (57), the values of which are always equal and opposite to the corresponding stress-energy-components \mathfrak{T}_{h^e} for the matter or the electromagnetic field.

It must be noticed that the four equations

$$\Sigma (e) \frac{\partial}{\partial x_e} (\mathfrak{T}_{h^e} + \mathfrak{T}_{(g)h}) = 0$$

always express the same relations, whether we choose t_{0h}^e , t_{h^e} , t'^{h^e} or $t'^{(E)h}$ as stress-energy-components $\mathfrak{T}_{(g)h}^e$ of the gravitation field. If however in a definite case we want to use the equations in order to calculate how the momentum and the energy of the matter and the electromagnetic field change by the gravitational actions, it is best to use t'^{e_h} or $t'^{(E)h}$, just because these quantities are homogeneous quadratic functions of the derivatives $g_{ab,c}$.

Experience namely teaches us that the gravitation fields occurring in nature may be regarded as feeble, in this sense that the values of the g_{ab} 's are little different from those which might be assumed if no gravitation field existed. For these latter values, which will be called the "normal" ones, we may write in orthogonal coordinates

$$g_{11} = g_{22} = g_{33} = -1, \quad g_{44} = c^2, \quad g_{ab} = 0, \quad \text{for } a \neq b. \quad (98)$$

In a first approximation, which most times will be sufficient, the deviations of the values of the g_{ab} 's from these normal ones may be taken proportional to the gravitation constant κ . This factor also appears in the differential coefficients $g_{ab,c}$; hence, according to the character of the functions t'^{h^e} mentioned above (and on account

of the factor $\frac{1}{x}$ in (96) and (97)) these functions become proportional to x , so that in a feeble gravitation field they have low values.

§ 56. Because of the complicated form of equations (96) and (97), we shall confine ourselves to the calculation for some cases of t'^4 , i.e. of the energy per unit of volume. This calculation is considerably simplified if we consider stationary fields only. Then all differential coefficients with respect to x_4 vanish, so that we have according to (96)

$$t'^4 = \frac{1}{2x} \left\{ -Q_1 + \sum (abfe) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,fe}} \right) g_{ab,fe} \right\} \quad (99)$$

We shall work out the calculation, first for a field without gravitation and secondly for the case of an attracting spherical body in which the matter is distributed symmetrically round the centre.

If there is no gravitation field we may take for the quantities g_{ab} the "normal" values. For the case of orthogonal coordinates these are given by (98). When we want to use the polar coordinates introduced into § 48 we have the corresponding formulae

$$\left. \begin{aligned} g_{11} &= -\frac{r^2}{1-x_1^2}, & g_{22} &= -r^2(1-x_1^2), & g_{33} &= -1, & g_{44} &= c^2, \\ g_{ab} &= 0, & & & & & & \end{aligned} \right\} (100)$$

If, using polar coordinates, we have to do with an attracting sphere and if we take its centre as origin, we may put

$$g_{11} = -\frac{u}{1-x_1^2}, \quad g_{22} = -(1-x_1^2)u, \quad g_{33} = -v, \quad g_{44} = w, \quad (101)$$

where u , v , w are functions of r . The g_{ab} 's which belong to an orthogonal system of coordinates may be expressed in the same functions.

These g_{ab} 's are

$$g_{11} = -\frac{u}{r^2} + \frac{x_1^2}{r^2} \left(\frac{u}{r^2} - v \right), \quad \text{etc.}$$

$$g_{12} = \frac{x_1 x_2}{r^2} \left(\frac{u}{r^2} - v \right), \quad \text{etc.}$$

$$g_{14} = g_{24} = g_{34} = 0, \quad g_{44} = w.$$

The "etc." means that for g_{22} , g_{33} we have similar expressions as for g_{11} and for g_{23} , g_{31} similar ones as for g_{12} .

§ 57. In order to deduce the differential equations determining u , v , w we may arbitrarily use rectangular or polar coordinates; the latter however are here to be preferred. If differentiations

with respect to r are indicated by accents, we have according to (40) and (101)

$$\begin{aligned} G_{11} &= \frac{1}{1-x_1^2} \left(-1 + \frac{u''}{2v} - \frac{u'v'}{4v^2} + \frac{u'w'}{4vw} \right), \\ G_{22} &= (1-x_1^2) \left(-1 + \frac{u''}{2v} - \frac{u'v'}{4v^2} + \frac{u'w'}{4vw} \right), \\ G_{33} &= \frac{u''}{u} - \frac{u'^2}{2u^2} - \frac{u'v'}{2uv} - \frac{v'w'}{4vw} + \frac{w''}{2w} - \frac{w'^2}{4w^2}, \\ G_{44} &= -\frac{u'w'}{2uv} + \frac{v'w'}{4v^2} - \frac{w''}{2v} + \frac{w'^2}{4vw}, \\ G_{ab} &= 0, \text{ for } a \neq b. \end{aligned}$$

So we have found the left hand sides of the field equations (65). Before considering these equations more closely we shall introduce the simplification that the g_{ab} 's are very little different from the normal values (100). For these latter we have

$$u = r^2, \quad v = 1, \quad w = c^2. \quad (102)$$

and therefore we now put

$$u = r^2(1+\lambda), \quad v = 1 + \mu, \quad w = c^2(1+\nu). \quad (103)$$

The quantities λ, μ, ν , which depend on r , will be regarded as infinitely small of the first order and in the field equations we shall neglect quantities of second and higher orders.

Then we may write for G_{11} etc.

$$\begin{aligned} G_{11} &= \frac{1}{1-x_1^2} (\lambda + 2r\lambda' + \frac{1}{2}r^2\lambda'' - \mu - \frac{1}{2}r\mu' + \frac{1}{2}r\nu'), \\ G_{22} &= (1-x_1^2)(\lambda + 2r\lambda' + \frac{1}{2}r^2\lambda'' - \mu - \frac{1}{2}r\mu' + \frac{1}{2}r\nu'), \\ G_{33} &= \frac{2}{r}\lambda' + \lambda'' - \frac{1}{r}\mu' + \frac{1}{2}\nu'', \\ G_{44} &= -c^2 \left(\frac{1}{r}\nu' + \frac{1}{2}\nu'' \right). \end{aligned}$$

On the right hand-sides of the field equations (65) we may take for g_{ab} the normal value; moreover we shall take for T_{ab} and \mathcal{T} the values which hold for a system of incoherent material points. We may do so if we assume no other internal stresses but those caused by the mutual attractions; these stresses may be neglected in the present approximation.

As we supposed the attracting matter to be at rest we have according to (10), (16) and (15) (1915) $w_1 = w_2 = w_3 = 0, w_4 = \rho, u_1 = u_2 = u_3 = 0, u_4 = c^2\phi, P = c\phi$.

In the notations we are now using we have further, according to (23) (1915),

$$\mathfrak{T}e_h = \frac{u_h w_e}{P},$$

so that of the stress-energy-components of the matter only one is different from zero, namely

$$\mathfrak{T}_4^4 = c\varrho.$$

Further (66) involves that, also of the quantities T_{ab} , only one, namely T_{44} , is not equal to zero. As we may put $\sqrt{-g} = cr^2$, we have namely

$$T_{44} = \frac{c^2}{r^2} \varrho, \quad T = \frac{1}{r^2} \varrho.$$

Finally we are led to the three differential equations

$$\lambda + 2r\lambda' + \frac{1}{2}r^2\lambda'' - \mu - \frac{1}{2}r\mu' + \frac{1}{2}rv' = -\frac{1}{2}\kappa\varrho, \quad (104)$$

$$2r\lambda' + r^2\lambda'' - r\mu' + \frac{1}{2}r^2v'' = -\frac{1}{2}\kappa\varrho, \quad (105)$$

$$rv' + \frac{1}{2}r^2v'' = \frac{1}{2}\kappa\varrho. \quad (106)$$

It may be remarked that $\varrho dx_1 dx_2 dx_3$ represents the "mass" present in the element of volume $dx_1 dx_2 dx_3$. Because of the meaning of x_1, x_2, x_3 (§ 48) the mass in the shell between spheres with radii r and $r + dr$ is found when $\varrho dx_1 dx_2 dx_3$ is integrated with respect to x_1 between the limits -1 and $+1$ and with respect to x_2 between 0 and 2π . As ϱ depends on r only, this latter mass becomes $4\pi\varrho dr$, so that ϱ is connected with the "density" in the ordinary sense of the word, which will be called $\bar{\varrho}$, by the equation

$$\varrho = r^2 \bar{\varrho}.$$

The differential equations also hold outside the sphere if ϱ is put equal to zero. We can first imagine ϱ to change gradually to 0 near the surface and then treat the abrupt change as a limiting case. In all the preceding considerations we have tacitly supposed the second derivatives of the quantities g_{ab} to have everywhere finite values. Therefore v and v' will be continuous at the surface, even in the case of an abrupt change.

§ 58. Equation (106) gives

$$v' = \frac{\kappa}{r^2} \int_0^r \varrho dr, \quad (107)$$

where the integration constant is determined by the consideration that for $r = 0$ all the quantities g_{ab} and their derivatives must be finite, so that for $r = 0$ the product $r^2 v'$ must be zero. As it is natural to suppose that at an infinite distance v vanishes, we find further

$$v = \kappa \int_{\infty}^r \frac{dr}{r^2} \int_0^r \rho dr \dots \dots \dots (108)$$

The quantities λ and μ on the contrary are not completely determined by the differential equations. If namely equations (105) and (106) are added to (104) after having been multiplied by $-\frac{1}{2}$ and $+\frac{1}{2}$ respectively, we find

$$\lambda + r\lambda' - \mu + rv' = 0 \dots \dots \dots (109)$$

and it is clear that (104) and (105) are satisfied as soon as this is the case with this condition (109) and with (106). So we have only to attend to (108) and (109). The indefiniteness remaining in λ and μ is inevitable on account of the covariancy of the field equations. It does not give rise to any difficulties.

Equation (107) teaches us that near the centre

$$v' = \frac{1}{2} \kappa \bar{\rho}_0 r$$

if $\bar{\rho}_0$ is the density at the centre, whereas from (108) we find a finite value for v itself. This confirms what has been said above about the values at the centre. We shall assume that at that point λ, μ and their derivatives have likewise finite values. Moreover we suppose (and this agrees with (109)) that λ, μ, λ' and μ' are continuous at the surface of the sphere.

If a is the radius of the sphere we find from (108) for an external point

$$v = -\frac{\kappa}{r} \int_0^a \rho dr.$$

Without contradicting (109) we may assume that at a great distance from the centre λ and μ are likewise proportional to $\frac{1}{r}$, so that λ' and μ' decrease proportionally to $\frac{1}{r^2}$.

§ 59. We can now continue the calculation of r_4^4 (§ 56). Substituting (101) in (99) and using polar coordinates we find

$$r_4^4 = -\frac{1}{2\kappa} u \sqrt{\frac{w}{v}} \left(\frac{1}{2} \frac{u^2}{u^2} + \frac{u'w'}{uw} \right),$$

whence by substituting (102) we derive for a field without gravitation

$$r_4^4 = -\frac{c}{\kappa}.$$

This equation shows that, working with polar coordinates, we

should have to ascribe a certain negative value of the energy to a field without gravitation, in such a way (comp. § 57) that the energy in the shell between the spheres described round the origin with radii r and $r + dr$ becomes

$$-\frac{4\pi c}{\kappa} dr.$$

The density of the energy in the ordinary sense of the word would be inversely proportional to r^2 , so that it would become infinite at the centre.

It is hardly necessary to remark that, using rectangular coordinates we find a value zero for the same case of a field without gravitation. The normal values of g_{ab} are then constants and their derivatives vanish.

§ 60. Using rectangular coordinates we shall now indicate the form of t'^4 , for the field of a spherical body, with the approximation specified in § 57. Thus we put

$$\left. \begin{aligned} g_{11} &= -(1 + \lambda) + \frac{x_1^2}{r^2}(\lambda - \mu), \text{ etc.} \\ g_{12} &= \frac{x_1 x_2}{r^2}(\lambda - \mu), \text{ etc.} \\ g_{14} &= g_{24} = g_{34} = 0, \quad g_{44} = c^2(1 + \nu). \end{aligned} \right\} \dots (110)$$

By (109) and (110) we find¹⁾

¹⁾ Of the laborious calculation it may be remarked here only that it is convenient to write the values (110) in the form

$$\begin{aligned} g_{11} &= -1 + \alpha + \frac{\partial^2 \beta}{\partial x_1^2}, \text{ etc.} \\ g_{12} &= \frac{\partial^2 \beta}{\partial x_1 \partial x_2}, \text{ etc.} \end{aligned}$$

where α and β are infinitesimal functions of r . We then find

$$\begin{aligned} t'^4 &= \frac{c}{2\kappa} \left\{ -\frac{1}{2} \Sigma(a) \left(\frac{\partial \alpha}{\partial x_a} \right)^2 + \Sigma(a) \frac{\partial \nu}{\partial x_a} \frac{\partial \alpha}{\partial x_a} + \right. \\ &\quad \left. + \frac{1}{4} \Sigma(a i k) \left[\frac{\partial^2 \beta}{\partial x_a \partial x_i^2} \frac{\partial^2 \beta}{\partial x_a \partial x_k^2} - \left(\frac{\partial^2 \beta}{\partial x_a \partial x_i \partial x_k} \right)^2 \right] \right\} \\ &\quad (a, i, k = 1, 2, 3) \end{aligned}$$

which reduces to (111) if the relations between ν , β and λ , μ , viz.

$$\alpha + \frac{1}{r} \beta' = -\lambda, \quad -\frac{1}{r} \beta' + \beta'' = \lambda - \mu$$

and the equality $\alpha' = \nu'$ involved in (109) are taken into consideration.

$$t'^4 = \frac{c}{4\pi} \left\{ v'^2 + \frac{1}{r} (\lambda - \mu) \left[\frac{1}{r} (\lambda - \mu) + 2(\lambda' - \mu') \right] \right\} \quad (111)$$

Thus we see (comp. § 58) that at a distance from the attracting sphere t'^4 decreases proportionally to $\frac{1}{r^4}$. Further it is to be noticed that on account of the indefiniteness pointed out in § 58, there remains some uncertainty as to the distribution of the energy over the space, but that nevertheless the total energy of the gravitation field

$$E = 4\pi \int_0^\infty t'^4 r^2 dr$$

has a definite value.

Indeed, by the integration the last term of (111) vanishes. After multiplication by r^2 this term becomes namely

$$(\lambda - \mu)^2 + 2r (\lambda' - \mu) (\lambda' - \mu') = \frac{d}{dr} [r (\lambda - \mu)^2].$$

The integral of this expression is 0 because (comp. §§ 57 and 58) $r(\lambda - \mu)^2$ is continuous at the surface of the sphere and vanishes both for $r = 0$ and for $r = \infty$.

We have thus

$$E = \frac{\pi c}{\pi} \int_0^\infty v'^2 r^2 dr, \quad (112)$$

where the value (107) can be substituted for v' . If e.g. the density $\bar{\rho}$ is everywhere the same all over the sphere, we have at an internal point

$$v' = \frac{1}{3} \pi \bar{\rho} r$$

and at an external point

$$v' = \frac{1}{3} \pi \bar{\rho} \frac{a^3}{r^2}.$$

From this we find

$$E = \frac{2}{15} \pi c \pi \bar{\rho} a^5.$$

§ 61. The general equation (99) found for t'^4 can be transformed in a simple way. We have namely

$$\begin{aligned} \Sigma (abfe) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,fe}} \right) g_{ab,f} &= \Sigma (abfe) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,fe}} g_{ab,f} \right) - \\ &- \Sigma (abfe) \frac{\partial Q}{\partial g_{ab,fe}} g_{ab,fe} \end{aligned}$$

and we may write $-Q_2$ (§ 54) for the last term. Hence

$$t_4^4 = \frac{1}{2\kappa} \left\{ -Q + \sum (abfe) \frac{\partial}{\partial x_e} \left(\frac{\partial Q}{\partial g_{ab,fe}} g_{ab,f} \right) \right\}, \dots \quad (113)$$

where we must give the values 1, 2, 3 to e and f .

The gravitation energy lying within a closed surface consists therefore of two parts, the first of which is

$$E_1 = -\frac{1}{2\kappa} \int Q dx_1 dx_2 dx_3 \dots \quad (114)$$

while the second can be represented by surface integrals. If namely q_1, q_2, q_3 are the direction constants of the normal drawn outward

$$E_2 = \frac{1}{2\kappa} \sum (abfe) \int \frac{\partial Q}{\partial g_{ab,fe}} g_{ab,f} q_e d\sigma \dots \quad (115)$$

In the case of the infinitely feeble gravitation field represented by λ, μ, ν (§ 57) both expressions E_1 and E_2 contain quantities of the first order, but it can easily be verified that these cancel each other in the sum, so that, as we knew already, the total energy is of the second order.

From $Q = \sqrt{-g} G$ and the equations of § 32 we find namely

$$\frac{\partial Q}{\partial g_{ab,fe}} = \frac{1}{2} \sqrt{-g} (2g^{ab} g^{fe} - g^{bf} g^{ae} - g^{af} g^{be}), \dots \quad (116)$$

so that we can write

$$E_2 = \frac{1}{4\kappa} \int \sqrt{-g} \sum (abfe) (2g^{ab} g^{fe} - g^{bf} g^{ae} - g^{af} g^{be}) g_{ab,f} q_e d\sigma.$$

The factor $g_{ab,f}$ is of the first order. Thus, if we confine ourselves to that order, we may take for all the other quantities these normal values. Many of these are zero and we find

$$E_2 = -\frac{c}{2\kappa} \sum (ae) \int g^{aa} (g_{aa,e} - g_{ae,a}) q_e d\sigma. \dots \quad (117)$$

Here we must take $a = 1, 2, 3, 4$; $e = 1, 2, 3$, while we remark that for $a = e$ the expression between brackets vanishes. For $a = 4$ the integral becomes $\int \frac{\partial v}{\partial x_e} q_e d\sigma$, which after summation with respect to e gives

$$\int \frac{\partial v}{\partial n} d\sigma, \dots \quad (118)$$

n representing the normal to the surface. If a and e differ from each other, while neither of them is equal to 4, we can deduce from (110) and (109)

$$g_{aa,e} - g_{ae,a} = \frac{\partial v}{\partial x_e}.$$

Each value of e occurring twice, i.e. combined with the two values different from e which a can take, we have in addition to (118)

$$- 2 \int \frac{\partial v}{\partial n} d\sigma,$$

so that (117) becomes

$$E_2 = \frac{c}{2\kappa} \int \frac{\partial v}{\partial n} d\sigma.$$

As now outside the sphere

$$v = -\frac{\kappa}{r} \int_0^a \rho dr$$

we have for every closed surface that does not surround the sphere $E_2 = 0$, but for every surface that does

$$E_2 = 2\pi c \int_0^a \rho dr \dots \dots \dots (119)$$

As to E_1 we remark that substituting (65) in (41) and taking into consideration (64) we find,

$$G = \kappa T \quad , \quad Q = \kappa \sqrt{-g} T \quad \dots \dots \dots (120)$$

From this we conclude that E_1 is zero if there is no matter inside the surface σ . In order to determine E_1 in the opposite case, we remember that G is independent of the choice of coordinates. To calculate this quantity we may therefore use the value of T indicated in § 56, which is sufficient to calculate E_1 as far as the terms of the first order. We have therefore

$$G = \frac{\kappa}{r^2} \rho$$

and if, using further on rectangular coordinates, we take for $\sqrt{-g}$ the normal value c ,

$$Q = \frac{c\kappa}{r^2} \rho.$$

From this we find by substitution in (114) for the case of the closed surface σ surrounding the sphere

$$E_1 = -2\pi c \int_0^a \rho dr.$$

This equation together with (119) shows that in (113) when integrated over the whole space the terms of the first order really cancel each other. In order to calculate those of the second order

and thus to derive the result (112) from (113), we should have to determine the quantity T (comp. 120), accurately to the order α . The surface integrals in (115) too would have to be considered more closely. We shall not however dwell upon this.

§ 62. From the expression for t'_4 given in (113) and the value

$$E = E_1 + E_2$$

derived from it, it can be inferred that, though t' is no tensor, we yet may change a good deal in the system of coordinates in which the phenomena are described, without altering the value of the total energy. Let us suppose e.g. that x_4 is left unchanged but that, instead of the rectangular coordinates x_1, x_2, x_3 hitherto used, other quantities x'_1, x'_2, x'_3 are introduced, which are some continuous function of x_1, x_2, x_3 , with the restriction that $x'_1 = x_1, x'_2 = x_2, x'_3 = x_3$ outside a certain closed surface surrounding the attracting matter at a sufficient distance. If we use these new coordinates, we shall have to introduce other quantities g'_{ab} instead of g_{ab} . As however outside the closed surface the quantities g_{ab} and their derivatives do not change, the value of E_2 will approach the same limit as when we used the coordinates x_1, x_2, x_3 , if the surface σ for which it is calculated expands indefinitely. The value which we find for E_1 after the transformation of coordinates will also be the same as before. Indeed, if $d\tau$ is an element of volume expressed in x_1, x_2, x_3 -units and $d\tau'$ the same element expressed in x'_1, x'_2, x'_3 -units, while Q' represents the new value of Q , we have

$$Qd\tau = Q'd\tau'.$$

It is clear that the total energy will also remain unchanged if x'_1, x'_2, x'_3 differ from x_1, x_2, x_3 at all points, provided only that these differences decrease so rapidly with increasing distance from the attracting body, that they have no influence on the limit of the expression (115).

The result which we have now found admits of another interpretation. In the mode of description which we first followed (using x_1, x_2, x_3), ρ ¹⁾ and g_{ab} are certain functions of x_1, x_2, x_3 ; in the new one ρ' , g'_{ab} are certain other functions of x'_1, x'_2, x'_3 . If now, without leaving the system of coordinates x_1, x_2, x_3 , we ascribe to the density and to the gravitation potentials values which depend on x_1, x_2, x_3 in the same way as ρ' , g'_{ab} depended on x'_1, x'_2, x'_3 just now, we shall obtain a new system (consisting of the attracting body and the gravitation field) which is different from the original system

¹⁾ By ρ we mean here what was denoted by $\bar{\rho}$ in § 56.

because other functions of the coordinates occur in it, but which nevertheless no observation will be able to discern from it, the indefiniteness which is a necessary consequence of the covariancy of the field equations, again presenting itself.

What has been said shows that the total gravitation energy in this new system will have the same value as in the original one, as has been found already in § 60 with the restrictions then introduced.

§ 63. If r' were a tensor, we should have for all substitutions the transformation formulae given at the end of § 40. In reality this is not the case now, but from (96) and (97) we can still deduce that those formulae hold for *linear* substitutions. They may likewise be applied to the stress-energy-components of the matter or of an electromagnetic system. Hence, if \mathfrak{E}_a^b represents the total stress-energy-components, i. e. quantities in which the corresponding components for the gravitation field, the matter and the electromagnetic field are taken together, we have for any linear transformation

$$\frac{1}{\sqrt{-g'}} \mathfrak{E}'_c{}^b = \frac{1}{\sqrt{-g}} \sum (kl) p_{kc} \pi_{lb} \mathfrak{E}^k{}^l \dots \quad (121)$$

We shall apply this to the case of a relativity transformation, which can be represented by the equations

$$x'_1 = ax_1 + bcx_4, \quad x'_2 = x_2, \quad x'_3 = x_3, \quad x'_4 = ax_4 + \frac{b}{c} x_1, \quad (122)$$

with the relation

$$a^2 - b^2 = 1. \dots \dots \dots (123)$$

In doing so we shall assume that the system, when described in the rectangular coordinates x_1, x_2, x_3 and with respect to the time x_4 , is in a stationary state and at rest.

Then we derive from (97)¹⁾

¹⁾ We have $g_{14} = g_{24} = g_{34} = 0$, while all the other quantities g_{ab} are independent of x_4 . Thus we can say that the quantities g_{ab} and $g_{ab,c}$ are equal to zero when among their indices the number 4 occurs an odd number of times. The same may be said of $g^{ab}, g^{ab,c}, \frac{\partial Q}{\partial g_{ab,cd}}$ (according to (116)), $\frac{\partial}{\partial x_k} \left(\frac{\partial Q}{\partial g_{ab,cd}} \right)$ and also of products of two or more of such quantities. As in the last two terms of (97) the indices a, b and f occur twice, these terms will vanish when only one of the indices e and h has the value 4.

As to the first term of (97) we remark that, according to the formulae of § 32, each of the indices a, b and e occurs only once in the differential coefficient of Q with respect to $g_{ab,e}$, while other indices are repeated. As to the number of

$$t'_{14} = t'_{24} = t'_{34} = 0; \quad t'_{41} = t'_{42} = t'_{43} = 0,$$

which means that in the system (x_1, x_2, x_3, x_4) there are neither momenta nor energy currents in the gravitation field.

We may assume the same for the matter, so that we have for the total stress-energy-components in the system (x_1, x_2, x_3, x_4)

$$\mathfrak{T}_{14} = \mathfrak{T}_{24} = \mathfrak{T}_{34} = 0; \quad \mathfrak{T}_{41} = \mathfrak{T}_{42} = \mathfrak{T}_{43} = 0.$$

Let us now consider especially the components \mathfrak{T}'_{14} , \mathfrak{T}'_{41} and \mathfrak{T}'_{44} in the system (x'_1, x'_2, x'_3, x'_4) . For these we find from (121) and (122)

$$\mathfrak{T}'_{14} = \frac{ab}{c} \mathfrak{T}_{11} - \frac{ab}{c} \mathfrak{T}_{44}; \quad \mathfrak{T}'_{41} = -abc \mathfrak{T}_{11} + abc \mathfrak{T}_{44} \quad (124)$$

$$\mathfrak{T}'_{44} = -b^2 \mathfrak{T}_{11} + a^2 \mathfrak{T}_{44} \quad (125)$$

It is thus seen in the first place that between the momentum in the direction of x_1 ($-\mathfrak{T}'_{14}$) and the energy-current in that direction (\mathfrak{T}'_{41}) there exists the relation

$$\mathfrak{T}'_{41} = -c^2 \mathfrak{T}'_{14}$$

well known from the theory of relativity.

Further we have for the total energy in the system (x'_1, x'_2, x'_3, x'_4)

$$E' = \int \mathfrak{T}'_{44} dx'_1 dx'_2 dx'_3,$$

where the integration has to be performed for a definite value of the time x'_4 . On account of (122) we may write for this

$$E' = \frac{1}{a} \int \mathfrak{T}'_{44} dx_1 dx_2 dx_3,$$

where we have to keep in view a definite value of the time x_4 .

If the value (125) is substituted here and if we take into consideration that, the state being stationary in the system (x_1, x_2, x_3, x_4) ,

$$\int \mathfrak{T}_{11} dx_1 dx_2 dx_3 = 0$$

we have

$$E' = aE,$$

if E is the energy ascribed to the system in the coordinates (x_1, x_2, x_3, x_4) .

By integration of the first of the expressions (124) we find in the same way for the total momentum in the direction of x_1

$$G' = \frac{b}{c} E.$$

times which e , h and the other indices occur we can therefore say the same of the first term of (97) as of the other terms. The first term also is therefore zero, if no more than one of the two indices e and h has the value 4.

That t'_{4e} vanishes for $e \neq 4$ is seen immediately.

§ 64. Equations (122) show that in the coordinates (x'_1, x'_2, x'_3, x'_4) the system has a velocity of translation $\frac{bc}{a}$ in the direction of x'_1 . If this velocity is denoted by v , we have according to (123)

$$a = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

If therefore we put

$$M = \frac{E}{c^2},$$

we find

$$E' = \frac{Mc^2}{\sqrt{1 - \frac{v^2}{c^2}}}, \quad G' = \frac{Mv}{\sqrt{1 - \frac{v^2}{c^2}}} \dots \dots (126)$$

When the system moves as a whole we may therefore ascribe to it an energy and a momentum which depend on the velocity of translation in the way known from the theory of relativity. The quantity M , to which the energy of the gravitation field also contributes a certain part, may be called the "mass" of the system. From what has been said in § 62 it follows that within certain limits it depends on the way in which the system and the gravitation field are described.

It must be remarked however that, if for the gravitation field we had chosen the stress-energy-tensor τ_0 (§ 52), the *total* energy of the system even when in motion would be zero. The same would be true of the *total* momentum and we should have to put $M = 0$.

At first sight it may seem strange that we may arbitrarily ascribe to the moving system the momentum determined by (126) or a momentum 0; one might be inclined to think that, when a definite system of coordinates has been chosen, the momentum must have a definite value, which might be determined by an experiment in which the system is brought to rest by "external" forces. We must remember however (comp. § 52) that in the theory of gravitation we may introduce no "external" forces without considering also the material system S' in which they originate. This system S' together with the system S with which we were originally concerned, will form an entity, in which there is a gravitation field, part of which is due to S' (and a part also to the simultaneous existence of S and S'). There is no doubt that we may apply the above considerations to the *total* system (S, S') without being led into contradiction with any observation.

Chemistry. — “*On the Saponification of Fats*”. I. By Dr. J. P. TREUB.
(Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of December 21, 1916).

INTRODUCTION.

§ 1. The saponification of esters of glycerine has been first experimentally studied by GEITEL.¹⁾ He determined the velocity of saponification of the three acetines in diluted acid solution, by titration of the split off acetic acid, and came to the result, that the ratio of the velocity constants of the reactions: triacetine → diacetine → monoacetine → glycerine is as 3 : 2 : 1, from which follows that the ester groups are all saponified with the same velocity, and that the velocity of saponification of a certain ester group is independent of a neighbouring group being saponified or not.

ABEL²⁾ advanced against this that good constants are likewise found when it is assumed that the saponification leads directly from triglyceride to glycerine, and that therefore GEITEL's measurements of velocity do not prove anything.

This is clear, as we arrive at the same equations of velocity in the two different cases as ABEL³⁾ has proved in another paper for the general case of a reaction in n stages.

However with his *measurements of velocity* GEITEL has not proved that the saponification of triacetine proceeds in stages, but only that if it proceeds in stages the velocity constants of the three stages must be in the ratio of 3 : 2 : 1.⁴⁾ This result on the contrary shows the impossibility to decide whether the process goes by stages or not from measurements of the velocity of the splitting off of fatty acid alone.⁵⁾

GEITEL proved that the acid saponification of glycerine esters actually takes place in stages by demonstrating that rancid fats contain more

¹⁾ Z. f. pr. Chem. (2) 55 429 (1897), 57 113 (1898).

²⁾ ULZER u. KLIMONT, *Chemie der Fette* 244 (1906).

³⁾ Z. f. phys. Chem. 56 553 (1906).

⁴⁾ J. MEYER has proved (*Z. f. Electrochem.* 13 485 (1907)), that this ratio only holds in approximation. For 18° C. the following ratio seems to hold more accurately: 3.10 : 2.00 : 1.14, for 25° C : 3.06 : 2.00 : 1.25.

⁵⁾ Cf. also § 12.

bound glycerine than agrees with an immediate splitting up into glycerine and three molecules of fatty acid. He could therefore assume analogous behaviour for the acetines.

JUL. MEYER ¹⁾ has mathematically examined the course of the saponification in acid solution of esters of bivalent acids or alcohols, and has brought this into equation in a very lucid form. It is evident from his formulae that when the first stage passes twice as quickly as the second, the whole saponification becomes seemingly monomolecular. Measurements of velocity carried out by him for the acid saponification of the glycol acetates and of esters of different symmetrically built bi-basic acids, confirm this fully.

Also to J. MEYER's conclusions the objection might be made that a simply monomolecular saponification explains his results equally well. J. MEYER has, however, also determined the velocities of saponification of the methyl esters of the asymmetrical camphoric acid. Of the dimethyl camphorate one ester group now appeared to be much more quickly split off than another. Hence the velocity constants in the saponification of di- and mono-ester are not in the ratio of 2:1, so that here the results of the measurements of velocity lead us to conclude directly to the process in stages of the reaction. The assumption that also in the saponification of glycol esters etc. the reaction takes place in stages, is then perfectly justified. Besides JUL MEYER's experiments support GEITEL's view that the acetines in acid solution are saponified stagewise.

THE SAPONIFICATION IN EMULSION.

§ 2. Both GEITEL's papers and those of JUL. MEYER treat the saponification in solution. In the saponification of fat, however, always more or less fine emulsions of fat and an aqueous solution are worked with, and it is, therefore, now the question in what way the reaction takes place in this case.

In the first place it is the question: Where does the reaction take place? There are, namely, three possibilities:

1. Reaction takes place in the water phase.
2. Reaction takes place in the fat phase.
3. Reaction takes place on the boundary of the two phases.

Let us consider each of these possibilities separately.

1. *The reaction takes place in the water phase.*

In this case the velocity with which the triglyceride is converted, is determined by the number of molecules dissolved in the water

¹⁾ Z. f. phys. Chem. 66 81 (1909).

phase. Now follows immediately another question, viz. may in this case an equation of velocity be applied which holds good for a solution? As NERNST¹⁾ has observed an equation of velocity holding for a homogeneous system leads to an entirely wrong conclusion in a heterogeneous system, when the velocity of reaction is dependent on the velocities of diffusion. This will always be the case where the velocity of reaction is great with respect to the velocity of diffusion.

When, however, on the contrary in a heterogeneous system the concentration equilibrium sets in rapidly, and the reaction proceeds comparatively slowly, the influence of the diffusion velocity is only slight, and can become quite imperceptible. This now is generally the case when both phases are liquid. When a substance *A* dissolved in a solvent *B* is shaken with a solvent *C*, which does not mix with *B*, only a very short time is required to establish the equilibrium between the two solutions.

H. GOLDSCHMIDT²⁾ has determined the velocity of saponification of ethyl acetate dissolved in benzine and shaken with about normal hydrochloric acid. Assuming that the reaction takes place in the aqueous solution he represented the velocity of saponification by the equation:

$$-\frac{dx}{dt} = K \cdot \frac{v_1 \cdot C}{v_2 + v_1 \cdot C} x \dots \dots \dots (1)$$

in which v_1 = volume of the aqueous solution, v_2 = volume of the benzolic solution, C = constant of partition of ethyl acetate between water and benzene. On the whole the reaction velocity appeared to be well represented by this equation.

Towards the end, the reaction in the opposite sense had to be taken into account.

It appears from this that when the velocity of reaction is not too great, the equations of velocity which hold in a homogeneous system may be applied in a heterogeneous system, consisting of two liquid phases.

Let us now return to the saponification of fat, and let us imagine the case that a triglyceride is saponified with diluted sulphuric acid according to the TWITCHELL process, in which fat and aqueous solution is held in emulsion by blowing in of steam, after addition of about $\frac{1}{2}$ % TWITCHELL reagent. GOLDSCHMIDT's formula may certainly not be used in this case for quantitative determinations. For

¹⁾ Z. f. phys. Chem. 47 55 (1904).

²⁾ Z. f. phys. Chem. 31 235 (1899).

NERNST'S law of partition cannot be applied here unreservedly, as the fat phase consists chiefly of triglyceride at the beginning of the saponification and chiefly of fatty acid at the end. The "constant" of partition C can, therefore, not be constant in this case. We can, however, draw a conclusion from equation (1) as to the probability or improbability of the supposition that the saponification takes place in the water phase. For at any rate there appears from it that if the said supposition is valid, the extent of the surface of contact between fat particles and water particles plays no part. But then the action of the TWITCHELL reagent must chiefly rest on this that it causes an increase of C , in other words, increases the solubility of the fat in the water phase. This is in itself very well possible, but seeing that the saponification without reagent practically does not take place, and obtains an efficient velocity on addition of not quite half a percentage to the emulsion, it is very improbable indeed, that increase of the solubility of the fat in the water phase should be the cause of it.

As will appear in § 4, the action of the TWITCHELL reagent can be quite plausibly accounted for by the supposition that the saponification takes place on the boundary of fat and water.

There is, however, another phenomenon that points to this. It appears namely, that, when triglycerides which contain little or no free fatty acid, are saponified, the reaction velocity is very small at first, then it increases and reaches a maximum. WEGSCHEIDER¹⁾, who assumes the reaction in the aqueous solution, wants to explain this by taking the concentration of the triglyceride in the water-phase constant. The increase of the reaction velocity would then be caused by the presence of lower glycerides in the waterphase. On this assumption WEGSCHEIDER comes to the following equation of velocity for the splitting off of fatty acid:

$$\frac{dx}{dt} = 9k \cdot C - 6k \cdot C \cdot e^{-kt} \dots \dots \dots (2)$$

In this C represents the not changing concentration of the triglyceride in the aqueous solution, k is a constant of velocity.

Equation (2) would really be able to explain the increase of the velocity of saponification, if it could be applied to the saponification of fat in this form. Now it is clear that (2) can only hold for the saponification by means of bases, as only in this case the fat phase which is in contact with the aqueous solution, consists practically exclusively of triglycerides, because of which the concentration of

¹⁾ Kais. Ak. d. Wissensch. Wien 116, II b. 1325 (1907).

the triglyceride in the waterphase may be taken constant. As will appear in § 19 the saponification in alkaline surroundings takes place however practically directly from triglyceride to glycerine + fatty acid. Then the second term of the second member of (2) disappears, and we should have a velocity of saponification which does not change with the time. The facts, however, are different.

If the reaction takes place on the boundary of the two phases, the increase of reaction velocity is at once apparent. At the beginning we have namely a not very intimate emulsion of lye and triglyceride. As the saponification advances, the soap concentration in the waterphase increases, the surface tension between fat- and waterphase accordingly decreases; hence the emulsion becomes more intimate, and the surface where the reaction can take place, becomes greater.

After what precedes we may, therefore, put aside the first possibility as very improbable.

§ 3. 2. *The reaction takes place in the fat phase.*

This supposition is still less tenable, as a reaction which is catalytically accelerated by H⁺ or OH⁻ ions, is very improbable in not aqueous surroundings.

§ 4. So the last possibility remains, namely:

3. *The reaction takes place on the boundary of the two phases.*

In the saponification in acid solution the velocity is a function of the number of collisions in the unity of time between an ester molecule and an H⁺ ion. For a given concentration and a definite temperature this number of collisions is fixed and therefore the velocity constant also.

If, however, as in the TWITCHELL process we have an emulsion of fat- and water particles, which move through one another in fine division, and if the reaction takes place on the boundary of the two phases, the velocity will be a function of the extent of the surface where the collisions can take place, i. e. of the fineness of the emulsion; hence the velocity constant will *not* be definite at a given temperature.

In the TWITCHELL process the accelerating influence of the reagent must chiefly, if not entirely, be found in the enlargement of the surface of contact between fat- and waterphase, in other words in the decrease of the surface tension between fat and water. That actually this surface tension is considerably decreased by traces of

reagent can be easily shown with DONNAN'S pipette.¹⁾ (see § 7).

It may seem arbitrary that where it appears that already traces of TWITCHELL reagent considerably decrease the surface tension between fat and water, it has been assumed in § 2, that those traces cannot practically influence the solubility of the fat in water. Yet this is by no means the case. In order to increase the solubility of fat in water sufficiently a solvent for triglyceride would have to be added to the waterphase, which mixes with water. Further the waterphase would have to exhibit a certain (pretty considerable) concentration of this solvent throughout its volume. For a substance, however, which lowers the surface tension between fat and water this need not be the case. For the action of a substance to lower the surface tension is accompanied with adsorption at the surface common to the two phases, in consequence of which such a substance, though if calculated over the whole mass, it is present only in traces, can occur in pretty considerable concentration at the common surface. It is exactly this surface layer that counteracts the tendency of two colliding drops to join to one whole.²⁾

The same considerations are also valid for the saponification in alcalic surroundings. Here the soap formed in the saponification acts so as to lower the surface tension between fat and water.

We arrive therefore at the conclusion that in the saponification in emulsion the reaction practically takes entirely place on the boundary of the fat and the water phase. We may then apply the equations of velocity holding in solution, when we take the fact into account that the constant of velocity depends on the fineness of the emulsion.

§ 5. Measurements of velocity have been carried out by M. NICLOUX³⁾, who studied the saponification of cottonseed oil by the aid of the ferment found in ricinus seed. He found for :

$$k = \frac{1}{t} \log \frac{a}{a-x}$$

a good constant especially at low temperature (15°). From this it appears that in this case the fineness of the emulsion does not appreciably change during the saponification and that the ratio of the saponification velocities of the three glycerides is as 3 : 2 : 1 or as 1 : ∞ : ∞.⁴⁾

1) Z. f. phys. Chem. **31**, 42 (1899).

2) DONNAN loc. cit.

3) Saponification des corps gras (1906).

4) See § 12.

As NICLOUX states¹⁾ that the quantity of glycerine split off after a certain time corresponds to the split off quantity of fatty acid, the latter ratio must be correct. In the experiments of M. NICLOUX triglyceride seems to have split off practically directly into fatty acid and glycerine.

In the saponification by means of bases the fineness of the emulsion does certainly not remain constant. For here the soap that is formed gives rise to a lowering of the surface tension between fat and aqueous solution, hence the fineness of the emulsion will increase during the saponification. The same thing holds, at least for the beginning of the reaction, for the autoclave saponification with zinc oxide and likewise for the saponification with lime. Nor does the fineness of the emulsion remain the same in the course of the TWITCHELL process. As can be shown with the aid of DONNAN'S pipette the surface tension between e.g. linseed oil fatty acid and water is smaller than between linseed oil and water. Here too the surface - of contact between fat and water phase will therefore become larger in the course of the reaction.

It is clear that in these cases measurements of velocity are of little use. The constant of velocity will always present a course, and then there is no criterion whether the equations of velocity that have been drawn up, are correct or not. We shall have to adopt another course here.

When we draw up equations of velocity for the splitting off of fatty acid in the saponification of triglyceride, and when there occurs in them only one constant k , which is dependent on the extent of the surface of contact of fat- and waterphase, and which therefore from the beginning of the saponification may be considered really constant only during a small period Δt_1 , we arrive after integration of the drawn up equations between the limits 0 and Δt_1 at a relation between the number of molecules of fatty acid (z) split off after the time Δt_1 and k and Δt_1 . Let this function be:

$$z = f(k \times \Delta t_1) \dots \dots \dots (3)$$

For stagewise saponification a second equation denotes: the number of molecules of glycerine (s) split off after the time Δt_1 as function of k and Δt_1 . Let this function be:

$$s = \varphi(k \times \Delta t_1) \dots \dots \dots (4)$$

If we now can eliminate $k \times \Delta t_1$ from the two equations (3) and (4), we find a relation:

$$\psi(z, s) = 0 \dots \dots \dots (5)$$

¹⁾ l. c. 52.

which indicates the relation between the number of molecules of glycerine and fatty acid split off after the time Δt_1 .

Let us now imagine that after the time Δt_1 has elapsed, the constant of velocity k changes into k' , and let us now consider a following period Δt_2 . At the beginning of this period the following equation holds:

$$\begin{aligned} z &= f(k \times \Delta t_1) \\ s &= \varphi(k \times \Delta t_1) \end{aligned}$$

The same values z and s could, however, have been obtained with the constant of velocity k' in a certain period $\Delta t'_1$, so that:

$$\Delta t'_1 = \frac{k}{k'} \cdot \Delta t_1 \quad \dots \dots \dots (6)$$

At the beginning of this period we have, therefore, also:

$$\begin{aligned} z &= f(k' \times \Delta t'_1) \\ s &= \varphi(k' \times \Delta t'_1), \end{aligned}$$

but then is after the lapse of the time t_2 :

$$z = f\{k' \times (\Delta t'_1 + \Delta t_2)\}$$

and

$$s = \varphi\{k' \times (\Delta t'_1 + \Delta t_2)\}.$$

From these last equations $k' \times (\Delta t'_1 + \Delta t_2)$ can be eliminated in the same way as $k \times \Delta t_1$ from (3) and (4), which proves, therefore, that (5) also holds after Δt_2 has passed.

Since the same reasoning may be extended over the whole saponification, it appears that when the number of molecules of split off fatty acid in the saponification of fat can be represented by:

$$z = f(k \times t)$$

and the number of molecules of split off glycerine by

$$s = \varphi(k \times t),$$

in which equations k varies with the time, we must be able to derive a function:

$$\psi(z, s) = 0$$

by elimination of $k \times t$, the form of which does not change during the saponification, and which is independent of the change of k .

Since in the saponification of fat both split off glycerine and free fatty acid can be determined separately, we have a means in this to examine the mechanism of the reaction.

It may still be pointed out here that in the change of k with the time must also be included the decrease of concentration of the lye taking place in the saponification in alkaline surroundings. We shall, therefore, have to arrive at analogous equations for acid and alkaline saponification.

§ 6. Before proceeding to the derivation of an equation $\psi(z,s) = 0$, we must first discuss the question what is to be expected in the saponification of fats in which *different* fatty acids are present.

The natural fats are, namely, mixtures of different triglycerides and in a molecule of triglyceride there are often found two, sometimes three different groups of fatty acid. Now it is first of all conceivable that e. g. the oleic acid group is more easily separated from a molecule of oleo-dipalmitine than a palmitinic acid group. Secondly, however, the possibility exists e. g. for a mixture of trioleine and tripalmitine that the surface tension of one of these glycerides in contact with the water surroundings with which the saponification is carried out, is lower than that of the other. The consequence of this would be that the triglyceride, which has the lowest surface tension in contact with the water phase, was adsorbed at the common surface, and was consequently more rapidly saponified.

Of this, however, nothing has ever appeared.

It has been shown by THUM.¹⁾ that in the saponification with bases as well as when palm oil and olive oil become rancid, the iodine value of the split off fatty acids agrees with that of the fatty acids that are still combined to glycerine.

STIEPEL²⁾ finds for autoclaved tallow fatty acids that the still combined fatty acids exhibit a somewhat higher iodine value than the split off ones; for the autoclavation of cocoanut oil and palm kernel oil he arrives, however, at the conclusion that the split off and the combined fatty acids have the same composition. STIEPEL finds a corroboration of this³⁾ in the fact that on distillation of partially saponified cocoanut and palm kernel oil the distillate presents the same acid values as that on second distillation of the fat mass that had first remained behind in the kettle, after this mass had been saponified anew, and now entirely.

It follows from this that a difference in saponifiability between ester groups of different fatty acids may in general be neglected, and further that the surface tensions of the glycerides occurring in the fats examined by THUM and STIEPEL in contact with the saponifying surroundings can be only little divergent.

CONNSTEIN, HOYER and WARTENBERG⁴⁾ have found that the fermentative saponification with the ricinus seed ferment proceeds more

¹⁾ Z. f angew. Chem. **3** 482 (1890).

²⁾ Seifens. Ztg. **31** 937, 965, 986, 1006, 1026 (1904), **36**, 788, (1909).

³⁾ Seifens. Ztg. **35** 1359 (1908).

⁴⁾ Ber. **35**. 3988. (1902).

slowly as the molecular weight of the combined acids is lower. It is therefore not excluded that also when glycerides of fatty acids of different molecular weight occur side by side, they will present here a specific saponification velocity. Experiments of the same nature as have been made by THUM and STIEPEL are not mentioned by CONNSTEIN c. s.

§ 7. In order to be able to form an opinion about the surface tensions of fats in contact with different media, I made the following experiments:

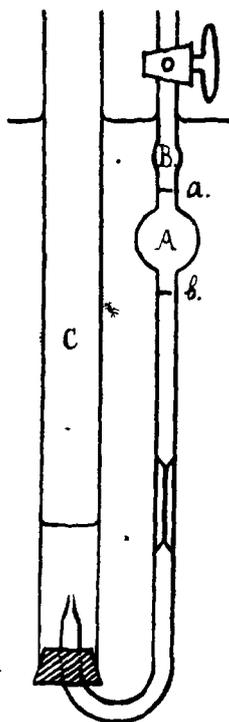


Fig. 1.

With the aid of DONNAN'S pipette the number of drops were counted which, when a definite volume of different triglycerides flowed from a thin walled capillary, mounted up in water and some solutions, all this at 100° C. The arrangement of the experiments follows from fig. 1. The pipette with the tube C which contained the aqueous solution, was heated to 100° in a large glass beaker with water. During the outflow of the fat the beaker was not heated to avoid shaking through the boiling of the water. The filling took place by the fat being sucked up into the bulb B. The mouth of the capillary was then cleaned as well as possible with a cloth, and the tube C was fastened with a rubber stopper. The whole was now carefully heated in the beaker till the fat just appeared from the capillary mouth, then the solution (always a same quantity) was poured into C along the wall.

When the whole had reached the temperature of 100° , then the level of the fat was reduced to *a* by opening of the cock, and then the number of drops was counted which mounted in the solution in C during the fall of the level of the fat from *a* to *b*. The diameter of the capillary mouth was about 1 mm. Trilaurine flowed out from *a* to *b* in about 4 minutes.

During the outflow of the fat every drop remains hanging at the capillary mouth till the upward pressure exceeds the tension of the surface. The greater, therefore, this surface tension is, the fewer drops will get detached when a definite volume of the fat substance flows out, and the smaller the number of drops that will mount in the aqueous liquid. When we disregard the difference in specific weight of the different triglycerides, the tension of the surface of

contact is roughly inversely proportional to the number of drops.

It is clear that the results obtained with the described apparatus give an indication only in rough approximation about the ratio of the surface tensions of different glycerides in contact with aqueous solutions. To determine this ratio quantitatively more accurate measurements are necessary than can be carried out with the DONNAN pipette. It will, however, appear in § 19 et seq. that the data obtained in the described way, can qualitatively entirely account for the phenomena that present themselves in the saponification of fats.

The obtained results are recorded in table I.

TABLE I.

1	2	3		4	5	6	7	8	9	10
Triglyceride	Acid value	Saponification value		Iodine value	Solidifying point of the fatty acids	Number of drops mounting at 100° C. in.				
		Calculated	Found			Water	1% solution of TWIRCHELL reagent in H ₂ O	10% solution of potassium laurate in H ₂ O	12.3% solution of potassium palmitate in H ₂ O	
Trilaurine	0.0	264.0	264.3	0.0	43.7	10	44	53	190	
Tripalmitinē	<0.2	208.9	208.3	0.8	62.0	12	45	(110)	(370)	
Tristearine	<0.2	189.2	190.0	0.0	68.7	13	50	(85)	—	
Olive oil	1.43	—	191.0	83.9	22.5	11	50	(100)	(340)	
Linseed oil	<0.2	—	191.3	182.3	20.6	15	48	(70)	(210)	

Trilaurine was obtained by recrystallisation of Tangkallak fat from alcohol, then from ether, tripalmitine by recrystallisation of Chinese vegetable tallow from benzene, then washing of the obtained product with alcohol, and again recrystallisation from ether. Tristearine by recrystallisation of catalytically hardened linseed oil from benzene, then also washing with alcohol and recrystallisation from ether. The olive oil used was oil sold for consumption from French origin. The linseed oil had been freed from free fatty acid as well as possible by treatment with lye. From the constants recorded in

columns 2—6 the purity of the examined triglycerides appears sufficiently.

It now appears from columns 7 and 8 that the surface tensions of the examined triglycerides in contact with water and a 1 % solution of TWITCHELL reagent diverge but little *inter se*, and it is clearly visible that in the presence of reagent the drops get sooner detached, the surface tension between fat and water phase has therefore decreased.

In alcalic surroundings greater divergencies were found between the different triglycerides *inter se* (see columns 9 and 10). It is, however, very much the question if they are essential. In triglycerides which cannot, like trilaurine, be purified by recrystallisation from alcohol, it is exceedingly difficult to remove the last traces of free fatty acid. In alcalic surroundings these traces cause a lowering of the surface tension, and give moreover rise to irregular moistening of the capillary mouth, which is the cause that often great deviations are found in repeated determinations. The values which are little reliable for this reason, have been placed between (). The lowest number of drops (rounded off to tens) that was found on repeated determination, has always been given. These values are of importance in so far, that they show clearly the influence of the molecular weight of the soap which is dissolved in the water.

As appears from THUM and STIEPEL's observations and from the results with DONNAN's pipette described in this §, no difference need in general be made in the derivation of an equation $\psi(z, s) = 0$ between natural fats and simple triglycerides. A function derived on this supposition must, however first be tested by different fats in the fermentative saponification, before further conclusions are drawn from it.

DERIVATION OF AN EQUATION $\psi(z, s) = 0$.

§ 8. As the reaction takes place on the boundary of fat and water phase, the velocity with which each of the stages of saponification proceeds, will be governed by the surface tension of tri-, di- and monoglycerides against saponifying surroundings. For if e. g. the surface tension of the diglyceride against the water phase is smaller than that of the tri-glyceride, the diglyceride will directly after its formation be adsorbed at the surface of contact, and therefore reach a greater concentration in the surface layer than when no adsorption took place. The consequence of this will be that an ester group of a molecule of diglyceride has on an average a greater

chance to be saponified than an estergroup of a molecule of triglyceride.

To be able to form an opinion about the surface tensions of tri-, di-, and monoglycerides against saponifying surroundings the behaviour of the laurines was examined by the aid of the apparatus described in the preceding §. The results are found in table 2.

TABLE 2.

1	2	3	4	5	6	7
Fat substance	Saponification value		Melting point	Number of drops flowing out at 100° C. into:		
	Calculated	Found		Water	1% solution of TWITCHELL reagent in H ₂ O	10% solution of potassium laurate in H ₂ O
Trilaurine	264.0	264.3	46°	10	44	53
Dilaurine	246.3	246.3	54	13.5	42	470
Monolaurine	205.0	204.4	62.8	—	—	—
90 Trilaurine + 10 Dilaurine	—	—	—	12	44	90
90 „ + 10 Monolaurine	—	—	—	80	280	flows!
Laurinic acid	280.7	280.4	43.7 ¹⁾	38	70	—

The laurinic acid was prepared by saponification of trilaurine, obtained from Tangkallak fat, followed by distillation in vacuo. The lower laurines were obtained by esterification of laurinic acid with excess of glycerine at about 200° in the way indicated by VAN ELDIK THIEME²⁾. To purify the dilaurine it was first recrystallized from alcohol (to remove monolaurine), then from benzene (to remove trilaurine). The monolaurine was first recrystallized from petroleum-ether (to remove di- and trilaurine), then from alcohol (to remove monolauryldiglycerine). All the glycerides were perfectly free from oleic acid and free fatty acid. For the rest the constants mentioned in columns 2—4 sufficiently express the purity of the substances used.

The number of drops of monolaurine rising in aqueous solutions could not be determined, as a skin is formed on the boundary of

¹⁾ Solidifying point.

²⁾ Thesis for the doctorate. Delft (1911).

monolaurine and water, so that there is no question of "drops". To be able to form in spite of this an opinion about the surface tension of monolaurine against aqueous solutions, the number of drops that mounted of a mixture of 90 % trilaurine and 10 % monolaurine, has been given in table 2, while for a comparison the thus obtained values of dilaurine have been given.

From table 2 the following conclusions can be drawn:

1. In acid and neutral surroundings the surface tensions of tri- and dilaurine in contact with the saponifying medium differ little, that of monolaurine is much less. We must therefore expect that in case of saponification in non alkaline surroundings the monoglyceride will be adsorbed at the boundary of fat- and water phase, and will, therefore, be saponified with a velocity greater than that with which it has been formed.

2. In alkaline surroundings both the surface tensions of di- and of monolaurine in contact with the saponifying medium are much smaller than that of trilaurine. Both di- and monoglycerides will, therefore, be absorbed here at the boundary layer; hence they are saponified with velocities greater than that with which they have been formed.

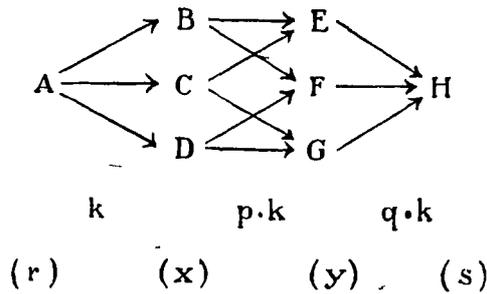
As appears from what precedes the increase of concentration of the lower glycerides at the surface of contact between fat and water phase must be taken into account in the derivation of an equation $\psi(z, s) = 0$. We now put:

p resp. *q* = the number of times that the concentration of the diglyceride, resp. monoglyceride at the boundary layer is greater in consequence of the adsorption than if no adsorption had taken place, and we put *p* and *q* both constant.

This assumption is an approximation, because the adsorption is not proportional to the total concentration of the adsorbed substance. ¹⁾ This approximation will be the closer as the concentration of the lower glycerides will vary between a narrower margin during the saponification.

§ 9. Since the difference in velocity of saponification between esters of primary and secondary alcohols is only slight, and the isomeric di- and monoglycerides can therefore be considered here as equivalent with close approximation (which also follows from GEITEL's and J. MEYER's results), we come to the following scheme for the saponification of fat:

¹⁾ See FREUNDLICH, Z. f. phys. Chem. 57, 385 (1907).



In this A represents a molecule of triglyceride, which can be converted into a molecule of diglyceride (B , C , or D) in three ways with a constant of velocity k . A molecule of diglyceride, e.g. B can give a molecule of monoglyceride (E or F) in two ways with a constant of velocity $p.k$, while finally every molecule of monoglyceride forms glycerine (H) with a velocity constant $q.k$. The number of molecules of A present after a time t will be expressed by r , the number of molecules of B , C , and D each by x , of E , F , and G each by y , and of H by s .

It is clear, that when there is no difference in saponifiability of the different ester groups, the concentrations of B , C , and D , and of E , F , and G are equal inter se at any moment.

Let us now suppose a molecules of triglyceride A to be present at the beginning of the reaction.

The velocity of saponification of A is now denoted by the equation:

$$-\frac{dr}{dt} = 3k \cdot r \dots \dots \dots (7)$$

When we integrate (7) and consider that for $t = 0$, $r = a$, then follows:

$$r = a \cdot e^{-3kt} \dots \dots \dots (8)$$

The variation of the number of molecules B (hence also of C and D) is represented by:

$$\frac{dx}{dt} = k \cdot r - 2pk \cdot x \dots \dots \dots (9)$$

When the value of r from (8) is substituted in (9), then follows:

$$\frac{dx}{dt} + 2pk \cdot x = a \cdot k \cdot e^{-3kt} \dots \dots \dots (10)$$

This equation can be solved by putting:

$$x = \tilde{m} \times n \dots \dots \dots (11)$$

in which, therefore, an arbitrary value can be given e.g. to m ; n is then fixed.

As

$$\frac{dx}{dt} = m \cdot \frac{dn}{dt} + n \cdot \frac{dm}{dt},$$

(10) passes into:

$$m \frac{dn}{dt} + n \left\{ \frac{dm}{dt} + 2pk \cdot m \right\} = a \cdot k \cdot e^{-3kt} \quad \dots \quad (12)$$

Let us now take m so that

$$\frac{dm}{dt} + 2pk \cdot m = 0.$$

On integration of this last equation we then find for m :

$$m = e^{-2pkt} \quad \dots \quad (13)^1$$

Introducing this value into (12), we get:

$$e^{-2pkt} \cdot \frac{dn}{dt} = a \cdot k \cdot e^{-3kt},$$

from which by integration:

$$n = \frac{a}{2p-3} \cdot e^{(2p-3)kt} + C \quad \dots \quad (14)$$

Now follows from equations (11), (13), and (14):

$$x = m \cdot n = \frac{a}{2p-3} e^{-3kt} + C \cdot e^{-2pkt} \quad \dots \quad (15)$$

Bearing in mind that for $t=0$ also $x=0$, we find for the integration constant C :

$$C = -\frac{a}{2p-3},$$

through which (15) passes into:

$$x = \frac{a}{2p-3} \cdot \{e^{-3kt} - e^{-2pkt}\} \quad \dots \quad (16)$$

The change of the number of molecules E (hence also of F and G) is represented by:

$$\frac{dy}{dt} = 2pk \cdot x - qk \cdot y \quad \dots \quad (17)$$

If the value of x from (16) is substituted in (17), then follows:

$$\frac{dy}{dt} + qk \cdot y = a \cdot \frac{2pk}{2p-3} \cdot \{e^{-3kt} - e^{-2pkt}\} \quad \dots \quad (18)$$

This differential equation can be solved in the same way as (10). We then find:

¹⁾ A constant of integration can of course be omitted here

$$y = a \cdot 2p \cdot \left\{ \frac{e^{-3kt}}{(2p-3)(q-3)} - \frac{e^{-2pkt}}{(2p-3)(q-2p)} + \frac{e^{-qkt}}{(q-3)(q-2p)} \right\}. \quad (19)$$

At last the number of molecules of split off glycerine (s) can be calculated from:

$$\frac{ds}{dt} = 3gk \cdot y,$$

or from:

$$s = a - r - 3(x + y).$$

We then find:

$$s = a \left\{ 1 - \frac{2pq}{(2p-3)(q-3)} e^{-3kt} + \frac{3q}{(2p-3)(q-2p)} e^{-2pkt} - \frac{6p}{(q-3)(q-2p)} e^{-qkt} \right\}. \quad (20)$$

The number of molecules of split off fatty acid is, as appears from the scheme at the beginning of this §.

$$z = 3x + 3 \cdot 2y + 3s.$$

When we substitute in this the equations (16), (19), and (20), we get:

$$z = 3a \cdot \left\{ 1 - \frac{1 + (2p-1)(q-2)}{(2p-3)(q-3)} e^{-3kt} + \frac{2(q-p)}{(2p-3)(q-2p)} e^{-2pkt} - \frac{2p}{(q-3)(q-2p)} e^{-qkt} \right\}. \quad (21)$$

Now we can eliminate $k \cdot t$ from the formulae (20) and (21) for definite values of p and q , which gives us a relation between s and z . It is however, more practicable to substitute two other quantities for s and z .

The total number of molecules of glycerine is a . If we now call that part of the total quantity of molecules of glycerine that is split off g , then

$$g = \frac{s}{a}.$$

The total number of molecules of fatty acid is $3a$. If we now call that part of the total quantity of molecules of fatty acid that is split off T , then:

$$T = \frac{z}{3a}.$$

Now follows from the equations (20) and (21):

$$g = 1 - \frac{2pq}{(2p-3)(q-3)} e^{-3kt} + \frac{3q}{(2p-3)(q-2p)} e^{-2pkt} - \frac{6p}{(q-3)(q-2p)} e^{-qkt} \quad (22)$$

and

$$T = 1 - \frac{1 + (2p-1)(q-2)}{(2p-3)(q-3)} e^{-3kt} + \frac{2(q-p)}{(2p-3)(q-2p)} e^{-2pkt} - \frac{2p}{(q-3)(q-2p)} e^{-qkt} \quad (23)$$

If now p and q are successively given different values, we obtain

4*

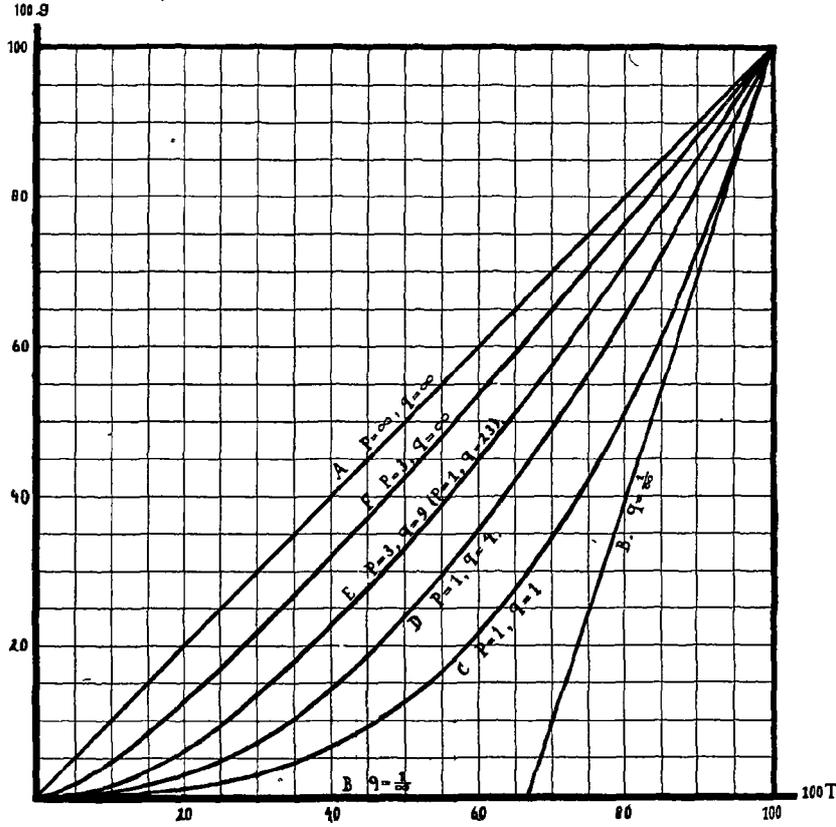


Fig. 2.

$$T = 1 - \frac{4p-3}{6p-9} e^{-3kt} + \frac{1}{2p-3} e^{-2pkt} - \frac{1}{3} \dots (28)$$

i.e. in finite time no glycerine is split off, the reaction goes no further than monoglyceride. In finite time T approaches $2/3$.

If $t = \infty$, (22) and (23) passes for $q = \frac{1}{\infty}$ into:

$$g = 1 - e^{-gkt} \dots (29)$$

$$T = 1 - \frac{1}{3} e^{-gkt} \dots (30)$$

from which:

$$T = 2/3 + 1/3g \dots (31)$$

For $q = \frac{1}{\infty}$ we find therefore the two boundary lines

$$g = 0 \text{ and } T = 2/3 + 1/3g;$$

both are indicated by B in fig. 2.

All the curves $\psi(T,g) = 0$ which are possible for different values of p and q , must therefore lie within the limits:

$$g = T, g = 0, \text{ and } T = 2/3 + 1/3g$$

§ 12. Let us now put $p = 1$, $q = 1$. The physical meaning of this is that there is no question of adsorption, because the surface tensions of all the glycerides in contact with the saponifying surroundings are the same. The velocity of saponification of an ester group is now independent of whether or no a neighbouring group is saponified.

For this case we find from (22) and (23):

$$g = (1 - e^{-kt})^3 \dots \dots \dots (32)$$

$$T = 1 - e^{-kt} \dots \dots \dots (33)$$

from which:

$$g = T^3 \dots \dots \dots (34)$$

This curve is indicated by C in fig. 2. It touches the boundary lines B at $g = T = 0$ and at $g = T = 1$.

Equation (34) is valid for the saponification in solution. From GETTEL's¹⁾ and J. MEYER's¹⁾ measurements follows that it holds for the saponification of triacetine, at least with close approximation. If it is possible to measure the split off quantity of glycerine in this

TABLE 3.

1	2	3	4	5	6	7	8
	Value of 100 T for:						
100 g	$p=1$ $q=1$	$p=2$ $q=2$	$p=1$ $q=4$	$p=3$ $q=9$ of $(p=1)$ $(q=23)$	$p=1$ $q=\infty$	$p=3$ $q=\infty$	$p=\infty$ $q=\infty$
0	0	0	0	0	0	0	0
10	46.42	39.03	34.29	25.99	22.66	17.20	10
20	58.48	51.90	45.99	37.56	34.59	28.24	20
30	66.94	61.45	55.20	47.25	44.73	38.26	30
40	73.68	69.27	63.17	55.99	53.92	47.75	40
50	79.37	75.98	70.37	64.12	62.50	56.90	50
60	84.43	81.89	77.02	71.83	70.63	65.82	60
70	88.79	87.17	83.24	79.21	78.41	74.55	70
80	92.83	91.94	89.15	86.34	85.88	83.15	80
90	96.55	96.22	94.73	93.26	93.10	91.62	90
100	100	100	100	100	100	100	100

¹⁾ loc. cit.

case, then the saponification of triacetine in stages can be *directly* proved by this way.

When the equations (25) and (33) are compared it appears¹⁾ that measurement of the velocity of fatty acid separation can never be conclusive with respect to the question whether or no the saponification of triacetine in acid solution takes place in stages²⁾.

In column 2 of table 3 (see p. 54) we find the values of 100 T corresponding to the given values of 100 g for the case that $p = q = 1$.

§ 13. Let us now put $p = 1, q = 4$, i.e. in consequence of the adsorption the concentration of the monoglyceride in the boundary layer is 4 times as great as it would be if no adsorption had taken place. For this case equations (22) and (23) become:

$$g = 1 + 8e^{-3kt} - 6e^{-2kt} - 3e^{-4kt} \dots \dots \dots (35)$$

$$T = 1 + 3e^{-3kt} - 3e^{-2kt} - e^{-4kt} = 1 - e^{-kt} \{1 - (1 - e^{-kt})^3\} (36)$$

From these two equations e^{-kt} can be eliminated by solving the fourth power equation (35) and substituting the found value in (36).

From (35) we find:

$$e^{-kt} = \frac{1}{4} \left\{ 4 - \sqrt{16 - 9z} + \sqrt{9z - 4 - 8\sqrt{16 - 9z} + 18\sqrt{(2-z)^2 + \frac{4}{3}(1-g)}} \right\} \quad (37)$$

in which:

$$z = \frac{2}{3} \cdot \left\{ 2 - \sqrt[3]{g(1 - \sqrt{1-g})} - \sqrt[3]{g(1 + \sqrt{1-g})} \right\}$$

In column 4 of table 3 are found the values of 100 T calculated by the aid of these equations.

These equations will be more fully discussed in § 22. The curve D of fig. 2 represents the corresponding values of 100 T and 100 g graphically. It touches the boundary line B at $g = T = 0$.

§ 14. If we put $p = 2, q = 2$, then

$$g = 1 + 8e^{-3kt} - 3e^{-4kt} - 6e^{-2kt} \dots \dots \dots (35)$$

$$T = 1 + e^{-3kt} - 2e^{-2kt} = 1 - e^{-2kt}(2 - e^{-kt}) \dots \dots \dots (38)$$

It appears that the split off quantity of glycerine is a same function of the time as in the case that $p = 1, q = 4$. This is a general property. If $p = 2m$ and $q = 2m$, or $p = m$ and $q = 4m$, in both cases we have:

$$g = 1 - \frac{8m^2}{(4m-3)(2m-3)} e^{-3kt} - \frac{3}{4m-3} e^{-4mkt} + \frac{6}{2m-3} e^{-2mkt}$$

¹⁾ In the acid saponification in solution k is invariable.

²⁾ Cf. § 1 The fatty acid splitting off likewise becomes seemingly monomolecular for $p = 1/p, q = \infty$ and for $p = \infty, q = 2$.

Hence in order to calculate T for a definite value of g , for the case $p = 2, q = 2$, we can make use of the equations (37) and (38). The thus obtained value is found in column 3 of table 3.

§ 15. If we put $p = 3, q = 9$, (22) and (23) change into:

$$g = (1 - e^{-3kt})^3 \dots \dots \dots (39)$$

$$T = \frac{1}{3} \{ (1 - e^{-3kt})^3 + (1 - e^{-3kt})^2 + 1 - e^{-3kt} \} \dots \dots (40)$$

from which:

$$T = \frac{1}{3} \cdot \{ g + g^{2/3} + g^{1/3} \} \dots \dots \dots (41)$$

In column 5 of table 3 are found the values of 100 T calculated by the aid of this equation. The curve E of fig. 2 represents the corresponding values of 100 T and 100 g for this case graphically. It touches the boundary line B at $g = T = 0$.

With a deviation $< 0,3\%$, equation (41) holds also for the case $p = 1, q = 23$. This will be more fully discussed in § 21.

§ 16. For $p = 1, q = \infty$ (22) and (23) change into:

$$g = 1 + 2 e^{-3kt} - 3 e^{-2kt} \dots \dots \dots (42)$$

$$T = 1 + e^{-3kt} - 2 e^{-2kt}, \dots \dots \dots (43)$$

from which

$$(1 + g - 2 T)^3 = (1 + 2 g - 3 T)^2 \dots \dots \dots (44)$$

If T is solved from this, we find:

$$T = \frac{1}{3} \{ 1 + 4g + 2\sqrt{1 + 8g} \cdot \cos(120^\circ - \frac{1}{3} \varphi) \},$$

in which:

$$\cos \varphi = - \frac{8g^2 + 20g - 1}{\sqrt{(1 + 8g)^3}} \dots \dots \dots (45)$$

The values of 100 T calculated from this are found in column 6 of table 3.

§ 17. If we put $p = 3, q = \infty$, (22) and (23) become:

$$g = 1 - 2 e^{-3kt} + e^{-6kt} \dots \dots \dots (46)$$

$$T = 1 - \frac{5}{3} e^{-3kt} + \frac{2}{3} e^{-6kt} \dots \dots \dots (47)$$

from which:

$$T = \frac{1}{3} (2g + \sqrt{g}) \dots \dots \dots (48)$$

In column 7 of table 3 are found the values of 100 T calculated from this. The curve F of fig. 2 represents the corresponding values of 100 T and 100 g for this case graphically. It touches the boundary line B at $g = T = 0$. Equation (48) will be more fully discussed in § 20.

Testing of the Derived Formulae.

§ 18. Measurements for the purpose of a comparison of the split off quantity of glycerine with the split off quantity of fatty acid have been carried out by KELLNER¹⁾, who determined free fatty acid and combined glycerine²⁾ of partially saponified palmkernel oil by different methods of saponification.

Let us first examine how T and g are to be found from KELLNER'S observations. For the calculation of the percentage of split off fatty acid the procedure is always as follows: The acid value is determined of a sample of the fat (which has first been washed with water and then dried), this is divided by the acid value of the esterfree fatty acid, and multiplied by 100. The value obtained (we shall call this 100 T') now indicates how much free fatty acid the sample contains in percentages, but only in approximation what percentage of the total fatty acid present occurs as free fatty acid (100 T'). The acid value of the esterfree fatty acid indicates how many mgr. KOH is required to neutralize 1 gramme of this fatty acid. If of a sample of partially saponified fat we want to determine what percentage of total fatty acid present occurs as free fatty acid, we must know, *not* the number of mgr. KOH (a), required to neutralise the free fatty acid of 1 gramme of fat, but the number of mgr. KOH (b) required for a quantity of fat which contains the same quantity of total fatty acid as 1 gramme of esterfree fatty acid. The value of saponification being a measure for the total fatty acid present, we get:

$$\frac{b}{a} = \frac{\text{saponification value of the esterfree fatty acid}}{\text{saponification value of the fat to be examined}} \quad (49)$$

It is clear that in consequence of the glycerine content of the partially saponified fat, always $b > a$. To find, therefore, T from T' , we multiply by b/a .

To calculate g we multiply the glycerine content of every sample again by b/a , and thus find the number of grammes of glycerine present in a quantity of the sample, which contains 100 grammes of total fatty acid. If we now also know the glycerine content of the triglyceride, hence also the quantity of glycerine present in so much triglyceride as contains 100 grammes of fatty acid, g can be directly determined.

§ 19. Let us now discuss KELLNER'S results.

¹⁾ Chemiker Ztg. 33, 453, 661, 993. (1909).

²⁾ According to the oxidationmethod.

We calculate from the given acid values and fatty acid contents (table 4—8):

Acid value esterfree fatty acid = 258.0, from this :
 Mol. weight „ „ „ = 217.8
 „ „ triglyceride „ = 691.4
 grammes of glycerine in 100 gr. triglyceride . . = 13.31
 „ „ „ „ triglyceride of 100 gr. fatty acid = 14.08.

For the saponification of palmkernel oil with aqueous *KOH* KELLNER now gives the values of columns 1, 2, 3, and 6 of table 4.

TABLE 4.

1	2	3	4	5	6	7
Acid value	Saponification value	% glyc. in the fat	% glyc. with resp. to total fatty acid	100 g	% free fatty acid in the fat	100 T
96.3	249	8.26	8.56	39.20	37.32	38.67
193.3	253.8	3.41	3.47	75.35	74.92	76.16

It appears from columns 5 and 7 that $g = T$, hence practically $p = q = \infty$ (cf. § 11 and fig. 2 line A), in other words, there practically directly takes place splitting up into fatty acid and glycerine.

The values found by KELLNER for the saponification of palm kernel oil with lime are found in columns 1, 2, 3, and 6 of table 5,

TABLE 5.

1	2	3	4	5	6	7
Acid value	Saponification value	% glyc. in the fat	% glyc. with resp. to total fatty acid	100 g	% free fatty acid in the fat	100 T
101.65	248.8	7.80	8.09	42.54	39.39	40.85
169.5	251.0	4.31	4.43	68.54	65.69	67.52

Here too it appears on comparison of columns 5 and 7 that $g = T$, and therefore $p = q = \infty$ must be practically valid also here. It follows therefore from KELLNER's experiments that in the saponification of palmkernel oil with aqueous lye, as well as with

lime, the triglyceride splits up practically directly into glycerine and fatty acid.¹⁾

This result is in conflict with the results of LEWKOWITZ²⁾, who in the alcalic saponification of tallow and cottonseed oil concluded to a saponification in measurable stages from the increase of the acetyl value. It is, indeed, not probable that tallow and cottonseed oil would have a stagewise saponification in alcalic surroundings, and palmkernel oil practically not.

As in the saponification of olive oil, tallow and tristearine with normal KOH R. FANTO³⁾ has found that here too the separated quantity of glycerine agrees with direct splitting up of the triglyceride into glycerine and fatty acid, in LEWKOWITZ's experiments, the increase of the acetyl value must be explained by other causes than the presence of lower glycerides. MARCUSSE⁴⁾ has shown that this is really the case. The increased acetyl value is as well caused by the *fatty acids*, as by the fat that has remained unsaponified. Probably the oxidation of the unsaturated fatty acids plays a part here, which also explains the irregularity of increasing and decreasing of LEWKOWITZ's acetyl values.

The results obtained by FANTO and KELLNER, perfectly confirm the conclusion drawn at the end of § 8. In alcalic surroundings the adsorption of the lower glycerides at the surface of contact between fat and water phase is so great that the chance to collision between an OH' ion and a molecule of di- and monoglyceride is practically ∞ compared with the chance to collision between an OH' ion and a molecule of triglyceride.

§ 20. For the fermentative saponification of palmkernel oil KELLNER found the values given in columns 1, 2, 3, and 6 of table 6. (See p. 60).

On comparison of columns 5 and 7 it appears that here $g \neq T$. In column 8 are recorded the values found for 100 T , when T is calculated from g by the aid of formula (48), i. e. on the assumption that $p = 3$ and $q = \infty$. (See § 17 and fig. 2 curve F').

It appears that the calculated and observed values of 100 T agree sufficiently, especially when we consider that g cannot be determined

¹⁾ KELLNER draws this conclusion by comparison of the found glycerine content of the partially saponified fat with that calculated on the assumption of a direct complete splitting up.

²⁾ Ber. **33**, 89 (1900); **36**, 175, 3766 (1903); **37**, 884 (1904); **39**, 4095 (1906).

³⁾ Monatshefte f. Chemie **25** 919 (1904).

⁴⁾ Ber. **39** 3466 (1906), **40** 2905 (1907).

TABLE 6.

1	2	3	4	5	6	7	8
Acid value	Saponifi- cation value	% glycerine in the fat	% glyc. with respect to total fatty acid	100 <i>g</i>	% free fatty acid in the fat	100 <i>T</i>	100 <i>T</i> calc. from (48)
66.7	241.5	10.63	11.36	19.32	25.86	27.63	27.53
78.4	243.3	9.95	10.55	25.07	30.39	32.23	33.40
84.27	243.6	9.63	10.20	27.56	32.66	34.59	35.87
116.10	247.2	7.92	8.27	41.26	44.99	46.96	48.92
165.15	250.8	5.38	5.53	60.72	64.01	65.85	66.45
234.22	252.7	1.41	1.44	89.77	90.78	92.68	91.43

more accurately than to about 1% (for smaller values of g a much greater error is even inevitable).

Of course the conclusion may *not* be drawn that in the said saponification $p = 3$ and $q = \infty$. Also by assuming other values of p and q equations can be drawn up (which however in general do not enable us to express T explicitly as function of g), which more or less accord with the values found experimentally¹⁾. Accordingly equation (48) and likewise the equations discussed in the following §§ must be considered as formulae of approximation, which roughly give an insight into the relations of the surface tensions of the three glycerides against the saponifying surroundings. When the relation between p and q on one side and the surface tensions between aqueous solutions and the three glycerides on the other side are quantitatively known, then we shall be able to decide in how far the here assumed values of p and q are conformable to the truth.

With regard to table 6 it may still be pointed out that the results obtained by KELLNER do not agree with what was found by M. NICLOUX for the fermentative saponification of cottonseed oil. From NICLOUX's values follows a practically direct splitting up into glycerine and fatty acid. (See § 5). Possibly the difference lies in this that KELLNER kept the emulsion in motion by blowing in air, NICLOUX on the other hand brought about the emulsion by stirring, and left it undisturbed after that.

¹⁾ It is the question whether p and q are *here* only functions of the surface tensions between glycerides and the *aqueous solution*, as the enzym is not in solution according to NICLOUX (loc. cit.). (See also § 7).

In conclusion it may still be pointed out here that the relation existing between free fatty acid and separated glycerine offers a chance to throw light on the mechanism of the splitting up of fat in germinating seeds. It is still an open question whether the reaction takes place there analogously to the saponification by the aid of the ferment from ricinus seed.

§ 21. In the saponification according to the TWITCHELL process KELLNER found for palmkernel oil the values from columns 1, 2, 3, and 6 of table 7.

TABLE 7.

1	2	3	4	5	6	7	8
Acid value	Saponification value	% glycerine in the fat	% glyc. with respect to the total fatty acid	100 <i>g</i>	% free fatty acid in the fat	100 <i>T</i>	100 <i>T</i> calc. from (41)
56.9	241.7	(11.36)	(12.13)	(13.85)	22.05	23.54	(30.79)
91.9	242.0	10.32	11.00	21.88	35.63	37.99	39.48
122.4	244.8	8.72	9.19	34.73	47.43	49.99	51.48
177.5	248.9	5.15	5.34	62.07	68.81	71.33	73.38
210.3	252.0	2.87	2.94	79.12	81.54	83.48	85.72

In column 8 are found the values of 100 *T* calculated from *g* by the aid of formula (41), which has been derived for the case that $p = 3$ and $q = 9$, but which with a deviation smaller than 0.3% is also valid for the case that $p = 1$, $q = 23$ (cf. § 15 and fig. 2 curve E).

In the first row the found and the calculated values of 100 *T* diverge greatly. This, however, says little, as this great difference already disappears if the glycerine content of the fat is 12.1% instead of 11.36%. When little glycerine has as yet been separated, a small error in the glycerine content of the concerned sample or of the triglyceride, on which the calculation of *g* is based, has a very great influence on the calculated value of *T*. The agreement between the other values of column 7 and 8 is satisfactory.

As it now appears from the experiments described in § 7 and § 8 that $p = 1$ in general in the TWITCHELL saponification, *q* must have a value in this case, which, as appears from the agreement

of columns 7 and 8 in table 7, differs little from the value $q = 23$ at the lower limit. ¹⁾

§ 22. The values found by KELLNER in the autoclave process of palmkernel oil are found in columns 1, 2, 3 and 6 of table 8.

TABLE 8.

1	2	3	4	5	6	7	8
Acid value	Saponification value	% glycerine in the fat	% glyc. with respect to total fatty acid	100 g	% free fatty acid in the fat	100 T	100 T calc. from (36) and (37)
55	242	(12.16)	(12.96)	(7.95)	21.30	22.71	(31.24)
131.5	247.5	9.84	10.26	27.13	50.96	53.12	52.72
193	251	5.28	5.43	61.43	74.80	76.89	77.94
212	252	3.75	3.84	72.23	82.17	84.13	84.89
218	253	2.83	2.89	79.47	84.48	86.15	88.85
229.5	254.7	2.11	2.14	84.80	88.94	90.09	91.86

In column 8 are found the values of 100 T calculated from g by the aid of the equations (36) and (37), i.e. on the assumption that $p = 1$ and $q = 4$ (see § 13 and fig. 2 curve D).

In the first row the deviation between the found and the calculated values of 100 T is again greatest. Much importance should not be attached to this here either, as this deviation already disappears when the glycerine content of the fat is 12.6% instead of 12.16%. The other values of columns 7 and 8 agree sufficiently.

It is not improbable that also in the autoclave saponification, where the saponification takes place in feebly acid surroundings, $p = 1$. Nothing can be said of this, however, with any certainty, as the influence of zinc soap has not been examined in the experiments of §§ 7 and 8. If really $p = 1$ also here, q must have a value which differs little from $q = 4$ in virtue of the agreement of columns 7 and 8 of table 1.

SUMMARY.

It has been shown in this paper that in the saponification in emulsion the reaction takes chiefly place on the boundary of the

¹⁾ A deviation upward has little influence. (See table 3 columns 5 and 6).

two phases and that in this case the process of the saponification is governed by the value of the surface tensions between the glycerides and the saponifying medium.

As velocities of saponification do not give an insight here in the mechanism of the reaction, because they are influenced by the variable fineness of the emulsion, equations were derived which give the relation between separated fatty acid and separated glycerine.

The equations, in which the increase of concentration of the lower glycerides at the surface of contact between fat and water-phase were taken into account, appeared to be able to account for the different course of the saponification in different surroundings.

In conclusion I gladly avail myself of the opportunity to express my thanks to Dr. GEITEL for the kind interest he has taken in my work.

*Laboratory of the Royal Stearine
Candle Works "Gouda".*

Gouda, November 1916.

Chemistry. — "*On Polymers of Methylchavicol*". (Preliminary communication). By Prof. P. VAN ROMBURGH and J. M. VAN DER ZANDEN.

(Communicated in the meeting of March 31, 1917.)

Some years ago one of us (v. R.) communicated that through heating of methylchavicol some products of polymerisation were obtained, viz. one that melts at 98°, and one that melts at 166°, while moreover still a very slight quantity of a compound melting above 200° could be separated. Elementary analyses and determinations of the molecular weight of the two first-mentioned products made it probable that these are dimers of methylchavicol.

The compound melting at 98° gave a dibromide melting at 87° with bromine.

Since then a greater quantity of these polymers has been prepared, so that a more extensive investigation was possible, some results of which will now briefly be communicated by us here.

In the first place it has been tried to augment the not very large yield of polymers. On change of the duration of the heating and of the temperature it appeared that a slight improvement of the yield can only be obtained by prolonging the former.

Besides the crystalline compounds a viscous syrup, which still contains large quantities of it, is formed. Now we tried to separate part of it by distillation in vacuo (15 m.m.), and we actually succeeded in getting a fairly large yield of crystals from the fraction 283°—313°. When the residue in the flask is heated to a higher temperature (to 350°), a reaction evidently sets in, at least the distillate becomes thinly liquid and the liquid that was distilled over goes over at ordinary pressure between 150° and 350°.

By continued fractionated distillation a product boiling between 175° and 178° was obtained, whose smell resembles that of the methylether of paracresol boiling at 175°.5. Oxidation of the compound formed with the mixture according to KILIANI yields an acid, which after recrystallisation melts between 178° and 181° and does not give lowering of the melting point when mixed with anisic acid.

If the substance is treated with conc. nitric acid (Sp. gr. 1.5), light yellow crystals are formed melting at 122°, which do not

exhibit lowering of the melting point when mixed with the dinitro compound obtained through the same treatment from p. cresyl methyl-ether. The liquid obtained is therefore undoubtedly p. cresyl methyl-ether. How this substance is formed, has not been explained as yet.

The polymer melting at 166° , dissolved in chloroform, gives with bromine a bromide, crystallising out from petroleum ether in fine needles, melting at 139° while assuming a black colour. About the experiments which have been made to determine the structure of the polymers, we may communicate what follows.

The product melting at 98° was oxidised with a solution of potassium permanganate in acetone. At this oxidation there is formed besides anisic acid, an acid which on recrystallisation separates from toluol into hard massive crystals. Melting point 113° . A micro-elementary analysis gave C 69.42 and 69.34 %. H 8.06 and 7.68%. These results point to a substance of the composition $C_{12}H_{16}O_3$ (Theory C 69.22 %, H 7.74 %).

We found 207 for the molecular weight, by titration, assuming the acid to be monobasic. Calculated for $C_{12}H_{16}O_3$: 208.

Continued oxidation, now with the mixture according to KILIANI, caused a new acid melting at 138° to be formed from this acid melting at 113° . We are still occupied with this research.

Oxidation of the product melting at 166° yielded only anisic acid.

Utrecht.

Org. Chem. Labor. of the University.

Chemistry. — “Action of Organo-magnesium Compounds on, and Reduction of Cineol.” By C. F. VAN DUIN, chem. docts. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of March 31, 1917).

The first communication in the literature about the action of organo-magnesium compounds on internal oxides is given by BLAISE ¹⁾, who found that on action of RMgBr on ethylene oxide, both a primary alcohol and the bromic hydrine of glycol are formed. The formation of these two products led him to assume that the organo-magnesium compound is added to part of the oxide according to equation $\text{RMgBr} + (\text{CH}_2)_2\text{O} = \text{RCH}_2 - \text{CH}_2\text{OMgBr}$ (I) and to another part according to the reaction scheme: $\text{RMgBr} + (\text{CH}_2)_2\text{O} = \text{CH}_2\text{Br} - \text{CH}_2\text{OMgR}$ (II).

GRIGNARD ²⁾, however, rightly pointed out that according to BLAISE's reaction scheme II the organo-magnesium compound splits up into RMg and halogen in its addition; a case which had never yet been observed. He then proved that in this first of all an oxonium

compound is formed of the formula $\begin{array}{c} \text{CH}_2 \quad \text{MgBr} \\ \diagdown \quad / \\ \text{O} \\ / \quad \diagdown \\ \text{CH}_2 \quad \text{R} \end{array}$, which on heating

passes into $\begin{array}{c} \text{CH}_2\text{OMgBr} \\ | \\ \text{CH}_2\text{R} \end{array}$ through an intramolecular conversion. The

appearance of the bromic hydrine of the glycol can then also be explained by action of HBr (formed at the hydrolysis of the MgBr^2) on oxide that has not reacted and had then split off. The mechanism of the reaction had been made clear by this. HENRY studied the action of organo-magnesium compounds on isobutylene oxide ³⁾, symm. butylene oxide ⁴⁾, and propylene oxide ⁵⁾; the first reacts then as the

¹⁾ BLAISE. C. R. d. l'Acad. des sciences **134**, 551 (1902).

²⁾ GRIGNARD C. R. d. l'Acad. des sciences **136**, 1260 (1903), Bull. Soc. chim. (3) **29**, 944 (1903).

³⁾ HENRY C. R. de l'Acad. des sciences **145**, 21 (1907); cf. *ibid.* **145**, 154 (1907).

⁴⁾ *Ibid.* **145**, 406 (1907).

⁵⁾ *Ibid.* **145**, 453 (1907).

isomeric isobutylaldehyde, the second as methylethylketon, the reaction for propylene oxide proceeding as for ethylene oxide.

Numerous are the investigations with epichloric hydrine; IOSITSCH ¹⁾ got on action of C_2H_5MgBr a chloric amylalcohol, and KLING ²⁾ obtained quantitatively the chloric iodine hydrine with C_2H_5MgI , IOSITSCH ³⁾. repeating his experiments, now got both the chloric bromic hydrine and a chloric amylalcohol. Then FOURNEAU and TIFFENEAU ⁴⁾ found that with aliphatic organo magnesium bromides only the chloric bromic hydrine is formed, while with aromatic organo-magnesium compounds chloric propanoles with the constitution $RCH_2 - C \begin{smallmatrix} H \\ COH \end{smallmatrix} CH_2Cl$ arise for which formerly the formula $CH_2Cl C \begin{smallmatrix} H \\ R \end{smallmatrix} CH_2OH$ had been assumed. ⁵⁾

In conclusion we may mention that FOURNEAU and TIFFENEAU ⁶⁾ drew the conclusion from their study on the action of organo-magnesium compounds on mono substituted and asymmetrically di-substituted ethylene oxides that for the former the general process of reaction is: $RC \begin{smallmatrix} \diagup H \\ \diagdown O \end{smallmatrix} CH_2 + R'MgBr \rightarrow RC \begin{smallmatrix} \diagup H \\ \diagdown OH \end{smallmatrix} CH_2R'$, whereas for the latter a previous isomerisation to the isomeric aldehyde must be assumed.

When we take the general result of the above mentioned researches into consideration, we should expect the primary formation of an addition product on the action of an organo-magnesium compound on cineol; that this is really so on action of CH_3MgI was already shown by GRIGNARD ⁷⁾, who also observed that on heating of this addition product a violent reaction sets in. This reaction, however, consists in more than only in an intra-molecular conversion; the reaction taking place at about 160° is very violent; the temperature rises to about 260° , while during violent gas generation a liquid distills over, which is coloured brown through free iodine. The reaction is not always equally violent; in connection with this the quantity of gas that escapes, and the quantity of liquid that distills

¹⁾ IOSITSCH, Journ. russ. phys. chem. Ges. **34**, 96. (1902).

²⁾ KLING, Bull Soc. chim. (3), **31**, 14 (1904) C. R. d. l'Acad. des sciences **137**, 756 (1903).

³⁾ IOSITSCH, Journ. russ. phys. chim. Ges. **36**, 6 (1904).

⁴⁾ FOURNEAU and TIFFENEAU, Bull Soc. chim. (4) **1**, 1227 (1907).

⁵⁾ J. D. RIEDEL, Akt. Ges. D. R. P. 183361; Ch. C. 1907 **1**, 1607.

⁶⁾ FOURNEAU et TIFFENEAU, C. R. d. l'Acad. des sciences **145**, 437 (1907).

⁷⁾ GRIGNARD, Bull Soc. chim. (3) **29**, 944 (1903).

over, varies. The latter is best obtained by adding 52 grammes of cineol to an etheric suspension of 56 grammes of CH_3MgI , obtained from 8 grammes of Mg and 48 grammes of CH_3I ; the whole mass is heated for a few hours and left for 3 or four days.

Then the ether is distilled off, in which but very little cineol goes over, the residue is heated up to $\pm 160^\circ$ on a sand bath, a very wide exit tube is placed on the flask and the reaction proceeds without further supply of heat. Thus from 30—40 grammes of distillate are obtained and from 4—5 L. of gas. There is, however, always some liquid left behind in the flask; it is obtained by treating the residue further in the usual way; the thus obtained liquid is the same as that which distills over. The latter is first washed with a thiosulphate solution and then fractionated in vacuo, collecting everything together that goes over at 21 mm. to 85° . Then the distillation is stopped, because then the residue begins to decompose with splitting off of iodine. What is distilled over is shaken a few times with a 50% resorcine-solution for the removal of unchanged cineol, which is present in a fairly large quantity; then it is dried on chloric calcium and finally distilled over metallic sodium. Then a liquid is obtained of b.pt. 170° — 178° at 759 mm., consisting of a mixture of hydrocarbons $\text{C}_{10}\text{H}_{16}$. The elementary analysis namely gave: (burned with lead chromate in a closed tube): C = 87, 84%; H = 12.00% (calculated for $\text{C}_{10}\text{H}_{16}$: C = 88.15%, H = 11.85%), the determination of the physical constants of the fractions obtained by repeated fractionation:

fraction b.pt. 170° — 172° , 5,	Sp. Gr. _{16°} = 0.841
	n_{D16° = 1.4679
	Mol. Refr. = 44.99
fraction b.pt. 172° 5— 175° :	Sp. Gr. _{16°} = 0.846
	n_{D16° = 1.4706
	Mol. Refr. = 44.94
fraction b.pt. 175° — 178° :	Sp. Gr. _{16°} = 0.853
	n_{D16° = 1.4752
	Mol. Refr. = 44.95

Calculated for $\text{C}_{10}\text{H}_{16}$ 2 F: Mol. Refr. = 45.25.

Besides, the fact that in not a single way a crystalline product could be obtained from any of these fractions points to the presence of a mixture. I tried the preparation of the tetrabromide according to WALLACH¹⁾ in alcohol ether, in sulphuret of carbon, and in

¹⁾ WALLACH, Annalen 227, 280 (1885).

methyl alcohol, of a nitrosochloride, and of a chloric hydrate, but could not obtain a crystalline product anywhere. Nor did oxidation with potassium manganate according to WAGNER¹⁾ lead to a result; the only products that could be identified were acetone and oxalic acid; hence I must rest satisfied with the communication that with generation of methane a mixture of hydrocarbons $C_{10}H_{16}$ is formed.

With C_2H_5MgBr the reaction takes place much less vigorously, and chiefly unchanged cineol distills over; the diminution of the specific gravity, as well as the reduction of an ammoniacal silver oxide solution pointed, however, to the presence of hydrocarbons $C_{10}H_{16}$.

The action of C_6H_5MgBr proceeds quite differently; it is true, here too an addition product is formed, but this remains unchanged on being heated, even up to 200° , so that when treating it we get back the cineol, besides diphenyl. Perhaps that here an intramolecular conversion may be obtained on continued action in the cold, for then crystals separate from the etheric solution of cineol and C_6H_5MgBr , if these crystals are treated separately, a little (3 grammes from 42 Gr. C_6H_5MgBr and 36 Gr. cineol after 3 months' standing) of a liquid that goes over between 80° and 90° at 21 mm., which with phenylisocyanate gave no crystalline urethane. The liquid which was poured off the crystals, yielded nothing but cineol.

With regard to the reduction of internal oxides according to the method of SABATIER and SENDERENS, there exists in the literature only one example, viz. the reduction of cyclohexene oxide to cyclohexanol²⁾, in which the yield was even quantitative. Besides SABATIER³⁾ expressed the opinion that all the ethylene oxides could be hydrated according to his method.

I could not get a reduction for cineol in this way; when at 170° this substance with an excess of hydrogen had been led twice through a tube 40 cm. long, filled with pumice nickel, the sp. gr. had not changed in the least.

These researches, both with cineol and with other oxides, are being continued.

Utrecht.

Org. Chem. Lab. of the University.

¹⁾ WAGNER, B. B. 23, 2315 (1896).

²⁾ BRUNEL, Ann. Chim. Phys. (8) 6, 237 (1905).

³⁾ SABATIER, Die Katalyse in der organischen Chemie Leipzig 1915, pag. 80.

Bacteriology. — “*On the nature and the significance of Volutin in Yeast-cells*”. By Miss M. A. VAN HERWERDEN M.D. (Communicated by Prof. C. A. PEKELHARING).

(Communicated in the meeting of April 27, 1917).

At the same time when the improvements in the technique of microscopical science enabled investigators to demonstrate a nucleus in a number of so-called non-nucleated unicellular organisms, attention was called to the presence of basophilic granules in the cell-plasma of bacteria, hypho- and blastomycetes, algae and protozoa, which behave towards various reagents in a similar way. Where there is a cell-nucleus, as is the case with the greater part of these unicellular organisms, these granules are disposed apart from it, and as to the affinity to stains they do not completely correspond with the chromatin of the nucleus.

Originally BABÈS looked upon these basophilic granules in bacteria as spores and described them afterwards as “Corpuscules métachromatiques”¹⁾, a name still in common use in the French literature up to this day. In Germany they are called “volutin-granules” since A. MEYER’S²⁾ extended investigation of their chemical nature. The name was borrowed from the *Spirillum volutans*, in which one of MEYER’S pupils, GRIMME³⁾ found the granules. Now, if we consider that this *Spirillum volutans* is only one out of many hundreds of bacteria, moulds, and algae in which similar corpuscles are found, the term is, surely, not well chosen. The objection to the term “metachromatic corpuscles” is that the granules or drops under consideration do not under all conditions stain metachromatically with methylene-blue, as also MEYER has remarked, and also that — as will be seen lower down — whether or no a change into a red-violet tint occurs, may, with most granules, depend not only on the condition of the cultures, but also in a great measure on the source of the methylene-blue preparation. In this paper I shall,

¹⁾ Zeitschr. f. Hygiene. Bd. XX, p. 412.

²⁾ Botanische Zeitung 1904, p. 113.

³⁾ Zentralblatt. f. Bakteriologie. Bd. XXXII 1902, p. 172.

therefore, adopt the term "volutin" as being generally received in the microbiological literature.

For a detailed morphological description of the volutin-granule I refer to the relative literature¹⁾. When fixing moulds or yeast-cells in formol, staining them by methylene-blue and differentiating them in 1 perc. sulphuric acid, the cell is decolorized, not however the spots containing the substance called volutin. This substance can be observed as fine granules scattered all over the cells, again coalesced to coarse granules, sometimes imbedded in a vacuole, varying much as to dispersion and quantity. A. MEYER²⁾, who realized the importance of subjecting to a close microchemical examination a substance of such frequent occurrence in the vegetable kingdom, has discovered other qualities in addition to the typical colour-reaction just mentioned. If e.g. we treat the methylene-blue preparation thus obtained with a solution of iodine in potassium iodide, the blue granules turn black and gradually lose the colour in 5 $\frac{1}{2}$ perc. sodiumcarbonate. The volutin rapidly dissolves in warm water, also in the fresh preparation in 5 perc. sulphuric- or hydrochloric acid. The digestibility by pepsin could not be made out, since 0.2 perc. hydrochloric acid will throw the substance into solution at bodily temperature. The behaviour of volutin towards dyes induced MEYER to compare it with that of nucleic acid prepared from yeast. He found the one to be very similar to the other. In 1904 MEYER, therefore, advanced the hypothesis that volutin is a nucleic-acid compound. This view has also been adopted in the later literature on the basis of MEYER's investigation, although MEYER²⁾ himself became aware that his reactions, from a chemical point of view, were not such as to prove his hypothesis, as witnesses his own pronouncement upon it on page 125, where he positively acknowledges that the question as to volutin being a nucleic acid compound has not yet been set at rest. Still, there was more ground, no doubt, for MEYER's supposition than for JANSSENS and LÉBLANCS³⁾, who, ten years before, in their morphological investigation of the nucleus of yeast-cells, consider basophilic granules in the cell-plasma, which they suppose to play the part of reserve-material, as nucleo-albumins.

¹⁾ CLIFFORD DOBELL. Quart. journal of micr. science, 1908, p. 121.

SWELLENGREBEL. Arch. f. Hygiene Bd. LXX, 1909, p. 380.

GUILLERMOND. Recherches cytologiques sur les levures etc, Thèse de Paris, 1902. Arch. f. Protistenkunde, Bd XIX, 1910, p. 298.

REICHENOW. Arbeiten aus dem kaiserl. Gesundheitsamte. Bd. XXXIII, 1910, p. 1.

²⁾ l. c. p. 1.

³⁾ La Cellule. T. XIV, 1898, p. 203.

The reactions, performed by MEYER in 1904, were in the main substantiated in 1913--by SUMBAL¹⁾ and in the same year by LINDE²⁾. LINDE points out that there is not any method to fix the volutin so as to prevent it from being ultimately dissolved in water at room-temperature. Besides MEYER himself also other investigators are wavering in their opinion about the chemical nature of this substance. GUILLIERMOND³⁾ for instance says that "though MEYER's hypothesis seems highly plausible, "aucune preuve décisive" has as yet been given" (p. 307). We quote from KOHL's⁴⁾ manual of yeast-cells (p. 40) the following passage: "Concerning the chemical nature we are still much in the dark. The assertions brought forward have not yet reached beyond the hypothetical stage."

Now, would it not be possible to settle this question with the aid of a subtler micro-chemical reagent than MEYER and his followers had at their disposal? If volutin is a nucleic-acid compound, it would presumably be dissolved by the enzyme that splits up nucleic acid, i. e. nuclease. If this could be demonstrated, the supposition would be proved. In connection with other experience of the action of nuclease on the nucleoproteins in the cell. I have also examined the volutin of various hypho- and blastomycetes and, as has been said elsewhere, I first made use of a nuclease prepared from the spleen of the ox. These efforts came to nothing, as volutin dissolves in water at bodily temperature inside the time required for a nuclease digestion. In glycerin the activity of the nuclease appeared to fall short. When following another way I came to the conclusion that MEYER's suggestion was perhaps right, as I found that the volutin was dissolved within a very short time by the nuclease-action of the living cells themselves, when brought in contact with coverslip-preparations fixed in alcohol. No such result was achieved with cells that were killed by formol-vapours and consequently had been deprived of their nuclease action.⁵⁾

The volutin-granules, which along with fat and glycogen often occupy such a considerable space in the cel-plasma of these unicellular organisms, prompted me to look at them more closely both morphologically and physiologically. The following questions arise: Is there no other way to establish the chemical nature than the

¹⁾ Zeitschr. f. allgem. Physiol. Bd XV, 1913, p. 456.

²⁾ Centralbl. f. Bakteriol. Abt. II. Bd. XXXIX, 1913--14, p. 369.

³⁾ Arch. f. Protistenkunde, Bd. XIX, 1910.

⁴⁾ Die Hefepilze 1907. QUELLE und MEYER. Leipzig.

⁵⁾ For a description of these experiments with *Ustilago maydis* and a species of *Torula*, see Anat. Anzeiger. Bd. XLVII, 1914, p. 312.

one just referred to? What is the function of these granules in the cell-body, does their presence depend on a special composition of the culture-medium? Do the various enzymic actions result from their presence? And as to their morphology: is there any connection between these granules and the development of reserve-materials such as fat and glycogen? and is there any reason for identifying them with mitochondria, as some researchers have done?

I have not carried out an extended cytological investigation. Still, I found that with *Torula monosa*¹⁾, the yeast-cell with which most of the experiments described lower down have been performed, the result of mitochondria-staining after BENDA is positive for the volutin-granules — another proof that all granules classed as “mitochondria” upon the basis of these colour-reactions alone, do not necessarily agree in composition; for these nucleinic-acid-containing granules e. g. stain in the same way as the mitochondria in the liver-cells, which very probably are compounds of phosphatids. When stained with methylene-blue and subsequently differentiated with 1 perc. sulphuric acid the volutin-granules do not at all appear to be metachromatic, as was also found by MEYER. The greater cells often show a diffusely coloured vacuole, which is stained violet-red, i. e. metachromatically; the granules often stain deep-blue as well in formol as in alcohol-fixation.

Nor is the methylene-blue-preparation used immaterial to the degree of metachromasia. With methylene-blue “ β -patent” for example a higher metachromasia was found than with GRUBLER’S methylene-blue for bacteria, the latter being probably purer. With toluidin-blue on the contrary nearly all granules are stained metachromatically. It is certain, therefore, that metachromasia cannot be taken as a criterion. This, as I said on page 70, also induced me to prefer the term “volutin-granules”. Besides with these anilin-dyes the granules can also be demonstrated with carbolic fuchsin; again also by UNNA’S staining-method (a mixture of two basic dyes: pyronin and methyl-green, of which only the former is taken up by the volutin-granules.)

With HEIDENHAIN’S ferric-hematoxylin the volutin-granules are not or hardly stained when the nucleus of the yeast-cell becomes clearly visible. In some cases we succeeded in identifying in the living cell, with dilute neutral-red, occasionally also with methylene-blue, granules disposed similarly to the volutin. This, however does not occur with

¹⁾ For further information regarding *Torula monosa* we refer to KLUYVER Biochemical Sugar-determinations. (Thesis. Delft 1914, p. 16.)

all cells¹⁾ nor always in such a quantity as is found in the fixed preparation after staining with methylene-blue and differentiation in sulphuric acid. Of course it is not outside the probabilities that, coincidentally with the fixation, compounds are isolated from the living matter, that contribute to the mass of volutin-granules. Allowance should always be made for such possibilities in the examination of fixed substances. It will no longer do, of course, to apply the term vital staining to the staining of living cells with methylene-blue + 5 perc. formol, as HENNEBERG does.²⁾

Fat may be stained in the yeast-cell at the same time with volutin. We need only apply Sudan III to the preparation treated with methylene-blue and sulphuric acid. As other researchers, among whom HENNEBERG, have also pointed out, the volutin-granules are, as regards their location, independent of the fat-drops; it can only be altered passively by the pressure of glycogen- or fat-drops, by which they may be pushed back to the periphery of the cell. In other respects their independence also appears from the presence of fat and glycogen in cultures where volutin is absent.

I here wish to emphasize that moulds as well as various other kinds of yeast may be cultivated and multiplied without any volutin being produced in the cell. Earlier researchers were also acquainted with the fact that in the case of insufficient nutrition the amount of volutin in the cell decreases, that some of the cells in the culture may even become completely devoid of volutin. In 1910 REICHENOW³⁾ has also demonstrated in *Haematococcus pluvialis*, that by not adding phosphate to the culture-fluid the volutin may be made to disappear ultimately, which, however, results in the death of the haematococci.

In my own culture-experiments with Ustilaginae and Torulaceae I have likewise watched the effect of the amount of phosphate in the culture-medium and endeavoured to obtain permanent cultures completely free from volutin. To accomplish this effect it will not suffice to omit the phosphate in the agar-cultures because, though in doing so the majority of the cells will indeed be free from volutin, still many volutin-bearers will be seen through the microscope in an alcohol-coverslip-preparation.

¹⁾ It is remarkable that in an agar-malt medium stained rather deep-red with neutral red, only a very small percentage of the growing cells had, after several weeks, taken up the dye.

²⁾ *Centralblatt f. Bact. Bd. XLV, 1916, s. 50; Wochenschrift f. Brauerei 1915, No. 36—42.*

³⁾ *l. c. page 71.*

I could not possibly detect volutin-granules among the glycogen-drops in the living cell-plasma. It is necessary, therefore, in watching the culture-experiments, to fix coverslip-preparations. With *Torula* and *Ustilago* absolute alcohol answered the purpose very well; not quite so well with *Saccharomyces* in which, as HENNEBERG ¹⁾ has also pointed out, the cell-body after fixation in alcohol and colouring in methylene-blue is not sufficiently decolourized by 1% sulphuric acid.

The culture medium was prepared by adding to the agar chemically pure substances; the agar was extracted for one hour with 0.5% acetic acid and subsequently washed out with distilled water. No tap-water was used ²⁾. As nutritive substances we first used 5 perc. glucose (pro analysi), 0.5 perc. peptone MERCK, 0.05 perc. Mg SO₄ (pro analysi) and a trace of KNO₃ (pro analysi). When examining this medium after NEUMANN ³⁾ to ascertain whether any phosphorus be present, this will be found to be the case and is chiefly due to the peptone. Neither was the albumose, obtained in the laboratory from the white of a hen's egg, found to be entirely free from phosphorus. When using pure glycocoll or asparagin as N-source, phosphorus is not found anymore macrochemically after NEUMANN, yet on a microchemical examination the analysis always brings to the front traces of phosphorus ⁴⁾.

On the medium carefully prepared with glycocoll or asparagin not a single yeast-cell containing volutin is to be found after some days at the second inoculation from a malt-agar-culture of *Torula monosa*. The growth, however, is slighter than in the phosphate-free cultures with peptone and since in the latter only a few volutin-containing cells were found in a field of thousands of volutin-free cells, they could safely be used for most of our experiments. Also in these almost phosphate-free peptone-cultures the growth, as

¹⁾ l. c. page 74.

²⁾ It should be noted that REICHENOW found the methylene blue sulphuric acid reaction absent in his experiments with *Haematococci*, even when simply omitting the phosphate. In the description of the culture fluids no mention was even made of the use of distilled water. Probably the hypho- and blastomycetes studied by me can seize upon smaller quantities of phosphorous-compounds present in the culture fluid than the *Haematococci* studied by REICHENOW.

³⁾ After this method the substance to be examined is incinerated with 10 c. c. of distilled nitric acid s. g. 1,4 and strong sulphuric acid aä. For further details we refer to HOPPE SEYLER, Hdb. d. Physiol. u. Pathol. Chemischen Analyse p. 359. After incineration and subsequent neutralization phosphoric acid was reacted upon with ammonium-molybdate.

⁴⁾ Here part of the nutrient medium was incinerated, the ashes were taken up in a drop of nitric acid and were put on an object-glass. Reaction was then performed under the microscope.

might be expected, is less rapid and less strong than on similar media with phosphate. I have not succeeded in making a nutrient medium that was microchemically completely free from P. The chances, indeed, are that on such a medium there is no increase of cells at all.

Volutin-free cultures were thus made from *Ustilago maydes*, from *Torula monosa*, from *Saccharomyces cerevisiae* and from a Lactose-yeast¹⁾ (also a *Torula*).

When transplanting the cells upon a phosphate-containing medium they were seen to be loaded again with volutin within a few hours, in a fluid medium even after a few minutes. This also applies to cultures that had been free from volutin for 8 or 9 months. That they have preserved the power to produce volutin is evidenced whenever an opportunity offers. The volutin-free yeast-cells react very rapidly on the addition of a small quantity of phosphate; for instance the addition of 0,04 m.grm KH_2PO_4 to 10 c.c. of fluid will evolve volutin in several cells. Also from purely organic compounds the phosphoric compound required for volutin-formation may be obtained in many cases. When using an albumose prepared from white of egg that contained 0.09 m.grm P. per test-tube, a large number of the cells were loaded with volutin. Volutin is also developed rapidly by the addition of nucleinic-acid-sodium to the culture-medium. As for the amount of fat and glycogen no difference worth mentioning could be made out, on microscopic examination, between phosphate-free and phosphate-containing cultures

In a *Torula monosa* culture upon a phosphate-free medium we observed in March 1916 a sudden formation of pigment in the yeast-cells. This could be made out macroscopically as a dark-grey to black coloration, microscopically from the presence of fine, brown pigment-granules in the living-cells, which did not disappear upon a short treatment with alcohol and that could be fixed in Canada-balsam-preparations. The pigment-production was arrested as soon as the pigmented cultures were transplanted on a phosphate-containing medium. It appears, therefore, that it is brought forth only in a phosphate-free medium. For five months this pigmented culture was maintained, then outside influences destroyed it. I never again detected this pigmentation in the same stock of *Torula monosa*.

As appears from the above, the presence of phosphorus-compounds is essential to the formation of volutin. They alone, and not as HENNEBERG asserts calcium-salts or ammonium-carbonate or sugar, can

¹⁾ Vide KLÜYVER, l. c. page 73.

regenerate this substance in volutin-free cells. It is not the calcium-salts, but the amount of phosphate in the tap-water that constitutes the causative agent. When HENNEBERG ¹⁾ reports that in a culture of beer-yeast, that has lost much of its volutin, a fresh volutin-formation takes place a short time after an incubation in sugar, notably after the addition of ammonium-carbonate, this is to be attributed, in my opinion, only to some degree of impurity of the preparation used. It is a fact that commercial glucose or cane-sugar, as I myself found experimentally, will produce an increase or a recovery of the volutin. In perfectly pure glucose (pro analysi), on the other hand, whether or not after the addition of ammonium-carbonate (pro analysi), the volutin is not recovered.

There is, therefore, no longer any room for doubt that volutin needs phosphorus for its formation. The question now arises: are there other methods by which its composition can be ascertained? When *Torula monosa* is treated for some time, say one hour, at room-temperature with $\frac{n}{15}$ NaOH, all the volutin is dissolved. By the same method nucleinic-acid may be prepared from yeast in the usual way. Does perhaps the volutin furnish the material for it? This hypothesis has been previously brought forward by MEYER also, as it seemed improbable to him that the comparatively slight portion of chromatin in the cell-nucleus — in connection with his reactions on volutin described above — could furnish all the nucleinic acid produced from yeast. Is there any foundation for this hypothesis, to which also other workers (among others REICHENOW ²⁾ and KOHL ³⁾) inclined? In order to ascertain this the following experiments were made.

Twenty-five malt-agar tubes were inoculated with *Torula monosa*; after 28 hours the strongly developed cultures were washed in $\frac{n}{15}$ NaOH. The suspension, thus obtained, was well stirred; one hour later (when all cells were free from volutin) it was filtered by suction through paper-pulp, after which 1 cc. 5 per cent. H₂SO₄ per 10 cc. filtrate was added. A precipitate was formed that was centrifugalized and washed out again in distilled water. When it was analysed this precipitate appeared to contain purin-bodies. It gave after hydrolysis in the autoclave with dilute sulphuric acid a distinct xanthin- and adenin-reaction and on further analysis a phosphate-

¹⁾ l. c. page 74.

²⁾ l. c. page 71.

³⁾ l. c. page 72.

reaction. According to what has been found in the preparation of nucleic acid from *Saccharomyces cerevisiae* we might expect the above mentioned precipitate originated by the addition of 5 perc. H_2SO_4 to contain nucleic acid (similar reactions I achieved afterwards also with commercial beer-yeast).

That the nuclease of yeast-cells is of itself capable of splitting up this nucleic compound and to set free phosphoric acid may now clearly be demonstrated. A suspension of the washed precipitate in 1 perc. glyose and 0,05 perc. $MgSO_4$ inoculated with *Torula monosa* does not give a phosphate-reaction; but this reaction is obtained when the yeast-cells are ground with quartz-sand and are then brought in contact with a suspension of the precipitate in water. After an incubation at 20° for 48 hours (with addition of a grain of thymol) a distinct phosphate-reaction with Mg-mixture takes place, which is absent in the precipitate itself (also after 48 hours) and is likewise absent in the ground *Torula*-cells. The impracticability of demonstrating the nuclease-action in the living cells by the phosphate-reaction is probably due to the fact that these cells immediately seize upon the phosphate they have isolated from the nucleic acid. By crushing the cells, however, we were in a position to prove the nuclease-action of *Torula monosa*. It appears that this enzymic activity was not lost in the cultures grown without volutin, for with these also phosphate could be isolated from the nucleic acid precipitate after grinding the cells with quartz-sand. I had ascertained beforehand that among thousands of cells at the most a single volutin-containing cell was present in coverslip-preparations of this culture.

Volutin is separated from the yeast-cells by $\frac{n}{15}$ NaOH while by the same process a nucleic acid compound is thrown into solution.

Though all this seems to point to the identity of these two substances, the decisive proof is furnished only when observing that phosphate-free cultures, not containing any volutin and extracted with $\frac{n}{15}$ NaOH, do not yield a precipitate with 5 perc. H_2SO_4 .

This was evidenced by me in the following way. Twenty-five culture-tubes with volutin-free *Torula monosa* (at most one granule of volutin per field of thousands of cells) were treated with $\frac{n}{15}$ NaOH, and the filtrate was passed through a filter by suction. With 1 cc. 5 perc. H_2SO_4 per 10 cc. of filtrate at most a trace of turbidity, never, not even after centrifugalizing, a precipitate was produced.

This does not imply that volutin-free yeast does not contain nucleinic acid, as in working with very large quantities of yeast, the nucleinic acid will also be isolated from the nuclei, and will be demonstrable in the filtrate. But it does imply that *Torula monosa*, devoid of volutin, produces much less nucleinic acid than the normal *Torula*. It is, therefore, quite justifiable to say that the volutin is answerable for by far the greater part of the nucleinic acid, generally prepared from yeast.

The fact that volutin-free cultures may be kept alive for months, moreover that, when transplanted on phosphate-free media, a fresh growth is developed, and lastly that on a phosphate-containing medium volutin is formed again directly, shows conclusively that the presence of this nucleinic acid compound is not essential to the vitality of these cultures. This does not mean, however that the conditions of life are not more favourable for the yeast-cells that contain volutin. On the contrary, with them the growth is more rapid and more abundant, the size of the cells is often larger. Nor is it to be expected, that a substance, present in each yeast-cell to such a considerable amount, has no function to perform in it.

In how far the absence of phosphate in the nutrient medium — aside from the volutin-production — is answerable for the decrease in the growth, could never be made out in these experiments. Theoretically speaking the protoplasm of the yeast-cell may, also apart from the volutin in consequence of the absence of this salt, lack a stimulant agent that cannot be replaced by other salts. It should not be forgotten, of course, that also in these phosphate-free nutrient media traces of phosphorus were always demonstrable microchemically, i. e. organic phosphorus-compounds that may be borne off and assimilated by the cell to render the multiplication of the nuclei possible. But for this the capacity of the yeast cells to grow and to multiply would be out of the question, as has been remarked above. The rare reports in the literature concerning a growth on a medium entirely free from phosphorus, cannot bear criticism as far as a careful analysis is concerned.

It stands to reason that, alongside of the efforts to detect the chemical nature of volutin, observers have always tried to establish its significance in the life of the yeast-cell. The first observers who studied these basophilic granules in moulds and bacteria naturally inclined to believe them to be a reserve-material. When upon the basis of MEYER'S investigation it was surmised that volutin was built up of nucleinic-acid compounds, it was natural that one should look for some relation with the nucleus. But when nothing was

found microscopically that indicated a production of the volutin granules from the nucleus, it was concluded that volutin-granules generated in the cell-body and formed a reserve-material from which the nucleus could draw at will. In this way REICHENOW¹⁾ e.g. represents in his culture-experiments with *Haematococcus pluvialis* the colligation of the larger clumps in the centre (initially on the side of the nucleus) and a breaking-up into smaller granules at the periphery during the growth of the cultures.

Of late HENNEBERG²⁾ went farther than the researchers who admitted volutin to have significance only as a reserve-material. According to him volutin plays an important part in the fermenting process of *Saccharomyces cerevisiae*. He even inclines to believe that the fermenting enzyme itself is to be found in the volutin and tries to support his view by a series of microscopic experiments tending to observe the abundance of volutin in the yeast-cell and its distribution in the cell-body, together with the fermenting power. He found that the yeast-cell during rest bears some spherical volutin-granules and that a dissemination into finer granules, rendered visible at the initial stage of the fermentation, indicates activity. The lower fermenting power (the carbonic acid production was taken as an index of the fermenting power) runs parallel with a diminution of the volutin. In a sugar-solution, as HENNEBERG asserts, the volutin is recovered. Before discussing HENNEBERG's results will return to my own investigation.

It being possible to make volutin-free cultures from moulds and yeast-cells that could be kept alive for a long space of time I put the simple question: Is the presence of volutin indispensable to fermentation? To answer it it was only necessary to use for the yeast-tests the volutin-free cultures under microscopic control.

First of all we had to find out whether fermentation can take place without volutin. When this appeared to be actually the case, the next thing of importance was to obtain some quantitative data regarding the relationship between the fermentation of a volutin-containing and of a volutin-free culture of the same age, both cultivated under the same circumstances (except the absence of phosphate in the culture medium).

For these experiments the rate of fermentation was estimated partly physically, partly chemically. In the first case the carbonic acid produced was collected above mercury; in the second, the reducing power of the remaining non-fermented sugar was determined

¹⁾ l.c. page 71.

²⁾ l.c. page 74.

after BENEDICT¹⁾. It goes without saying that sterilisation was applied in these experiments. The fermentation-flasks connected with the mercury tube were kept at a temperature of 23°—25° and the fermentation took place at the same temperature in the flasks used for the determination after BENEDICT.

These series of experiments go to show by either method that a distinct fermentation takes place in the volutin-free cultures of *Torula monosa*, *Saccharomyces cerevisiae* and Lactose-yeast. The fluid used was free from phosphate and contained 1 to 2½ perc. glucose, 0.05 perc. MgSO₄, a trace of KNO₃, 0.2 perc. peptone or, to make sure of the absence of any volutin in thousands of yeast-cells, 0.2 perc. asparagin or glycocoll instead of peptone. Peptone, however, serves our purpose quite well, especially in comparative fermentation-tests it was quite immaterial whether over against the richly filled yeast-cells of the volutin-containing culture an occasional cell containing a few volutin-granules, emerges in the volutin-free culture. As said before, peptone yields the advantage of a larger growth. Into the culture-fluid thus prepared, yeast-cells were inoculated from a culture-tube. At the commencement as well as at the end of each experiment the absence of volutin was verified. In the experiments with asparagin or glycocoll the same substance was also made use of for the culture of the volutin containing yeast with the addition of 0.1 perc. KH₂PO₄. Occasionally also the entire volutin-free culture was transferred from a tube to a flask of a phosphate-free fluid, and the fermentation was compared with that which was brought about also in a phosphate-free fluid by a nearly equal quantity of *Torula monosa* loaded with volutin-granules. In this way a greater uniformity was obtained in the medium in which the fermentation took place, than with a phosphate-containing control-fluid; still, a perfect uniformity was never obtained, since it may be possible that these volutin-containing cells, rich in nucleinic acid, as has been said on page 9, of themselves furnish phosphate to the medium on which they have been planted. I subjoin some of my experiments and their results:

1 October 1916. Two flasks *A* and *B* each with 25 c.c. 2 perc. glucose, 0.05 perc. MgSO₄, 0.1 perc. glycocoll and a trace of KNO₃ (consequently phosphate-free). The preparations used are all chemically pure. To *A* is added a culture of *Torula monosa* cultivated on a phosphate-free medium, (only a few cells with volutin, at most one in a thousand); to *B* is added a culture full of volutin-granules,

¹⁾ Vide NAGASAKI, Zeitschr. für physiol. Chem. Bd. 95, p. 61.

the culture being grown on a phosphate-containing medium. The amounts are such as to render the turbidity in the two flasks apparently equal. Temperature 20° — 25° . The carbonic acid output is read above the level of the mercury. After the lapse of five hours not yet an appreciable fall of the mercury-column, after 48 hours with *A* a fall of 4 c.c., with *B* $4\frac{1}{2}$ c.c. (to the level of the mercury-reservoir¹⁾). At the termination of the experiment in *A* exclusively yeast-cells without volutin; in *B* a large part with volutin.

26 January 1917. In flask *A* 25 c.c. 0,5 perc. glyose, 0,05 perc. $MgSO_4$, 0,5 perc. asparagin and a trace of KNO_3 , in flask *B* the same liquid + 0,1 perc. KH_2PO_4 . In *A* inoculation with *Torula monosa* without volutin from a phosphate-free asparagin medium. In *B* *Torula monosa* that has been incubated from 29 June 1916 to 23 Jan. 1917 with a phosphate-free medium and by transplanting into malt-agar has again grown rich in volutin. Carbonic-acid production read above the level of the mercury. Temperature 20° — 25° . Fall of the mercury-column with *A* in 6 hours $2\frac{1}{2}$ c.c. with *B* 3 c.c..

3 April 1917. A flask of 25 c.c. 2,5 perc. glyose, 0,2 perc. peptone, 0,05 perc. $MgSO_4$ and a trace of KNO_3 . Inoculation with volutin-free culture of *Torula monosa*, which had been transplanted on March 30 on a phosphate-free medium and which originates from a phosphate-free culture dating from June 19, 1916. After two hours fall of the mercury-column = $3\frac{1}{2}$ c.c. (which means fermentation of a volutin-free culture of rather more than nine months).

13 March 1917. In flask *A* and *B* each 25 c.c. 2,5 perc. glyose, 0,2 perc. peptone, 0,05 perc. $MgSO_4$ and a trace of KNO_3 . *A*. inoculated with a second inoculation from a volutin-free culture, *B*. from a volutin-rich culture. Apparently equal turbidity in the two flasks at the commencement of the experiment. After one hour both mercury-columns are fallen 1 c.c., after 18 hours *A* = 3 c.c. *B* = $4\frac{1}{2}$ c.c. (down to the mercury level in the reservoir.¹⁾)

March 1917. Beer-yeast from the brewery, kept under 10 perc. cane-sugar, in which initially a marked fermentation has taken place (microscopically coarse volutin-granules; no appreciable contamination

¹⁾ The determinations were read from non-graduated tubes, on which the level of the mercury was marked with anilin pencil. The fall was expressed in centimetres; 4 cm. corresponded with a fall of 4 c.c. of mercury. Minute quantitative determinations cannot be made in this way, which indeed was not aimed at. In the case of a fall down to the level of the mercury-reservoir, the amount of carbonic acid given off may, of course, have been larger than we were able to read. Therefore, for a more accurate quantitative comparison some determinations were made after BENEDICT (vide p. 83).

of the yeast-cells. through bacteria or moulds). After three days' incubation in canesugar, inoculated in flask *B* with 0,5 perc. glycoſe, 0,5 perc. peptone, 0,05 perc. $MgSO_4$ and a trace of KNO_3 . In flask *A*, filled with the ſame fluid, alſo beer-yeaſt from the ſame ſource, which, however, has already twice been tranſplanted on a phosphate-free medium, and does not contain any more volutin. After 18 hours both mercury columns fallen $4\frac{1}{2}$ c.c. (to the mercury level in the reſervoir).¹⁾ In a ſubſequent ſimilar experiment both fallen 2 c.c. after one hour's fermentation.

Reduction teſts after BENEDICT.

July 1915. *A* 20 c.c. culture fluid with glycoſe, 0,05 perc. $MgSO_4$ and a trace of KCl . *B* ſimilar fluid + 0,1 perc. KH_2PO_4 .

Before the fermentation determination of reduction = 0,5 glycoſe.

A inoculated with volutin-free, *B* with volutin-containing culture of *Torula monosa*. After 48 hours' fermentation

A = 0,15 perc. glycoſe.

B = 0,15 perc. glycoſe.

March 1917. *A* 20 c.c. of culture-fluid with glycoſe, 0,5 perc. aſparagin and a trace of KNO_3 . *B* ſimilar fluid + 0,1 perc. KH_2PO_4 .

Before fermentation determination of reduction = 2,25 perc. glycoſe.

A inoculated with volutin-free culture, *B* with volutin-containing culture of *Torula monosa*. After 48 hours in *A* ſtill 2,06 perc. glycoſe
in *B* alſo 2,06 perc. glycoſe.

March 1917. *A* 15 c.c. of culture-fluid with glycoſe, 0,2 perc. aſparagin, 0,05 perc. $MgSO_4$ and a trace of KNO_3 . *B* ſimilar fluid + 0,1 perc. KH_2PO_4 .

A inoculated with volutin-free, *B* with volutin-containing culture of Lactose-yeaſt. Before the fermentation determination of reduction = 2,04 perc. glycoſe. After 48 hours in *A* ſtill 1,53 perc. glycoſe.

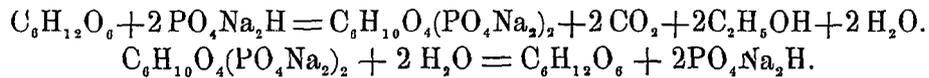
B 1,44 perc. glycoſe.²⁾

It cannot be doubted therefore, that with *Torula monosa*, *Saccharomyces cerevisiae* and Lactose-yeaſt fermentation takes place independently of volutin, the ſame holding perhaps for other zymaſe-containing hypho- and blaſtomycetes. It is not ſurprising that in ſome experiments the fermentation in the phosphate-containing control-cultures is ſomewhat ſtronger in the ſame ſpace of time. As I ſtated before, the growth of yeaſt is more intense on a phosphate-containing medium, ſo that the number of the cells, participating in the fermentation-proceſſe muſt be more conſiderable. We alſo

¹⁾ See preceding note p. 82.

²⁾ I am endeſted to Mr. J. W. Bſer for the laſt two determinations.

know that the presence of phosphate aids the fermentation. The experiments cannot be arranged so as to enable the investigator to study this influence irrespective of the volutin-production. HARDEN and YOUNG¹⁾ have even rendered it very probable that phosphates are indispensable to fermentation. According to them the course of the fermentation is represented by their well-known equation:



In connection with this my experiments go to show that (if HARDEN and YOUNG are right) traces of phosphorus-compounds in a culture-fluid, too small to cause the formation of volutin, bring about these chemical changes. That they are organic and not anorganic phosphorus-compounds is of no consequence; we need only think of the nuclease-action, which, as described above, also belongs to the volutin-free yeast-cells.

Zymase-action therefore does not depend on the presence of volutin, no more does the nuclease-action; I have been able to prove the same for katalase-action. Yeast-cells, entirely free from volutin, suspended in 3 perc. H_2O_2 , evolve immediately an abundance of oxygen. No gas-formation takes place in H_2O_2 when the yeast-cells have been previously destroyed by boiling.

HENNEBERG's totally different results with the zymase-action of *Saccharomyces cerevisiae* may be attributed to the fact that such problems can be solved only when, as was the case in my experiments, the volutin-production can be absolutely precluded, for, as HENNEBERG himself asserts on page 15, the volutin-contents of the cells could in his experiments be replenished from the medium in which they live.

When HENNEBERG observes regeneration of the volutin in a solution of sugar in water without the addition of salts, it is not the sugar that constitutes the active substance, for in glucose pro analysi no fresh production of volutin takes place, as I found over and over again. When some months ago commercial glucose was sold in a somewhat impure condition, numerous volutin-containing cells appeared in all my cultures without addition of phosphate.

As for HENNEBERG's microscopic findings during the fermentation, viz. a finer distribution of the volutin-granules in the initial phase of the fermenting process, the question may be asked whether these changes may perhaps be connected with other life-symptoms in the

¹⁾ Proceedings of the Royal Society Vol. LXXXII p. 361. See also EULER and HAMMARSTEN *Bioch. Zeitschr.* Bd. LXXVI, 1916, p. 314.

protoplasm during the transplantation into a fresh culture-fluid (preparation to the division of the cell etc.).

I have myself repeatedly made microscopic preparations in different phases of the fermentation. In a beer-yeast, kept for two weeks under 10 perc. cane-sugar, I found along with volutin-free cells many with one or more coarse volutin-granules, also a few with a great number of scattered fine granules. When they were incubated in a phosphate-free fluid, fermentation set in at once. After 20 minutes (1 c.c. fall of the mercury-column) the same picture was seen under the microscope as before the fermentation. After 1 hour (fall of the mercury-column 2 c.c.) some cells had begun to germinate. They were obviously richer in coarse volutin-granules than the other cells. The bridge between the knob and the mother-cell was also stained deep blue. Just as in this case the cells in a volutin-containing culture generally exhibit a picture differing so much the one from the other that, in my judgment, it is impracticable to point out a distinct change in connection with the fermentation. True, with the *Torula monosa* in a fresh phosphate-containing culture-fluid faint-violet coloured vacuoles, which have generated after a long incubation in the same malt-agar medium, are often seen to disappear, but there is nothing whatever that points to a correlation with fermentation. On the contrary, what goes very much against such a correlation with the fermentation as such, in the case of *Torula monosa*, is the discovery that when these yeast-cells are incubated with a fluid containing 2.5 perc. lactose instead of 2.5 perc. glucose (along with peptone, $MgSO_4$ and KNO_3) exactly the same picture is presented by the spreading volutin-granules in the coverslip-preparations, made during some hours. Now it is well-known that *Torula monosa*, as the very name indicates, attacks exclusively monose not lactose. In a similar way I examined at the same time the beer-yeast-culture mentioned above, which had been incubated under 10 perc. cane-sugar, as well with 2.5 perc. lactose as with 5 perc. glucose (both with an equal amount of peptone, $MgSO_4$ and KNO_3). Fermentation-experiments taught that, as might be expected, only in the latter case an evolution of carbonic acid occurred, since lactose is not fermented. A convincing difference between the yeast-cells in these two fluids was not noticeable. True, after 1, 2, and 3 hours a more diffuse dissemination of the volutin-granules was to be seen in part of the cells, but only in a very small percentage of the cells, which was perhaps a little higher in the glucose-containing fluid. The difference was, however, not such as to point to a close relation to the fermentation.

To ascertain whether volutin is indispensable to the fermenting process we had to follow up another plan. It then appeared that the zymase as well as the nuclease and the katalase do not depend on the presence of this substance. The question might now be asked whether — though the material that exhibits the colour-reactions, demonstrated by MEYER, is not the mother-substance of the enzymes — it may be that the principal constituents of the volutin still remain in the cell after the said reactions have disappeared. To this question we can say that — as seen on page 80 — in extracting volutin-containing *Torula monosa* with dilute alkali we get a nucleic acid compound, not to be obtained by the same method from an approximately equal amount of volutin-free *Torula*. It follows then that it is not only a colour-reaction, which gets lost through unknown chemical changes in the cell, but undoubtedly a nucleic acid compound which the *Torula* loses in a phosphate-free medium. We are, therefore, justified in assuming that this nucleic-acid compound is not indispensable for the enzymic action. Nor is it indispensable to sustain the stock, for the *Torula monosa* maintains the properties of the stock after a nine months' incubation in a phosphate-free medium; also the multiplication continues to proceed regularly, though at a somewhat slower rate. Such a culture transplanted after 9 months upon a phosphate-free medium is still capable of fermenting (experiment page 85); in a phosphate-containing medium volutin is formed again directly in the usual way. This substance, which appeared indeed to be a nucleic-acid compound, we can hardly consider to be anything else but a reserve-material, and most likely one of a peculiar nature. If namely we bear in mind that most probably phosphates must always be present for the cells to draw from in the fermenting process, it will be an advantage to the cell when it can draw this phosphate immediately from that reservoir of nucleic-acid in virtue of its nuclease, the quantity of this phosphate may be ever so small, as after being set free, it can be utilized again. It is obvious, therefore, that the presence of volutin in hypho- and blastomycetes may be of great significance for the fermenting process without however being indispensable to the fermentation, as it has been proved that even the merest traces of phosphorus, demonstrable only under the microscope, in a volutin-free culture, suffice to render fermentation possible.

S U M M A R Y.

The production of volutin-granules in moulds and in yeast-cells depends on the presence of anorganic or organic phosphorus-compounds in the culture-medium. In a phosphate-free medium *Ustilago*

maydes, *Torula monosa*, *Saccharomyces cerevisiae* and Lactose-yeast can be cultivated, without volutin being generated in the cells. On transplantation into a phosphate-containing medium a fresh formation of volutin ensues.

With dilute alkali a nucleinic-acid compound is extracted along with volutin from *Torula monosa* and *Saccharomyces cerevisiae*, which cannot be obtained from an approximately equal quantity of volutin-free culture. The hypothesis, never proved before, though indirectly supported, that volutin consists of a nucleinic-acid compound, has thus been placed beyond dispute. Nucleinic-acid prepared from yeast in the usual way originates no doubt chiefly from volutin.

The nucleinic-acid compound dissolved from the volutin-containing cells, is decomposed by a nuclease formed in the *Torula*-cells themselves, in which process the development of phosphoric acid could be demonstrated. Also the volutin-free cultures of *Torula monosa* still contain a nuclease. Other enzymic actions also continue, e. g. the katalase- and the zymase-action. Contrary to HENNEBERG's recent pronouncement that the zymase-action of the yeast depends on the presence of volutin, that the latter is probably to be considered as the enzyme itself, it may be proved that volutin-free cultures still evolve a very distinct fermentation. Considering the slower growth in a phosphate-free medium, this fermentation is not appreciably inferior to the fermenting power of the volutin-cultures of *Torula* and *Saccharomyces*. Even after a sojourn of 9 months in a phosphate-free environment a volutin-free culture of *Torula monosa* is still liable to fermentation.

Volutin is a nucleinic-acid compound which is presumably nothing but a reserve-material. The presence of this reserve-material though it is not indispensable to the life and the multiplication of cells, is no doubt of great moment for their individual development. There is reason to believe that, though not being required for the fermentation, it facilitates the fermenting process by continually supplying small amounts of phosphate, which can be liberated from the nucleinic-acid by the nuclease. The relationship of the volutin to the multiplication of the cells is a subject that must be left for further investigation.

Upon a phosphate-free medium with *Torula monosa* a pigmented variation was once developed with fine brown pigment-granules. This pigment disappeared after transplantation upon a phosphate-containing medium but recurred repeatedly in a phosphate-free medium. Also these pigment-containing cultures had retained the glucose-splitting enzyme.

Chemistry. — *“Influence of different compounds on the destruction of monosaccharids by sodiumhydroxide and on the inversion of sucrose by hydrochloric acid. Constitution-formula of α -amino-acids and of betain”*. By Dr. H. I. WATERMAN. (Communicated by Prof. J. BOESEKEN).

(Communicated in the meeting of April 27, 1917).

The destruction of monosaccharids, such as glucose, galactose etc., by basic substances, is accompanied by a decrease of polarisation of the solution in question whilst at the same time the colour becomes brown.

The action of hydroxylions is measured by the rapidity of diminution of polarisation and by the colour-intensity of the solution. I have noticed that different substances belonging to a series of compounds which generally have no or only a slightly acidic character, for instance amino acetic acid and α -aminopropionic acid, are able to neutralize the destructive action on glucose of considerable concentrations of alkali¹⁾.

In order to increase the general importance of my observations I have repeated the experiments with solutions of galactose instead of glucose. The results obtained are quite the same as with glucose (See table I). The action of hydroxylions on galactose is retarded too by different “neutral” substances. Whereas the addition of 5 cm³. 1,06 normal NaOH-solution in the experiments mentioned in table I after three hours has lowered polarisation from + 12,4 to + 9,3 and + 9,4, in the presence of 500 milligrams of alanin the same concentration of alkali has lowered polarisation only to + 11,1. After 24 hours and especially after 48 hours the phenomenon could be observed much better still. So, after 48 hours, without the addition of alanin the polarisation had diminished from 12,4 to 4,0 respectively 4,3; in the presence of alanine the polarisation had only diminished to 9,7.

The difference in colour-intensity of the solutions examined was in accordance with these facts. After \pm 48 hours, in presence of sodium hydroxide, but without alanine, the colour was brown yellow, with alanine only pale-yellow.

¹⁾ H. I. WATERMAN, *Chemisch Weekblad* 10, 739 (1913); 14, 119 (1917).

From these and other experiments described in previous communications it follows that the quantity of alkali, which is fixed by glycine and alanine is very important.

TABLE I. *Retarding action of alanine on the destruction of galactose by alkali.*

		A	B	C	D
		40 cm ³ of a solution containing $\pm 3,5\%$ galactose ¹⁾			
Quantity of alanine added		0	0	0	500 milligram
Number of cm ³ 1,06. normal NaOH-solution added		0	5	5	5
		Filled up with H ₂ O to 50 cm ³			
		A, B, C and D were at the same time placed in a thermostat with watermantle (temperature: 33°)			
Polarisation in grades VENTZKE (length of the polarisation- tube 2 dm.)	At the beginning (temp. of the polarisa- tion-solution: 18,5°)	+ 12,3	+ 11,1	+ 11,1	+ 12,3
	After ± 3 hours (temp. of the polarisation- solution: 20°)	+ 12,4	+ 9,3	+ 9,4	+ 11,1
	After ± 24 h. (temp. of the polarisation- solution: 18,5°—19°)	+ 12,5	+ 5,6	+ 5,8	+ 9,9
	After ± 48 h. (temp. of the polarisation- solution: 18°)	+ 12,4	+ 4,0	+ 4,3	+ 9,7
Colour of the solution	At the beginning	colourless	colourless	colourless	colourless
	After ± 3 hours	colourless	pale yellow	pale yellow	colourless
	After ± 24 hours	colourless	yellow	yellow	colourless
	After ± 48 hours	colourless	brown- yellow	brown- yellow	scarcely pale yellow

The number of cm³. alkali used for titration of the same quantity of these amino acids dissolved in water (with phenolphthalein as indicator) can practically be neglected with regard to the above.

By further experiments it has appeared that glycine and alanine behave under the circumstances belonging to these researches as one-basic acid.

¹⁾ Before using this solution, it was boiled for a moment and afterwards cooled.

Some of the observations referring to this are united in table II.

TABLE II. *Determination of the quantity of alkali fixed by glycine and alanine.*

		A	B	C	D	E	F	G	H	I	J
		80 cm ³ of a solution containing $\pm 5\%$ glucose									
Number of cm ³ 1,06 normal NaOH-solution added		0	2	3	4	5	6	10	10	10	10
Added									500 milligr. glycine		500 milligr. alanine
		Filled up to 100 cm ³ and placed in thermostat with watermantle (temperature 33°)									
Polarisation in grades VENTZKE (2 dm. tube)	At beginning	+ 11,0							+ 10,6	+ 9,7	+ 10,5
	After 2 h.	+ 10,9	+ 10,5	+ 10,1	+ 9,9	+ 9,6	+ 9,3	+ 8,3	+ 10,0	+ 8,5	+ 9,6
Colour of the solution	After 40 hours	colourless	scarcely pale yellow	pale yellow	pale yellow (C)	yellow	yellow-brown	brown	pale yellow (little deeper than D)	yellow-brown deeper than F.	pale yellow (= D)

A solution of glucose in water of fixed concentration was under comparable circumstances submitted to the action of different quantities of alkali. The number of cm³. normal NaOH-solution added varied between 0 and 10 cm³. per 100 cm³. solution.

The most important decrease and the darkest yellow colour occurred there, where most alkali had been added (experiments G and I). After about two hours the polarisation of G and I had diminished from + 10,9 to + 8,3 and + 8,5. By the experiments H and J was proved once more the protective influence of glycine and alanine; the polarisation was respectively + 10,0 and + 9,6.

The polarisation of H lay between that of C and D. From this it is apparent that 500 milligram glycine has fixed $10 - 3\frac{1}{2} = 6,5$ cm³. 1,06 N.NaOH = almost 7 cm³. N.NaOH. The intensity of colour was in accordance with this. In an analogous way it was demonstrated that 500 milligrams of alanine had fixed about $5 \times 1,06 = 5,3$ cm³. N.NaOH.

Glycine and alanine regarded as monobasic acid, 500 milligrams

of these compounds would fix respectively $\frac{500}{75} = 6,7 \text{ cm}^3$. and

$\frac{500}{89} = 5,6 \text{ cm}^3$. N. alkali, so the agreement is sufficient.

On the other hand amino acetic acid and α -aminopropionic acid behave in hydrochloric acid containing solution as monacidic alkali, so that these aminoacids slacken the velocity of inversion of sucrose by hydrochloric acid considerably (Table III).

TABLE III. *Slackening influence of glycine and alanine on the inversion of sucrose by hydrochloric acid.*

130 Gr. sucrose was dissolved in H ₂ O and filled up to 500 cm ³ (solution R.)										
	A	B	C	D	E	F	G	H	I	
50 cm ³ of solution R										
Added						500 milligr. glycine	500 milligr. alanine	500 milligr. phenol		
Number of cm ³ 1,01 Normal hydrochloric acid added	0	2	4	6	10	10	10	10	10	
Filled up with H ₂ O to 100 cm ³ and placed in thermostat with watermantle (temperature 33°)										
Polarisation in grades VENTZKE (2dm tube)	At the beginning of the experiments	+ 49,6	+ 49,4	+ 49,4	+ 49,5	+ 49,3	+ 49,4	+ 49,1	+ 49,0	+ 49,0
	after about 2 hours	+ 49,8	+ 48,5	+ 47,6	+ 46,3	+ 43,9	+ 47,2	+ 46,4	+ 43,1	+ 43,4
	after ± 43 hours	+ 8,3 (temp. 13°)	- 8,3	- 13,8 (temp. 13°)	- 16,7 (temp. 13°)	- 6,0	- 10,5	- 16,6 (temp. 14,5)	- 16,1 (temp. 14°)	- 16,1 (temp. 14°)
	after ± 3 × 24 hours	- 2,9 (temp. 17°,5)	- 13,9 (temp. 18°,5)	- 16,1 (temp. 17°,5)	- 16,5 (temp. 17°,5)	- 13,1 (temp. 18°,5)	- 14,9 (temp. 18°,5)	- 16,4 (temp. 18°)	- 16,4 (temp. 18°)	- 16,4 (temp. 18°)
	after ± 4 × 24 hours	not determined	- 14,8 (temp. 21°,5)	not determined	not determined	- 14,7 (temp. 21°,5)	- 15,2 (temp. 21°)	not determined	not determined	not determined
	after ± 6 × 24 hours	not determined	- 16,0 (temp. 18°,5)	not determined	not determined	- 16,0 (temp. 18°,5)	- 15,9 (temp. 18°)	not determined	not determined	not determined

As follows from the survey given in table III the protective action of glycine and alanine on sucrose corresponds with respectively $\pm 6 \text{ cm}^3$. and $\pm 5 \text{ cm}^3$. N.HCl.

It is thus proved that under the circumstances of these experiments both aminoacids behave as monacidic basic substances.

Phenol has no protective influence; from the results obtained the opposite would sooner be inferred.

In acidic solution the properties of phenol differ widely from those of glycine and alanine, in alkalic solution on the contrary phenol behaves as monobasic acid just as glycine and alanine.

TABLE IV. *Influence of phenol on the destruction of glucose by alkali.*

		A	B	C	D	E	F	G
		80 cm ³ of a solution containing $\pm 5\%$ glucose						
cm ³ 1,06 normal NaOH-solution added		0	3	5	10	10	10	10
quantity of phenol added		0	0	0	0	500 milligr.	1500 milligr.	0
		Filled up with H ₂ O to 100 cm ³ . Placed in thermostat with watermantle (temperature 33°).						
Polarisation in grades VENTZKE (2 dm-tube)	At beginning of the experiments	+ 11,1	+ 10,6	+ 10,3	+ 9,8	+ 10,2	+ 10,9	not determined
	After $\pm 3\frac{1}{2}$ hours	+ 11,1	+ 9,6	+ 8,7	+ 6,9	+ 8,5	+ 10,6	+ 6,9
	Temp. of the polarisation-solution	(19°,5)	(19°)	(19°)	(19°)	(19°)	(18°)	
	After ± 24 hours	+ 11,0	+ 3,0	+ 0,4	- 1,0	+ 0,6	+ 9,5	- 0,7
	Temp. of the polarisation-solution			(20°)	(20°)	(19°,7)		
	After $\pm 2 \times 24$ h.	not determined	+ 0,3	- 0,2	- 0,7	- 0,6	+ 8,1	- 0,6
	Temp. of the polarisation-solution				(17°,5)		(17°,5)	
Colour	After ± 24 hours	colourless	pale yellow	yellow	deep yellow	yellow	almost colourless	deep yellow

500 milligram phenol neutralizes the action of about 5 cm³. 1,06 N. NaOH-solution = $\pm 5,3$ cm³. N. NaOH.

Regarding phenol as monobasic acid 500 milligram corresponds with $\frac{500}{94} = 5,3$ cm³. N.acid. So the agreement is sufficient.

In the above we have made acquaintance with two sensible methods, which enable us to determine the acidic or basic character

of a compound in another way than this has usually happened up to now.

Besides they give us an important indication about the condition of the amino acids in watery solutions.

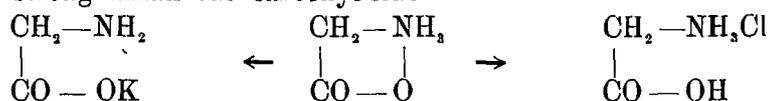
These amphoter electrolytes have apparently a neutralising influence in two directions. This can only be understood well, when we suppose that the action of the alkalic substances and of the acids on the destruction of the monosaccharids and on the inversion of sucrose is caused by molecules or molecule-fractions, which can be fixed by the amino acid.

From these results we may conclude that with these reactions under the influence of strong acids the amino acids assume the character of rather strong basic substances and under influence of strong alkali they act as rather strong acids.

These *two* opposite properties of the amphoter substance come very distinctly to the front, which can best be symbolized by the supposition of *the open chain* as well in strong acidic as in alkalic medium.

When we suppose the ring-constitution in pure water, against which no decisive difficulty exists because the electric conductive power is so small, the above can also be defined as follows:

By strong alkali the carboxyl-side



of the ring is opened, by strong acids the ammonium-side.

Now it was interesting to know how betain should behave; this compound has no doubt in pure water the ring-constitution and it could be expected that this ring should not open on the two sides as easily, at least not in an equally strong degree, as this proved the case with the amino-acids.

Really, the experiments joined in tables V^a and V^b show that betain does not hinder the destructive action of alkali on glucose, whereas betain acts as monacidic alkali on hydrochloric acid during the inversion of sucrose. Accordingly in presence of alkali the ring-formula must be assigned to betain; in presence of strong acids this compound has an open chain.

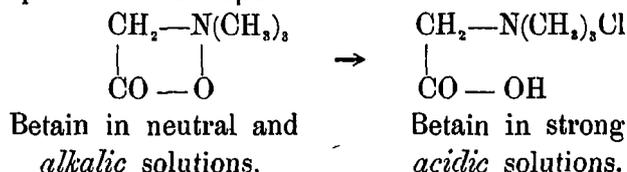


TABLE Va. Behaviour of betain in alkalic solution.

		A	B	C	D	E
		40 cm ³ of a solution containing $\pm 5\%$ glucose				
Quantity of betain-hydrochloric acid added					499 milligr.	
Number of cm ³ 1,06 Normal NaOH-solution		0	2,5	5	5	5
		Filled up to 50 cm ³ and placed in thermostat with watermantle (temperature 33°)				
Polarisation in grades VENTZKE (2 dm. tube)	At beginning of the experiment	+ 12,4	+ 11,8	+ 11,0	+ 11,8	+ 11,2
	After ± 3 hours	+ 12,5	+ 9,7	+ 7,5	+ 10,2	+ 7,6
	After ± 6 hours	+ 12,5	+ 7,4	+ 4,1	+ 8,0	+ 4,1
	After ± 24 hours	+ 12,5	+ 1,8	- 0,8	+ 3,2	- 0,5
Colour of the solution	After ± 3 hours	colourless	hardly pale yellow	pale yellow	hardly pale yellow	pale yellow
	After ± 24 hours	colourless	pale yellow	yellow	hardly pale yellow	yellow

499 milligram betain-hydrochloric acid correspond with $\frac{499}{153,5} =$ almost 3,3 cm³. normal HCl. If in alkalic medium betain behaves as a neutral compound, the action of the added 5 cm³. 1,06 N. NaOH = 5,3 cm³. N. NaOH must be diminished by that of 3,3 cm³.; then 5,3—3,3 = 2 cm³. N. NaOH remains. From the experiments it follows indeed that 499 milligrams of betain-hydrochloric acid and 5 cm³. 1,06 N. NaOH act together as something less than 2,5 cm³. 1,06 N. NaOH.

Whilst in alkalic solution betain behaves neutral, in acidic solution it acts like one-acidic alkali.

From this results that the betain-hydrochloric acid-complex behaves as practically neutral.

Hence the inversion of sucrose by hydrochloric acid is accelerated but little by betain-hydrochloric acid.

TABLE Vb. Behaviour of betain in acidic solution.

		130 Gr. sucrose was dissolved in H ₂ O and filled up to 500 cm ³ (R)							
		A	B	C	D	E	F	G	H
		50 cm ³ of liquid R							
Quantity of betain-hydrochloric acid added						500 milligr.		500 milligr.	
Number of cm ³ 1,01 normal HCl-solution added		0	3	5	7	7	10	10	10
		Filled up with H ₂ O to 100 cm ³ , placed in thermostat with watermantle (temperature : 33°)							
Polarisation in grades VENTZKE (2 dm) tube	At beginning	+ 49,8	+ 49,4	+ 49,3	+ 49,2	+ 49,3	+ 49,2	+ 49,1	+ 49,1
	Temperature of the polarisation liquid			(17°)	(17°)	(17°)	(18°)	(18°)	(18°)
	After ± 2 ³ / ₄ hours	+ 49,7	+ 46,7	+ 45,0	+ 42,5	+ 41,9	+ 40,2	+ 39,5	+ 39,4
	Temperature of the polarisation liquid			(19°)	(19°)	(19°)	(19°)	(19°)	(18°)
	After ± 3 ¹ / ₂ hours	+ 49,8	+ 45,5	+ 43,1	+ 39,9	+ 39,1	+ 36,7	+ 35,8	+ 36,0
	Temperature of the polarisation liquid			(19°)	(19°)	(19°)	(18,5°)	(19°)	(19°)
	After ± 72 hours	not determined	not determined	- 16,2	- 16,4	- 16,2	- 16,6	- 16,3	not determined
	Temperature of the polarisation liquid			(17°)	(17°)	(17°)	(17°)	(17°,5)	

The summary of the above mentioned results becomes as follows :

1. Amino acetic acid and α amino propionic acid retard the destruction of glucose by sodiumhydroxide.

2. This phenomenon is independent of the presence and the quality of the monosaccharid, for the destruction of galactose by sodium-hydroxide is retarded too by the substance mentioned.

3. Amino acetic acid and α -aminopropionic acid behave in alkalic medium as acids. By further examination it was demonstrated that they behaved as about one-basic acid.

4. Just on the other hand these aminoacids in presence of hydrochloric acid behave as monacidic alkali, so that they considerably

retard the rapidity of inversion of sucrose by hydrochloric acid.

5. The behaviour of glycine and alanine deserves special attention because these compounds behave by the usual way of titration as practically neutral.

The number of cm³. alkali necessary for colouring pink a solution of glycine or alanine, which contains phenolphthalein, is insignificant if compared with the quantity of alkali which would be necessary when both compounds should behave in this case as one-basic acids. The same holds for phenol (Compare 7°).

6. The destructive influence of sodium-hydroxide on monosaccharids and the inversion of sucrose by hydrochloric acid can be used for the edification of two sensible methods, which enable us to judge in another way than was usual up to now, whether a compound has acidic or basic properties¹⁾.

7. Remarkable too is the behaviour of phenol in alkalic solution. Phenol acts then as about a one-basic acid, whilst this compound practically has no influence on the inversion of sucrose by hydrochloric acid.

8. The pure amphoter behaviour of glycine in alkalic and in acidic solution, together with the behaviour of betain, which compound in alkalic solution is practically neutral and in acidic solution acts as one-acidic basic substance, make it probable that glycine as well as alanine possess in alkalic and acidic solution the open formula of constitution. In entirely neutral solution the ring formula is sufficient. To betain the ring-formula must be granted in neutral and alkalic solution, in acidic solution the open constitution-formula.

This research will be continued in different directions in order to study the acidic and basic character of the substances and at the same time to determine how far their usual constitution-formula corresponds with this character.

Dordrecht, February 1917.

¹⁾ These methods can only be used if we know with certainty that the substance to be examined is not destroyed in acidic or alkalic solution and has for the rest no disturbing influence.

Physics. — “*Sur les équations différentielles du champ gravifique.*”

By Mr. TH. DE DONDER. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 26, 1917).

En étudiant le champ gravifique dans l'univers stellaire, M. EINSTEIN a été amené tout récemment ¹⁾, à adopter l'hypothèse que j'avais faite antérieurement, en la considérant comme nécessaire dans tous les cas ²⁾, à savoir que la courbure totale C de l'espace-temps doit être nulle.

D'autre part, M. EINSTEIN modifie ses équations du champ gravifique: dans chacune d'elles, il introduit un terme nouveau; je démontrerai dans cette note que les équations ainsi corrigées d'EINSTEIN sont identiques aux équations que j'ai données le 12 juin 1916 ³⁾, à savoir:

$$\bar{k} (-g)^{\frac{1}{2}} \sum_k \sum_l g^{kl} (i k, l m) = \sum_k (g_{km} T_{ik} - \frac{1}{4} g_{im} T_{kk}) \quad . \quad . \quad (1)$$

$i, k, l, m = 1, 2, 3, 4.$

Dans ces dix équations différentielles, les symboles g_{im} représentent les dix potentiels d'EINSTEIN; g est le déterminant symétrique formé au moyen de ces g_{im} ; chacun des g^{kl} représente le mineur algébrique de g_{kl} , divisé par g ; $(i k, l m)$ est une parenthèse à quatre indices de CHRISTOFFEL ou de RIEMANN; \bar{k} est une constante universelle; les T_{ik} sont 16 fonctions qui dépendent du champ électromagnétique ⁴⁾ de MAXWELL-LORENTZ et du mouvement de la matière ⁵⁾ dans le champ gravifique. La configuration de l'espace-temps est déterminée

¹⁾ Sitzungsberichte der Akademie der Wissenschaften, Berlin, 8 février 1917.

²⁾ Zittingsverslag Amsterdam XXV, 1916, p. 156.

Archives du Musée TEYLER, Série 2. T. III (voir la fin de ce mémoire).

Dans la suite de cette note, nous désignerons le mémoire précédent sous le nom de: mémoire (Archives TEYLER).

³⁾ Voir la fin de mon mémoire (Archives TEYLER).

⁴⁾ Voir équation (355) de mon mémoire (Archives TEYLER).

⁵⁾ Voir mémoire de M. EINSTEIN, p. 799 (Sitz.ber. Akad. Wiss., Berlin, 4 novembre 1915). Remarquons que quand M. EINSTEIN écrit

$$\mathfrak{E}_i^k \equiv (-g)^{\frac{1}{2}} T_i^k \equiv (-g)^{\frac{1}{2}} \sum_{\sigma} g_{i\sigma} T^{\sigma k} \equiv (-g)^{\frac{1}{2}} \sum_{\sigma} g^{k\sigma} T_{i\sigma},$$

nous employons le symbole T_{ik} .

7

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par la forme différentielle quadratique :

$$ds^2 \equiv \sum_i \sum_k g_{ik} dx_i dx_k \dots \dots \dots (2)$$

Démonstration. M. EINSTEIN a proposé, dans son récent travail cité, d'étendre le principe d'HAMILTON de la manière suivante: il annule la variation

$$\delta \iiint (\bar{\mathcal{L}} + \bar{l} + \lambda(-\bar{g})^{\frac{1}{2}}) dx dy dz dt, \dots \dots \dots (3)$$

où $\bar{\mathcal{L}}$ est une fonction qui joue un rôle analogue à celui de \bar{L} dans l'étude du champ électromagnétique dépourvu de matière¹⁾; où $\bar{l} \equiv k C (-\bar{g})^{\frac{1}{2}}$, et où λ est une fonction de x, y, z et t , que nous déterminerons plus loin²⁾; dans le calcul de la variation δ , on prend, comme on sait, $\delta x = \delta y = \delta z = \delta t = 0$. Les tirets horizontaux qui surmontent les symboles employés servent à rappeler qu'on a fait usage des variables g^{ik} et de leurs dérivées.

Les 10 équations différentielles des extrémales de (3) sont³⁾:

$$\overset{im}{\Delta} [\bar{\mathcal{L}} + \bar{l} + \lambda(-\bar{g})^{\frac{1}{2}}] = 0, \dots \dots \dots (4)$$

$i, m = 1, 2, 3, 4$

où

$$\overset{im}{\Delta} \equiv \frac{d}{dg^{im}} - \sum_{\sigma} \frac{d}{dx_{\sigma}} \left(\frac{d}{dg^{im, \sigma}} \right) + \sum_{\sigma\tau} \frac{d^2}{dx_{\sigma} dx_{\tau}} \left(\frac{d}{dg^{im, \sigma\tau}} \right).$$

Remarquons que

$$\overset{im}{\Delta} (-\bar{g})^{\frac{1}{2}} = \frac{d(-\bar{g})^{\frac{1}{2}}}{dg^{im}} = -\frac{1}{2} (-\bar{g})^{-\frac{1}{2}} \frac{d\bar{g}}{dg^{im}}.$$

Grâce au déterminant réciproque de \bar{g} , on trouve aisément que :

$$\frac{d\bar{g}}{dg^{im}} = - (2 - \epsilon_{im}) \bar{g} g_{im}$$

où $\epsilon_{ii} \equiv 1$, et $\epsilon_{im} \equiv 0$, quand i est différent de m .

Donc :

$$\overset{im}{\Delta} (-\bar{g})^{\frac{1}{2}} = -\frac{1}{2} (2 - \epsilon_{im}) (-\bar{g})^{\frac{1}{2}} \bar{g} g_{im} \dots \dots \dots (5)$$

Les équations (4) et (5) donnent :

$$\overset{im}{\Delta} \bar{l} = - \frac{d\bar{\mathcal{L}}}{dg^{im}} + \frac{\lambda}{2} (2 - \epsilon_{im}) (-\bar{g})^{\frac{1}{2}} \bar{g} g_{im} \dots \dots \dots (6)$$

Par extension⁴⁾, on aura encore dans le cas d'un champ gravi-

¹⁾ Voir équations (324) à (329) de mon mémoire (Archives TEYLER).

²⁾ M. EINSTEIN supposait que λ était une constante.

³⁾ Pour les détails, voir le chapitre VII de mon mémoire (Archives TEYLER).

⁴⁾ Voir l'équation (353) de mon mémoire (Archives TEYLER).

fique contenant de la matière :

$$\frac{d\bar{\mathcal{L}}}{dg^{im}} = \left(\frac{\epsilon_{im}}{2} - 1 \right) \sum_k g_{mk} T_{ik} \dots \dots \dots (7)$$

On a d'autre part l'identité remarquable ¹⁾ :

$$(1 + \epsilon_{im}) \sqrt[im]{\bar{l}} \equiv \bar{k} (-\bar{g})^{\frac{1}{2}} \sum_k \sum_l g^{kl} (ik, lm) - \bar{k} (-\bar{g})^{\frac{1}{2}} C g_{im} \dots (8)$$

Rapprochons les relations (6), (7) et (8); les 10 équations différentielles du champ gravifique prennent la forme :

$$\bar{k} (-\bar{g})^{\frac{1}{2}} \sum_k \sum_l g^{kl} (ik, lm) - \bar{k} (-\bar{g})^{\frac{1}{2}} C g_{im} = \sum_k g_{km} T_{ik} + \lambda (-\bar{g})^{\frac{1}{2}} g_{im} \dots (9)$$

Multiplions ces équations (9) par g^{im} , et sommons par rapport à i et à m ; d'où, en vertu de ²⁾ :

$$C \equiv \frac{1}{2} \sum_i \sum_m \sum_k \sum_l g^{kl} g^{im} (ik, lm), \dots \dots \dots (10)$$

on trouve la relation

$$\bar{k} C (-\bar{g})^{\frac{1}{2}} = -\frac{1}{2} \sum_k T_{kk} - 2\lambda (-\bar{g})^{\frac{1}{2}} \dots \dots \dots (11)$$

Rappelons que dans le champ électromagnétique de MAXWELL-LORENTZ, on a ³⁾

$$\sum_k T_{kk} = 0. \dots \dots \dots (12)$$

D'autre part, les T_{ik} provenant de la matière valent, d'après EINSTEIN ⁴⁾ :

$$T_{ik} = (-\bar{g})^{\frac{1}{2}} \rho \sum_{\sigma} g_{i\sigma} \frac{dx_{\sigma}'}{ds} \frac{dx_k}{ds}, \dots \dots \dots (13)$$

où ρ désigne la densité de la matière: c'est une fonction de x, y, z , et t . On en déduit que (2) :

$$\sum_k T_{kk} = (-\bar{g})^{\frac{1}{2}} \rho; \dots \dots \dots (14)$$

d'où, en vertu de (11) et (14),

$$\lambda = -\frac{\rho}{4} - \frac{\bar{k}}{2} C. \dots \dots \dots (15)$$

Il résulte de (15) que, pour que λ soit fonction de x, y, z, t *seulement*, c'est-à-dire pour que λ soit indépendant des g_{im} et de leurs dérivées, *il faut et il suffit que* :

$$C = 0. \dots \dots \dots (16)$$

¹⁾ Voir la fin de mon mémoire (Archives TEYLER).
²⁾ Dans la formule (8) qui se trouve à la fin de mon mémoire (Archives TEYLER), il y a une erreur typographique: le facteur $1/2$ a été omis.
³⁾ Voir la relation (7) à la fin de mon mémoire (Archives TEYLER).
⁴⁾ Voir p. 799. Sitz.ber. Akad. Wiss. Berlin, 4 novembre 1915.

J'ai donc démontré que mon équation complémentaire est *nécessaire* et *suffisante*.

En vertu de (15) et (16), on a donc, enfin :

$$\lambda = -\frac{\rho}{4}; \quad (17)$$

et les équations du champ gravifique deviennent [(9), (16) et (17)] :

$$\bar{k} (-\bar{g})^{\frac{1}{2}} \sum_k \sum_l g^{kl} (i k, l m) = \sum_k g_{km} T_{ik} - \frac{\rho}{4} (-\bar{g})^{\frac{1}{2}} g_{im} . . (18)$$

ou encore, en vertu de (14)

$$\bar{k} (-\bar{g})^{\frac{1}{2}} \sum_k \sum_l g^{kl} (i k, l m) = \sum_k (g_{km} T_{ik} - \frac{1}{4} g_{im} T_{kk}); \quad . (19)$$

ce sont *textuellement* les équations que nous avons données le 12 juin 1916 ¹⁾; elles entraînent *comme conséquence* ¹⁾ l'équation complémentaire

$$C = 0 .$$

Remarquons enfin, que le principe d'HAMILTON généralisé pourra s'énoncer comme suit :

Les équations différentielles de tout champ gravifique et électromagnétique expriment que, dans un espace-temps euclidien, l'intégrale :

$$\iiint \left[\bar{\mathcal{L}} - \frac{\rho}{4} (-\bar{g})^{\frac{1}{2}} \right] dx dy dz dt$$

est extrémée.

Remarque I. L'hypothèse (14), ainsi que nos équations ²⁾ (353) (Archives TEYLER), sont satisfaites dans le cas où l'on prendrait $\bar{\mathcal{L}} = \frac{1}{4} \rho (-\bar{g})^{\frac{1}{2}}$; alors, on aura $T_{\nu\mu} = \frac{1}{4} \rho (-\bar{g})^{\frac{1}{2}} \epsilon_{\nu\mu}$.

Remarque II. Si l'on n'introduit pas l'hypothèse (14), la relation (11) montre qu'en vertu de $C = 0$, on aura :

$$\lambda = -\frac{1}{4} (-\bar{g})^{-\frac{1}{2}} \sum_k T_{kk} (20)$$

En substituant cette valeur de λ dans les équations (9), on obtient encore mes équations (19). Pour l'application du principe d'HAMILTON (3), on devra dans le second membre de (20) exprimer toutes les quantités en fonction de x, y, z et t ; on obtiendra ainsi le λ attaché au système considéré.

¹⁾ Voir la dernière page de mon mémoire (Archives TEYLER).

²⁾ Nos conclusions précédentes sont *indépendantes* de l'hypothèse (13).

Mathematics. — “*On Elementary Surfaces of the third order*”.
(First communication). By B. P. HAALMEIJER. (Communicated
by Prof. BROUWER).

(Communicated in the meeting of May 26, 1917).

Introduction. The existence of certain numbers of real straight lines on cubic surfaces is well known. In Math. Ann. 76 C. JUEL makes a clever attempt to prove the existence of straight lines on certain surfaces of the third order which are non-analytically defined and which he calls elementary surfaces. His methods however are not always convincing and some conditions he puts to his surfaces seem to be artificial and out of place. The object of this note is to introduce elementary surfaces of the third order in a natural way and to prove the existence of at least one straight line on such a surface. Our starting point is formed by the elementary curves of the third order which are extensively dealt with by JUEL in the Proc. of the R. Acad. of Denmark, 7th series, t. 11 N^o. 2. Besides this we shall principally use well known theorems of the analysis situs and the theory of sets of points.

In carrying out the following researches I am indebted for many suggestions to Prof. L. E. J. BROUWER, who also has attracted my attention to this subject.

Definitions and exposition of the problem. An open JORDAN curve, which, together with the linesegment ¹⁾ between its endpoints, forms the boundary of a convex region, is called *convex arch*. These convex arches form the building material for the elementary curves. Let a set of points be composed of a finite number of convex arches, in such a way that it forms the continuous representation of a circle. To every point of the circle is to correspond one and only one point of the set under consideration. Besides, the *tangent (touching line, Stutze)* is to change continuously with the corresponding point of the circle and lastly the set of points is not to contain linesegments, but may include entire lines. A closed set of points consisting of a finite or countably infinite number of these above defined sets is called *elementary curve*. Isolated points are admitted though tangents in the ordinary sense disappear.

¹⁾ In the following *line* will be used for *straight line*.

An elementary curve is said to be of the n^{th} order, when lines exist which have n , but no lines which have more than n points in common with the curve (unless the curve includes the entire line).

In this note we chiefly consider elementary curves of the third order. Some of the results obtained by JUEL which shall prove most useful are the following:

The possible forms of elementary curves of the third order are:

1. One connected curve of the third order without double point or cusp.
2. One connected curve of the third order with a cusp (the two branches arrive at the cusp from different sides of the tangent, cusps where the two branches meet from the same side cannot exist on curves of the third order, as a slight change in the position of the tangent would produce 4 points of intersection).
3. One connected curve of the third order with double point, (this variety can be considered as composed of a curve of the third order and one of the second ¹⁾ having only the double point in common and each forming an angle at that point).
4. One connected curve of the third order and one of the second ¹⁾ (that is: oval, boundary of convex region) having no points in common.
5. One connected curve of the third order and isolated point.
6. Straight line and oval ¹⁾.
7. Straight line and isolated point.
8. Three straight lines.

As points of intersection with a line are counted:

double: ordinary point (that is: internal point of a convex arch) on the tangent, isolated point on every line, cusp on every line except the tangent and double point on every line except on either of the tangents.

triple: point of inflexion on tangent, cusp on tangent and double point on both tangents.

All other modes of intersection are counted single.

We define as *elementary surface of the third order* F^3 any set of points in the projective R_3 , possessing the two following properties ²⁾:

¹⁾ These curves of the second order of course need not have finite breadth, but can have one or two points in common with the line at infinity. (We always consider projective space).

²⁾ Ultimately it may be advisable to make this definition less restricting. In order to admit conical points it will be necessary to extend the first condition and to make it possible that the surface degenerates both conditions have to be revised.

The ultimate definition must be couched in such terms that no essential alterations are required for defining elementary surfaces of order higher than the third.

1. F^3 is to answer the most general definition of a twodimensional continuum ¹⁾).

2. Every plane section of F^3 is an elementary curve of the third order.

This note is divided into two parts:

In the first part we shall prove: *The tangents to plane sections passing through an arbitrary point A of F^3 , not situated on a line of F^3 , form one plane*, which may be called *tangent plane* to F^3 in A . Only one exceptional point is possible having the following character: It is isolated in every plane except the planes through one line, and in these it is cusp with that line as cuspidal tangent.

In the second part we begin by proving some further theorems concerning points of F^3 not situated on a line of F^3 . At the end we assume that no point of a certain plane section is situated on a line of F^3 . By showing that this leads to contradictory results, the existence of at least one straight line on F^3 is established.

First part. We divide the proposition as follows:

§ 1. If A is isolated in a plane α , then α is tangent plane to F^3 in A or A is exceptional point.

§ 2. Only one exceptional point is possible.

§ 3. If A is double point in a plane α and cusp in not more than one plane, then α is tangent plane.

§ 4. If A is cusp in one and not more than one plane α , then α is tangent plane.

§ 5. If A is cusp in two different planes, then A is exceptional point.

§ 6. Through A passes at least one plane in which A is either isolated point, double point or cusp.

§ 1. *If A is isolated in a plane α then α is tangent plane or A is exceptional point.*

The first thing to be done is to construct a plane in which A is not isolated. The vicinity of A on F^3 is the (1,1) continuous representation of the vicinity of a point in a plane, hence a sequence of points A_1, A_2, A_3, \dots of F^3 can be chosen having A for sole limiting point. Let α be an arbitrary line through A in α and $\beta_1, \beta_2, \beta_3, \dots$ the planes passing through α and A_1, A_2, A_3, \dots respectively. These planes have at least one limiting plane β passing through α also. In case A is isolated in each of the planes $\beta_1, \beta_2, \beta_3, \dots$ it can be shown that A is not isolated in β .

¹⁾ BROUWER, Math. Ann. 71, p. 97.

In a plane in which A is isolated the remaining points belonging to F^3 form a connected curve of the third order or a straight line. This restcurve is a closed set of points (it is the continuous representation of a circle), hence A has a finite minimum distance from it. Let this minimum distance be ε_1 in β_1 , ε_2 in β_2 etc. When a point B moves along the restcurve in β_1 the distance AB changes continuously from ε_1 to ∞ , in β_2 from ε_2 to ∞ etc. (when a point A is situated at distances b_1 and b_2 from two points B_1 and B_2 belonging to a connected set of points then to every distance b_3 such that $b_1 > b_3 > b_2$ corresponds at least one point B_3 of the set such that $AB_3 = b_3$).

The sequence $\varepsilon_1, \varepsilon_2, \varepsilon_3 \dots$ has zero for limit. Let $\sigma_1, \sigma_2, \sigma_3 \dots$ be a decreasing sequence chosen from it and let the corresponding planes be represented by $\beta_{\sigma_1}, \beta_{\sigma_2}, \beta_{\sigma_3} \dots$.

In β_{σ_2} we choose a point B_2' of F^3 such that $\sigma_1 > AB_2' > \sigma_2$
 „ β_{σ_3} „ „ „ „ B_2'' „ „ „ „ $\sigma_1 > AB_2'' > \sigma_2$
 and „ „ „ B_3' „ „ „ „ $\sigma_2 > AB_3' > \sigma_3$
 In β_{σ_4} we choose a point B_2''' „ „ „ „ $\sigma_1 > AB_2''' > \sigma_2$
 and „ „ „ B_3'' „ „ „ „ $\sigma_2 > AB_3'' > \sigma_3$
 and „ „ „ B_4' „ „ „ „ $\sigma_3 > AB_4' > \sigma_4$

etc.

$B_2', B_2'', B_2''' \dots$ have a limiting point B_2 in β such that $\sigma_1 \geq AB_2 \geq \sigma_2$
 $B_3', B_3'', B_3''' \dots$ „ „ „ „ B_3 „ β „ „ $\sigma_2 \geq AB_3 \geq \sigma_3$
 etc.

F^3 is a closed set of points, hence $B_2, B_3, B_4 \dots$ all belong to F^3 . Besides $\sigma_1, \sigma_2, \sigma_3 \dots$ is a decreasing sequence having zero for limit hence A is limiting point of F^3 in β .

We now proceed to construct a finite sphere round A inside of which F^3 is entirely situated on one side of the plane α (except the point A in α). A is isolated in α , hence with A as centre there exists in α a finite circle c containing no other points of F^3 . Let b be the sphere with A as centre passing through c . The vicinity of A on F^3 is the (1,1) continuous representation of the vicinity of a point in a plane. Let A_1 be the point corresponding to A . The correspondence is (1,1) continuous, hence a finite circle c_1 round A_1 can be found in the plane such that all internal points of c_1 have corresponding points inside the sphere b and a sphere b' concentric with b can be found such that all internal points of b' belonging to F^3 have corresponding points inside c_1 .

Inside b' F^3 lies on only one side of α for if this were not the case, a contradiction might be obtained as follows: Two points B

and C of F^3 are chosen, both internal to b' and on different sides of a . The corresponding points B_1 and C_1 are situated inside c_1 and can be joined by an open JORDAN curve not passing through A_1 and entirely internal to c_1 . The set of points K corresponding to this curve is closed and connected (both these properties are invariants for (1,1) continuous transformations). K is situated entirely inside b , contains points on both sides of a but no points of a itself (A is the only internal point of c belonging to F^3). Hence K is composed of two closed sets of points, one on each side of a , but this is impossible, because K is connected.

The above results may be taken together as follows:

Through the line a passes a plane α , in which A is isolated, and a plane β , in which A is not isolated. Besides, inside a sufficiently small neighbourhood of A the surface F^3 lies entirely on one side of α , let us say below α . Hence inside that neighbourhood of A the intersection of β and F^3 lies entirely below α (always excepting the point A itself, which is situated on a). Considering the possible forms of elementary curves of the third order, there remain two possibilities:

1. A is ordinary point in β with a as tangent.
2. A is cusp in β .

Let A be cusp in β with b as cuspidal tangent. In no plane through b can A be isolated, because the two branches meeting at the cusp in β furnish points of F^3 on both sides of each of these planes inside every vicinity of A . But above α there is a finite neighbourhood of A containing no points of F^3 , hence in every plane through b , A is either cusp or ordinary point with the tangent in α . We proceed to show that *if A is cusp in β it cannot be ordinary point in two other planes through b* .

Let $\alpha_1, \alpha_2, \alpha_3, \dots$ be a sequence of parallel planes each of which lies above all preceding ones and which have α for limiting plane. Let the points of intersection of b and $\alpha_1, \alpha_2, \alpha_3, \dots$ be respectively B_1, B_2, B_3, \dots . If the sequence is started high enough every plane $\alpha_1, \alpha_2, \dots$ has a point in common with each of the branches meeting at the cusp in β . Let these points be B_1' and B_1'' , B_2' and B_2'' , B_3' and B_3'' , None of these points B_1', B_1'', \dots can be isolated in the planes $\alpha_1, \alpha_2, \dots$ considering the branches meeting at the cusp in β furnish points on both sides of each of these planes in every vicinity of B_1', B_1'', \dots .

A sequence of connected sets of points, each having a breadth $> p$, has for limit a connected set of points with breadth $\geq p$. From this follows that when n increases the points B_n' and B_n''

cannot continue to be situated on odd curves in α_n , for an odd curve is never entirely internal to a finite region (in other words: always has infinite breadth), so the limiting set would be a curve in α passing through A . But if for n larger than some finite value the points B_n' and B_n'' can neither be isolated nor situated on odd curves, they must lie on even curves, which in this case must be ovals. Obviously these ovals contract when n increases and A is the sole limiting point. Let γ and δ be the planes through b in which A is supposed to be ordinary point (with the tangents in α).

Let a_n, c_n and d_n be the lines of intersection of α_n and β, γ, δ respectively. Obviously a_n intersects the oval in plane α_n at B_n' and B_n'' .

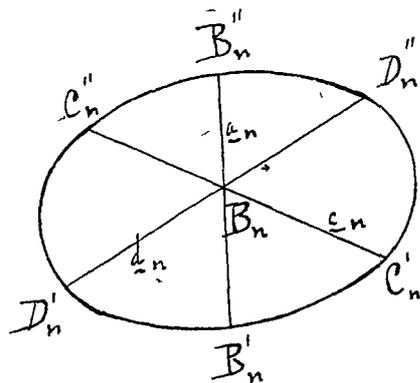


Fig. 1.

B_n is a point of the cuspidal tangent in β and B_n' and B_n'' are points of the branches meeting at the cusp from different sides of the tangent, so on line a_n , B_n is situated between B_n' and B_n'' , hence B_n is internal point of the oval in α_n . From this follows that the lines c_n and d_n passing through B_n have each two points in common

with the oval, one on either side of B_n . Let these points be C_n', C_n'' and D_n', D_n'' .

In plane β A is cusp with b as tangent, but in γ and δ A is supposed to be ordinary point with the tangents in α . From this follows that by taking n large enough the ratios $\frac{B_n B_n'}{B_n C_n'}$ and $\frac{B_n B_n''}{B_n D_n''}$ may be made as small as desired, even of the second order with respect to the distance of the planes α and α_n . Besides the angles of a_n, c_n and d_n are the same for every n , hence for n large enough, the line segments $C_n' D_n'$ and $B_n B_n'$ will have no point in common and this result contradicts one of the fundamental properties of ovals.

The following question arises: Is it possible that A is ordinary point in γ and δ and cusp in β , but with a cuspidal tangent not coinciding with b ? We shall show that the answer must be negative. The notation of points of intersection etc. is kept the same as above. In β the branches meeting at the cusp would arrive from the same side of b , but in γ and δ the branches meeting at A arrive from different sides of b . Hence for n large enough the oval in α_n would be such that on the lines c_n and d_n the point B_n is situated *between*

the points of intersection with the oval, but on the line α_n both points of intersection lie on the same side of B_n . This means that B_n is at the same time internal and external to the oval, and this is impossible.

The above results may be taken together as follows: A is supposed to be isolated in plane α , and b is a line through A not situated in α . Now, if A is ordinary point in two different planes through b , it cannot be cusp in any other plane through b . But if A is ordinary point in a plane through b , the branches meeting at A in this plane furnish points of F^3 on both sides of every plane through b inside every vicinity of A . Hence in no plane through b can A be isolated. Besides above α there is a finite vicinity of A containing no points of F^3 ,¹⁾ so in no plane can A be double point, point of inflexion or ordinary point with tangent not situated in α . Hence when A is supposed to be isolated in α , and b is a line through A not situated in α , the final result may be formulated as follows: *If through b pass two different planes in which A is ordinary point, then in every plane through b , A is ordinary point and all the tangents are situated in α .*

Above we found that in β the point A is either:

1. Ordinary point with a as tangent.
2. Cusp.

Let the first possibility be assumed. We turn the tangent a in the plane β round the point A in both directions to the positions a' and a'' . Provided these rotations be small enough the lines a' and a'' have each three different points in common with F^3 .¹⁾ Hence in no plane through a' or a'' can A be isolated point, double point or cusp. Points of inflexion are also excluded, because one of the branches meeting at such a point would arrive from above α , but above α there is a finite neighbourhood of A containing no points of F^3 . The only remaining possibility is that in every plane through a' or a'' , A is ordinary point and the tangents must all be situated in α because above α there is a finite neighbourhood of A containing no points of F^3 .

Let c be an arbitrary line through A , not situated in α or β . The

¹⁾ JUEL, loc. cit. Acad. of Denmark. When points of intersection are counted as explained, an elementary curve of the third order and an arbitrary line in its plane have in common either three points or one point. Hence a tangent at an ordinary point A carries one point more of the curve. Now if this tangent be turned round A over a sufficiently small angle, A is replaced by two points of intersection A and B each counting single. But there must be still another point of intersection, as there are to be three altogether, so the line in its new position has three different points in common with the curve.

two planes passing through c and through a' and a'' respectively show ordinary points in A . Hence (using the results obtained above) every plane through c shows an ordinary point in A and all the tangents are situated in α .

But c is an arbitrary line through A only subjected to the condition not to lie in α or β , so it follows that in every plane, except α and β , A is ordinary point with tangent in α . Besides in β A was assumed to be ordinary point and the tangent was found to lie in α , hence the only remaining exception is α in which plane A is isolated and which has now been proved to answer our definition of tangent plane.

We now assume the second possibility given above:

The point A is isolated in α and cusp in β . Let b be the cuspidal tangent. In no plane through b can A be ordinary point, for if this were the case, it might be shown in the same way as above that A cannot be cusp in β . Also in no plane through b can A be isolated because b has only the point A in common with F^3 . Taking into consideration that above α there is a finite vicinity of A containing no points of F^3 , the only remaining possibility is that A is cusp in every plane through b . b must be cuspidal tangent in every one of these planes because b has only the point A in common with F^3 . Now a cusp counts double as point of intersection on any line except the tangent, hence every line through A ($\neq b$) has one and only one other point in common with F^3 , because in the plane through that line and b the point A is cusp with b for tangent. Thus in a plane through A which does not contain b , every line through A has one and only one other point in common with F^3 , hence A is isolated in every plane which does not contain b . Thus it has been shown that A is exceptional point.

Before proceeding further we shall just rehearse what has been done in § 1:

A was assumed to be isolated in plane α . Then a plane β was constructed in which A was *not* isolated. From the assumed isolation in α it followed that only two things were possible, namely that A is ordinary point in β with tangent in α or that A is cusp in β . Assuming the first possibility we proved that α must be tangent plane, while the second assumption lead to the conclusion that A is exceptional point.

§ 2. *Only one exceptional point is possible.*

Suppose there could be two: A and B . In a plane through A and B there are a priori four possibilities:

1. A and B are both isolated.
2. A and B are both cusps.
3. A is isolated and B is cusp.
4. A is cusp and B is isolated.

But no elementary curve of the third order can have two isolated points, two cusps or one of each, hence the required contradiction is obtained.

§ 3. *If A is double point in a plane α and cusp in not more than one plane, then α is tangent plane.*

The points of F^3 situated in the plane α form an elementary curve of the third order K , which has a double point in A . A

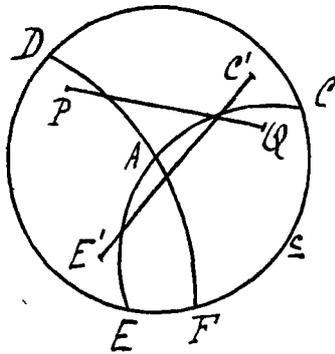


Fig. 2.

is the point of intersection of two convex arches K_1 and K_2 . Let c be a circle round A in α , such that all points of K which are internal to c belong to $K_1 + K_2$ and besides c must be such that it has only two points: C and E in common with K_1 and only two points: D and F with K_2 . All these conditions can be fulfilled by taking c small enough.

Now the branches AC , AD , AE and AF are connected by four sets of points I, II, III and IV, having no points in common, all belonging to F^3 and each of which is entirely situated on one side of α . Respecting these four sets of points, the JORDAN theorem for threedimensional space¹⁾ leaves only two possibilities.

The first possibility comes to the following: AC and AD are connected by I, and AD and AE by II, AE and AF by III, and lastly AF and AC by IV. If the concave side of EC faces F , let us assume for a minute that III and IV are both situated above α . Now if a parallel linesegment converges from above towards $E'C'$ it would end up by having at least two points in common with both III and IV, and this is impossible. Hence III and IV cannot lie on the same side of α . If the concave side of DF faces E then II and III must also be situated on different sides of α . Hence II and IV lie on the same side of α , but then I is certainly situated on the other side, for suppose all three were on the same side then a parallel linesegment converging from that side towards PQ would

¹⁾ BROUWER, Math. Ann. 71, p. 314.

finish up by having at least one point in common with each of II and IV, and at least two with I, and this again cannot be as no line carries four points of F^3 . Hence the final result is that I and III are situated above α and II and IV below α or vice versa.

A representative case of the *second possibility* is the following: AC and AE are connected by I above α , AE and AF above or below α by II, AF and AD below α by III and lastly AD and AC above or below α by IV. If IV be situated below α we choose in α a point A' near A and a point D' near D , such that the line-segment $A'D'$ intersects the arch AD at a point near A and at another point near D . Now a parallel line-segment converging from below towards $A'D'$ would end up by carrying at least two points of III and two of IV: a contradiction¹⁾. Hence the second possibility left by the JORDAN theorem is excluded and we need only consider the first. In the following it will be assumed that I and III are situated above, and II and IV below α .

Obviously the set of points $I + AC + AD$ is the (1,1) continuous representation of a plane region and part of its boundary. Besides, inside a finite neighbourhood of the point corresponding to A , this region has the character of a JORDAN region, because the arches AC and AD are JORDAN curves, and the same holds for the (1,1) continuous representations. The same things can be said of $II + AD + AE$, $III + AE + AF$ and $IV + AF + AC$.

Lastly we remark that inside a finite neighbourhood of A all points of F^3 , not situated in α belong to $I + II + III + IV$.

Let b be a line in α through A such that the branches FA and EA arrive at A from different sides of this line. Then the branches CA and DA will do the same. Let β be a plane through b ($\neq \alpha$). AC and AD are joined above α by I. $I + AC + AD$ is the continuous (1,1) representation of a plane region and part of its boundary. Let I_1 correspond to I, A_1C_1 to AC , and A_1D_1 to AD . Inside a finite neighbourhood of A_1 , the region I_1 has the character of a JORDAN region.

We shall now have to use a property of JORDAN regions called the "Unbewalltheit".²⁾ For two dimensions it may be formulated as follows: Let J be a closed JORDAN curve, I the internal and E the external region. Two points Q and R of J can always be joined by an open JORDAN curve belonging entirely to I and by an open

¹⁾ By using this last reasoning the *first possibility* might have been dealt with in a more simple fashion.

²⁾ BROUWER, Math. Ann. 71, p. 321.
SCHOENFLIES, Mengenlehre 2, chapter 5.

JORDAN curve belonging entirely to E . Let P be a third point of J and c an arbitrary circle round P . Now the "Unbewalltheit" says that if Q and R are chosen close enough to P , the joining curves may be kept entirely inside c .

Applying this to our case it follows that points of A_1C_1 and A_1D_1 can be joined by open JORDAN curves entirely belonging to I_1 , inside any vicinity of A_1 . Hence in the *continuous* (1,1) representation AC and AD can be joined by open JORDAN curves entirely situated on I inside any vicinity of A . Now every one of these curves has at least one point in common with β , because AC and AD lie on different sides of that plane, hence in plane β the point A is limiting point of I , and in the same way can be proved that A is limiting point of III in β . But I and III have no points in common, hence in β one branch departs from A on I and another on III . I and III are both situated above α so in β two branches depart from A above α .

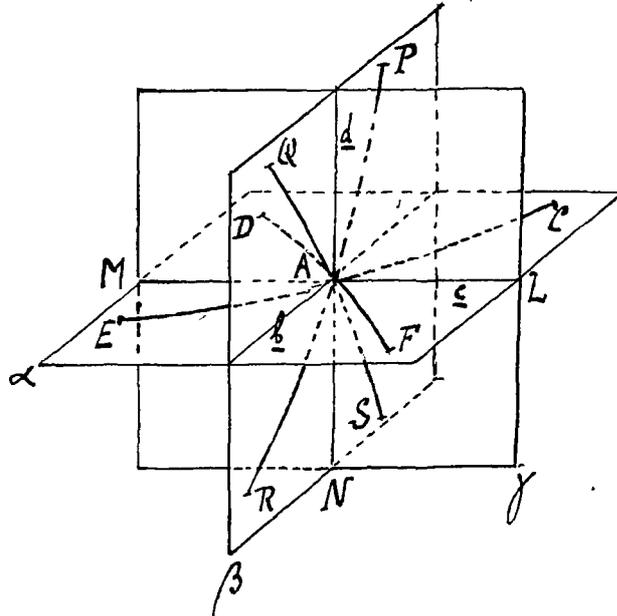
In β two branches arrive at A from the same side of b . Considering the possible forms of elementary curves of the third order, there are a priori three possibilities:

1. A is double point in β .
2. A is cusp in β .
3. A is ordinary point in β with b for tangent.

1. Suppose A is double point in β . Two branches AP and AQ arrive in A from above b , hence two more AS and AR arrive from below b (three from one side and one from the other is impossible because b has, besides A , another point in common with F^3). We proceed to show that the branches AR and AS are at first both situated on II or both on IV . Suppose AR and AS were situated respectively on II and IV . Then AR and AS could not be connected below α , because II and IV have no points in common. But AS would be connected via AC and AF with AP and AQ and AR would be connected via AD and AE with AP and AQ . From this follows that AR and AS would only be connected via AP and AQ . This however leads to a contradiction, because the four branches meeting at A in β must be connected in an analogous way as those in α hence AR and AS are joined by a set of points situated entirely on one side of β . Thus it has been shown that AR and AS are situated either both on II or both on IV , let us assume on II .

The vicinity of A on F^3 is the (1,1) continuous representation of the vicinity of a point in a plane. Let A correspond to A_1 , AE to A_1E_1 , AD to A_1D_1 , II , to II_1 , AR to A_1R_1 , and AS to A_1S_1 . Inside a finite neighbourhood of A_1 the region II_1 is divided by the

open JORDAN curves A, R_1 and A, S_1 in three regions having no points in common. In the vicinity of A_1 all these regions have the character



Ffg. 3.

of JORDAN regions. We consider the two outside regions, namely those connecting respectively A_1E_1 with A_1R_1 and A_1S_1 with A_1D_1 ¹⁾. The (1,1) continuous representations of these regions of F^3 connect respectively AE with AR and AS with AD . That this connection exists inside any neighbourhood of A , again follows from the “Unbewalltheit”. Hence in any plane through b (fig. 3) such that AE and AR are situated on different sides, at least two branches arrive at A from below α . But we also know that in each of these planes two branches arrive in A from above α (one on I and the other on III), hence the following result has been obtained: When the plane β is turned round b (fig. 3) in such a way that the lower half moves to the left, then in every position as far as α the point A remains double point.

Let c be a line in α through A , passing between the branches AE and AD , and let d be a line in β through A , separating the branches AR and AS . The plane through c and d is denoted by γ (fig. 3). In γ two branches arrive in A from below α , one on II and the other on IV. The branch situated on II arrives in A from the right

¹⁾ A priori it would be possible that A_1E_1 is connected with A_1S_1 and A_1R_1 with A_1D_1 , but when we consider the representations on F^3 , this leads to contradiction with the JORDAN theorem for threedimensional space

hand side of AN , because the component region of Π which forms the direct connection between AR and AS , is situated on the right hand side of β . This branch on Π cannot have AL for tangent because in that case the branch on IV would also have AL for tangent and cusps where both branches arrive from the same side of the tangent, are excluded. Hence the branch in γ on Π forms at A finite angles with both AM and AL .

The line c has, besides A , another point in common with F^3 , and for this reason can never be tangent at a double point. Hence the branch in γ situated on IV cannot have AL as tangent, so it must arrive in A under a finite angle with AL , and it follows that if the plane α be turned round line b in such a way that the right hand side moves downwards (fig. 3), the point A will at first remain double point. The above results may be taken together as follows: *α cannot be limiting plane of planes through b in which A is not double point.* But by reversing α and β in our reasonings, the same can be said of plane β . Hence: If α be turned round b in either direction, A at first remains double point. In neither direction can there be a *last* plane in which A is double point, so either there is a *first* in which A is not double point, or all planes through b show a double point in A .

In a *first* plane in which A is not double point, there still arrive two branches in A from above α (one on I and the other on III) hence in such a plane A would be either ordinary point with b as tangent or cusp. The case that A is cusp shall be dealt with sub 2. So at present only two assumptions need be made, namely that there is a *first* plane in which A is not double point, but ordinary point with b for tangent, or that all planes through b show a double point in A . We shall successively show that both these assumptions lead to contradictions.

Let σ be first plane in which A is ordinary point with b for tangent and $\sigma_1, \sigma_2, \sigma_3 \dots$ a sequence of converging planes (all passing through b) in which A is double point. In σ a finite neighbourhood of A exists containing no points of F^3 on one side of the tangent b , in this case *below* b . Considering F^3 is a closed set, this is only possible when in the converging planes the loop of the curve (that is the part of the second order) ends up by being situated in the semiplane of σ_n which converges towards the lower semiplane of σ . Besides these loops must contract towards A and nothing but A . Hence for $n >$ some finite number the branches in σ_n belonging to the part of the third order depart from A above b . At first the *concave* side of these branches faces b . Both branches have infinite

breadth, hence each has an infinite limiting branch. In the limiting plane σ the branches departing from A at first face b with their *convex* side (b is tangent at an ordinary point). But a sequence of finite concave branches cannot have a convex limiting branch hence a contradiction is obtained. The possibility might be put forward that on the converging branches points of inflexion may converge towards A , but a curve of the third order with double point has only *one* point of inflexion¹⁾, hence it may be assumed that only on either the left or the right hand branch points of inflexion converge towards A and the contradiction remains with regard to the other branch.

We now proceed to show that not all planes through b can have a double points in A . Again AE and AD are supposed to be joined by II below α and AC and AF by IV below α (fig. 3). AR and AS are situated on II. We found that if α be turned round b in such a way that the right hand side moves downwards, then at first A remains double point and the branches arriving in A from below remain situated on IV. In the same way as AC and AF are connected by IV below α , the branches AR and AS are connected by a component region of II on the right hand side of β . Taking in consideration this analogy it is obvious that if β be turned round b in such a way that the lower half moves to the right, then at first A not only remains double point, but the branches meeting at A from below α are still situated on II. This may be expressed as follows: *There cannot be a last plane in which the branches are situated on II, and the same can be said of IV.*

Let us now consider the set of semiplanes through b and situated below α . If every plane through b has a double point in A , then in each of these semiplanes two branches would arrive in A from below α . It was found that if these branches are both situated on II, then the same holds for the branches in all semiplanes situated more to the left. In the same way if both branches lie on IV this is also the case in all semiplanes more to the right. Besides the set of semiplanes with branches on II cannot have a last element on the right side and those with branches on IV cannot have a last element on the left side. But all semiplanes have two branches below α , hence the two kinds of semiplanes with branches on II and IV respectively must be separated by a semiplane with one branch on II and one on IV, and this is impossible according to page 111. Thus the assumption that *all* planes through b have double points in A leads to a contradiction.

¹⁾ JUEL loc. cit. Acad. of Denmark § 5.

2. We now come to the second possibility given on page 111, namely that A is cusp in β . Again α denotes the plane in which A is double point and b the line of intersection of α and β . In the proposition of § 3 it was assumed that A is cusp in not more than one plane. Hence if c is a line in α ($\neq b$) the point A can never be cusp in any plane through c . Provided c does not coincide with one of the tangents in α either, the reasoning given sub 1 shows that A cannot be double point in any plane through c (except in α). Considering the possibilities given on page 111 it follows that A must be ordinary point in every plane through c (except α), with c for tangent.

Let AF be the cuspidal tangent in β (fig. 4). The line c in α we choose in the same angle of the tangents in A , in which the line

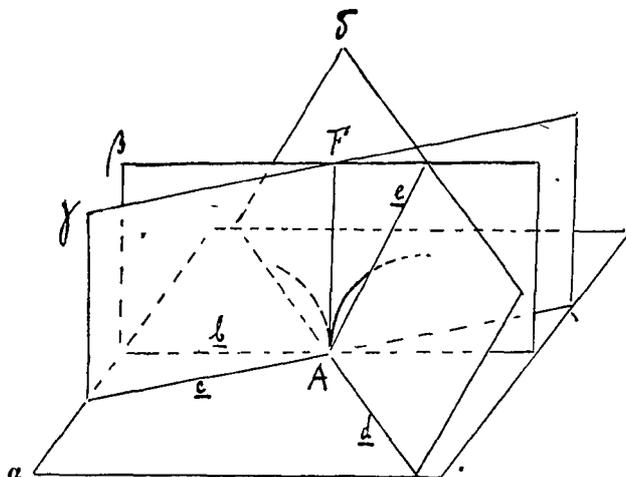


Fig. 4.

b is situated. Besides we choose in α a line d through A , not being tangent in A and in β a line e , not coinciding with AF or b . The plane through d and e is denoted by δ , that through c and AF by γ .

The branches meeting at the cusp A in β arrive from above α (one on I and the other on III). We consider a sequence of planes $\gamma: \gamma_1, \gamma_2, \gamma_3, \dots$ turning round AF and converging towards β . In each of these planes A is ordinary point with tangent (c_1, c_2, c_3, \dots) situated in α . The branches meeting at A in each of these planes arrive from above α (one on I and the other on III), because the branches in β arrive from above and none of the lines c_1, c_2, c_3, \dots is separated from b by a tangent in A .

Each of the lines c_1, c_2, c_3, \dots has, except A , another point in common with F^3 . The distance from A to these points cannot tend towards zero, because if the second point of F^3 on b is added, they form

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a closed set of points to which A does not belong, none of the lines c_1, c_2, c_3, \dots, b being tangent.

Let e_1, e_2, e_3, \dots be the lines of intersection of δ and $\gamma_1, \gamma_2, \gamma_3, \dots$ respectively. These lines e_1, e_2, e_3, \dots converge towards e .

In γ_1 a branch departs from A between c_1 and e_1 , in γ_2 between c_2 and e_2 etc. The distance from A at which these branches can cross c_1, c_2, c_3, \dots cannot tend towards zero, hence to make it possible that in plane β no branch departs from A between b and e it is unavoidable that the branches in the converging planes cross e_1, e_2, e_3, \dots in points converging towards A . This means that in plane δ the line e would be tangent in A . But considering d does not coincide with b or either of the tangents in α , the plane δ through d must show an ordinary point in A with d for tangent. Thus a contradiction has been obtained.

It has been shown successively that the a priori possibilities 1 and 2 given on page 111 lead to contradictory results. Hence only the third possibility remains, namely that A is ordinary point in β with b for tangent. But b is an arbitrary line in α through A , only subjected to the condition not to coincide with either of the tangents in A , and β is an arbitrary plane through b , only supposed not to coincide with α , hence the results obtained so far may be expressed as follows: *In every plane through A which does not coincide with α and does not contain a tangent in α , the point A is ordinary point with tangent situated in α .*

Thus to complete the proof that α is tangent plane, it only remains to consider the sections of F^3 in planes through a tangent at A in α .

In α the point A is point of intersection of two convex arches, parts of which are indicated by QS and PR in fig. 5. Let α ($= DC$) be tangent at A to PR , and let β be an arbitrary plane through α ($\neq \alpha$). We assume the senses of curvature of the convex arches to be as indicated in fig. 5.

In β we choose a line AB ($\neq \alpha$) and we consider a sequence of planes $\beta_1, \beta_2, \beta_3, \dots$ all passing through AB and converging towards β , in such a way that the back part converges towards β from the right hand side (see fig. 5). The line of intersection of α and β_n is denoted by AC_n (a_n).

Let the part of F^3 connecting AP and AS be situated above α (the other case is treated in a strictly analogous way). In every plane β_n a branch departs from A above α in the direction AC_n . These branches have a limiting set in β belonging to the closed set F^3 . Applying the same reasoning given above to show that A cannot be cusp in any plane, it can be shown that this limiting branch

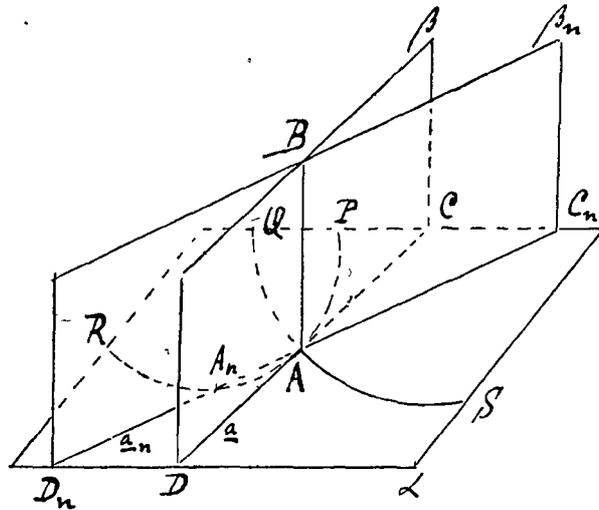


Fig. 5.

in β' departs from A above α in the direction AC . If this branch formed at A a finite angle with AC , then every line inside this angle would be tangent at A in every plane except β , and this is obviously at variance with the results already obtained. For the complete demonstration it is necessary to know that the linesegment AC_n cannot have points in common with F^3 , converging towards A . Now this is obvious if we remember that when the lines a_n converge towards α , the point A_n on AB converges towards A , and that the point A only counts double on α .

The possibility might be put forward that the branches in the converging planes β_n have only A as limiting set in β . Then however, it is unavoidable that the converging planes show ovals, contracting from above towards A . Now all these ovals would cross AB , hence A would be limiting point of F^3 on AB and the entire line AB would belong to F^3 , a possibility excluded at the outset.

Between the branches AP and AS the surface F^3 was assumed to be situated above α , hence the part of F^3 connecting AS and AR lies below α . Now if the planes $\beta_1, \beta_2, \beta_3, \dots$ converge towards β from the other side and if we consider the front halves of these planes (fig 5), it may be shown in exactly the same way that in β a branch departs from A below α in the direction AD .

Taking these results together, it is found that A is point of inflexion in β with α for tangent.

Before passing on to § 4 we shall prove the following theorem:
It is impossible that a point of intersection A counts double on α

line b in some planes through b and single in other planes through b . To prove this it obviously is sufficient to show that when a point of intersection A counts double on a line b in a sequence of planes $\delta_1, \delta_2, \dots$ through b , converging towards a limiting plane δ , then A also counts double on b in δ .

Let us imagine two parallel planes, also parallel to b , situated close to b and on different sides of that line. The lines of intersection with $\delta_1, \delta_2, \dots, \delta$ are respectively denoted by b'_1, b'_2, \dots, b' and b''_1, b''_2, \dots, b'' . Now if the above proposition were false, then in at least one of the two planes, for instance the first, there would be every time *two* points of intersection with b''_n , converging together towards *one* point of intersection with b' . This would remain the same when the plane, parallel to itself, moves towards b . But then it is unavoidable that two branches departing from A in δ_n which keep finite breadth, converge towards one single finite branch departing from A in δ , hence the two sectors of the surface, meeting at that branch, would be situated on the same side of δ and this has been shown to be impossible at the beginning of § 3.

Meteorology. — “*The semi-diurnal horizontal oscillation of the free atmosphere up to 10 km. above sea level deduced from pilot balloon observations at Batavia.*” By Dr. W. VAN BEMMELEN and Dr. J. BOEREMA. (Communicated by Dr. J. P. v. D. STOK).

(Communicated in the meeting of May 26, 1917).

The great regularity of the semi-diurnal variation of the air pressure in the whole equatorial zone, as well as the constancy of its amplitude and phase all over the earth prove that the atmosphere as a whole also performs a regular semi-diurnal oscillation. Above all it was JUL. HANN who brought to light the simple laws commanding this phenomenon, while MARGULES proved this phenomenon probably to be a phenomenon of resonance by making it evident that an infinitely thin shell of the atmosphere has a period of oscillation of its own of nearly 12 hours and consequently will resound to a diurnal disturbance as caused by the sun's radiation.

From the wind observations on mountain tops in Europe and North America and also on those in southern British India HANN¹⁾ deduced that this variation of the air pressure is accompanied by a horizontal wind oscillation possessing an amplitude of some decimeters pro sec.

This horizontal atmospheric oscillation may be called an important geophysical phenomenon. Thus ARTH. SCHUSTER founded his theory of the diurnal variation of terrestrial magnetism on the presence of the above oscillation also in the very upper layers of the atmosphere, and it might, therefore, be desirable to try and obtain more information by observations in the free atmosphere, where disturbances caused by convection will be of less influence than they must be on high mountain tops.

Though this has already been done to some extent by means of cloud observations, no exhaustive nor distinct results could be obtained in this way.

The only suitable method of observation consists in a series of pilot balloon observations, which, however, are so complicated that

¹⁾ Sitzungsber. d. Ak. d. W. in Wien 1908.

they can only be applied in those regions where the atmospheric conditions are quiet enough to retain the series of observations within practicable limits.

Experience gained by means of pilot balloon observations at Batavia justified the supposition that here favourable results might be acquired by such investigation, and therefore during the last few years we have continued the ascension of pilot-balloons started in 1909. As early as 1912 ascensions at 2 p.m. and 7 p.m. were added by the first mentioned of us to the ascensions which before that date usually took place at 8 a.m., in order to gather further knowledge of the phenomenon of land and sea breezes. The results obtained induced him to start in 1913 an extensive series of observations at different hours between 6 a.m. and 6 p.m., more in particular with a view to study the diurnal and semi-diurnal variation of the wind. However, at the time he was not able to have nocturnal ascensions made of balloons carrying lights, like those that first took place in 1912, but in 1914 we again proceeded to these nocturnal observations, when the latter of us joined the investigation.

A continuation of these nocturnal observations was checked, however, by the outbreak of the war in August 1914, so that only a series of day balloons could be sent up and not before the latter part of 1915 was it possible to have an extensive series of nocturnal ascensions made.

From the above it will appear that on account of various circumstances, partly not under our control, the ascensions have by no means been conducted in such a manner as would have been most suitable to the investigation, i.e. equally distributed over the day and during the same season.

These drawbacks have partly been neutralized by the following circumstances.

For the deduction of the semi-diurnal variation, which is the most important and which it is our aim to investigate, it is sufficient to divide the observations over half a whole-day, as was usually done before.

The observations were made in periods as little disturbed by showers as possible, this being even more feasible for half days, or shorter parts of a day, than for whole-days.

The ascensions took place within the semester May/November, i.e. principally with northern declination of the sun and eastern winds.

Of the greater part of the ascensions the altitude reached by the balloons has been calculated trigonometrically from double-observation.

The direction and length of the bases were the following:

1912	311°	1860 m.
1914 (night balloons)	„	„
„ (day balloons)	348	908 „
1915 (night balloons)	296	2640 „

During 1913 single-observation only has been applied, and during the other years the same has been applied mostly for ascensions between 6 a. m. and 9 a. m., during which hours the lower layers are little or not disturbed by convection currents.

The material of observation consisted of the direction and velocity of the wind at various heights and at various hours, derived from series of consecutive balloon ascensions and the problem remained to deduce therefrom the diurnal and semi-diurnal oscillations.

To this end it was assumed in the first place that these oscillations are constant for each height. However, this is certainly not the case with the diurnal oscillations in the lower layers, because the latter are influenced by land and sea breezes, the intensity of which varies from day to day; but the departures from an average might be classified among all non-periodical variations of the wind.

However, the semidiurnal variation of the East-West-component might be surmised to possess a great constancy and also the North-South-component to retain the same sign during, at least a semester.

In the second place the "difference method" was applied; each time two ascensions, succeeding each other at a short interval, were joined and by doing so it might be expected that the non-periodical variations would be eliminated for the greater part; moreover, ascensions with intervals not disturbed by showers were mostly joined and, as regards the lower layers, with intervals no longer than 24 hours. In case of the upper layers longer intervals were admitted.

Therefore, each couple of ascensions yielded the value of the following expression for each height and for each of the two components (E. W. and N. S.):

$$x_1(\sin t_1 - \sin t_2) + y_1(\cos t_1 - \cos t_2) + x_2(\sin 2t_1 - \sin 2t_2) + y_2(\cos 2t_1 - \cos 2t_2)$$

and the values of x_1 , y_1 , x_2 and y_2 were calculated from the whole for each height and for each of the two components according to the method of least squares.

When performing the ascensions, which took place by day and night, and the enormous amount of calculations attending the deduction of wind components and the making up and solving of the normal-equations, we have been greatly assisted by the staff of

the Batavia Observatory, especially by Observer J. H. KATS, to all of whom we herewith desire to express our thanks

In order to gather further knowledge of the air currents in the lower layers, we collected and worked out particulars for each 100 m., up to 1500 m.; upwards of 1500 m. for each 500 m.

The following is a synopsis of the number of cases on which finally the normal-equations are based. In order to somewhat neutralize the diminution of those numbers in the higher levels, groups were formed for the deduction of the coefficients, resulting in the following figures:

0.1 km.	406	3.5 km.	302
0.5 "	406	4.0 "	284
1.0 "	400	4.5 & 5 "	509
1.5 "	387	5.5 & 6 "	432
2.0 "	357	6.5 & 7 "	341
2.5 "	338	7.5, 8 & 8.5 "	318
3.0 "	320	9-11 "	199

This compensation was also necessary to meet the growing uncertainty of the observation with increasing height and the increase of the (non-periodical) velocity of the wind.

However, the number of cases of such a combined group may not be regarded as being equivalent to a non-combined one of the same number, seeing that the non-periodical velocities of the wind — here appearing as accidental errors — are not independent of each other for successive heights.

It is, however, impossible to ascertain this difference quantitatively, although it should be remarked that it is principally dependent on two circumstances.

In the first place on the variability of the wind which the balloon encounters when ascending. As a rule this variability will be somewhat less in the higher layers than in the lower ones.

Secondly on the manner of combining the ascensions, i. e. whether the differences of the wind have been deduced from the same couple of ascensions or from various ones. E g. a balloon sent up at 3 a.m. is compared up to 6 km. with one sent up at 0 a.m., but higher up with one sent up the day before at 6 p.m. In this case the differences for e.g. 4.5 km. and 5 km. will be more dependent on each other than those for 5.5 km. and 6 km. The latter case will be more frequent in the upper layers.

From the above it will appear that it is impossible to state this dependency quantitatively to any amount.

The mean errors have been calculated for the groups 4 km. (6.5—7) km. and (9—11) km. as follows:

	4 km.		6.5—7 km.		9—11 km.	
	North	East	North	East	North	East
(x_1)	17	18	20	22	30	32
(y_1)	30	32	37	40	63	67
(x_2)	17	18	21	22	32	34
(y_2)	17	18	21	22	30	32

The equality of the mean errors of x_1 , x_2 and y_2 and the greater value of the m. e. of y_1 are striking; this being a consequence of the distribution of the ascensions over the day.

The mean errors of x_1 , y_1 , x_2 and y_2 are mainly in inverse proportion to respectively $[\sin t \sin t]$, $[\cos t \cos t]$, $[\sin 2t \sin 2t]$ and $[\cos 2t \cos 2t]$, and the greater part of the couples consisted of one ascension between the hours of 6—12 or 18—24 together with one between the hours of 0—6 or 12—18. For such a combination the values of $[\sin t \sin t]$, $[\sin 2t \sin 2t]$ and $[\cos 2t \cos 2t]$ are indeed about the same, but $[\cos t \cos t]$ is much smaller, which may be easily ascertained when making up the limits between which the values for $\sin t$, $\cos t$, $\sin 2t$ and $\cos 2t$ are fluctuating.

	$\sin t$.	$\cos t$.	$\sin 2t$.	$\cos 2t$.
6 ^h —12 ^h	1.0 to 0.0	0.0 to -1.0	0.0 over -1.0 to 0.0	-1.0 to 1.0
12 ^h —6 ^h	0.0 to -1.0	-1.0 to 0.0	0.0 over 1.0 to 0.0	1.0 to -1.0
(difference) absolute value	0.0 to 2.0	0.0 to 1.0	0.0 to 2.0	0.0 to 2.0

As regards the values determined for y_1 , these show indeed — in accordance with the mean errors, which are nearly twice as large — a greater spreading than those for x_1 , x_2 and y_2 . The values determined are shown in the following table and graphic.

The figures in the table (p. 124) show, first: that the influence of land and sea breezes is distinctly visible in the curves for the diurnal variation of the N.-component; this influence seems to make itself felt up to 4 k.m. Together with this influence is mixed up the one, which

Coefficients of the sinus formula for the diurnal and semidiurnal wind oscillations at various heights, expressed in centimeters pro sec⁴.

	Northcomponent				Eastcomponent			
	x_1	y_1	x_2	y_2	x_1	y_1	x_2	y_2
0.1 km.	-270	-240	165	-25	-23	1	-45	-20
0.2 "	-300	-198	168	-73	3	74	-34	-44
0.3 "	-231	-120	178	-60	15	130	-18	-26
0.4 "	-223	-120	149	-50	15	114	-33	-40
0.5 "	-193	-65	115	-40	9	110	-32	-35
0.6 "	-167	-27	70	-50	21	111	-49	-33
0.7 "	-145	-22	47	-49	33	90	-34	-32
0.8 "	-119	-15	23	-39	38	63	-30	2
0.9 "	-100	28	5	-35	64	62	-31	-6
1.0 "	-85	40	-18	-19	56	36	-31	6
1.1 "	-36	41	-11	-7	68	13	-46	21
1.2 "	-15	66	-29	-11	90	19	-33	39
1.3 "	15	67	-36	-9	90	-38	-26	41
1.4 "	40	46	-49	5	92	-23	-44	30
1.5 "	62	43	-57	14	71	-58	-50	25
2 "	138	-13	-47	44	16	-36	-46	13
2.5 "	116	3	-46	46	1	-1	-8	5
3 "	86	47	4	-1	-38	-17	-45	38
3.5 "	39	0	8	-8	6	5	-52	21
4 "	9	-47	4	0	14	-12	-40	43
4.5-5 "	32	-7	17	7	-25	-35	-43	27
5.5-6 "	-13	16	-15	19	-12	43	-31	23
6.5-7 "	-2	-81	-6	1	22	35	-34	2
7.5-8.5 "	13	37	-27	-1	-6	-72	-12	-26
9-11 "	-14	137	9	-21	22	78	50	-23

is the result of the intermixing of the layers of the air by convection (Espy-Köppen effect).

As regards the East component the land and sea breezes ought

to be of small account, the direction of the coastline being mainly E.-W.; on the other hand the Espy-Köppen effect ought to be fairly well the same for both components. However, the sea wind blowing N.-S. exercises its influence on the East West component, in such a manner that the air above the sea, which is little or not susceptible to the Espy-Köppen effect, is forced landward, thereby diminishing its effect above the land in those layers where sea breezes occur.

The following phases of the diurnal oscillation of the East component clearly show the influence of the Espy-Köppen effect.

Phase of the diurnal oscillation of the East component.

Height	Phase	Height	Phase
0.1 km.	178°	0.9 km.	44°
0.2 "	88	1.0 "	33
0.3 "	84	1.1 "	11
0.4 "	82	1.2 "	12
0.5 "	85	1.3 "	337
0.6 "	79	1.4 "	346
0.7 "	70	1.5 "	321
0.8 "	59	2.0 "	294

Though in a smaller degree, the curves of the semidiurnal variation also distinctly show the influence of both phenomena of land and sea breezes and of the Espy-Köppen effect.

The main reason for this is probably that both phenomena do not run purely sinus-like, but deviate from it sufficiently to produce an important semi-diurnal term when applying harmonic analysis. Indeed both phenomena chiefly originate in insolation to and radiation from the earth, which do not run purely semidiurnal.

The graphs distinctly show that these influences make themselves felt principally below 3 km. and may be neglected above 4 km. Therefore, if we wish to arrive at results for the lower layers, not disguised by either of these effects, it will be necessary to operate far from the land and above the open sea, because here they are both absent.

Eventually we proceeded to these observations and the last mentioned of us together with the observator J. H. KATS started a series of ascen-

sions from a small coral island in the Java Sea (one most north of the Duizend-Eilanden¹⁾); moreover he erected an anemograph (recording velocity and direction) on the neighbouring Noordwachter light house (50 m. above sea level). These balloon observations are still in hand, but of the wind records the results of a few months are available.

These, however, have shown that there also, i. e. at a distance of no less than 68 km. from the Sumatra coast, still considerable land and sea breezes, are found and, seeing that the islet whence the balloons were sent up is situated respectively 60 km and 70 km from the Java and Sumatra coasts, the results there obtained will neither be free from the effect of land and sea breezes²⁾.

We trust to obtain and publish in due course the various results for land and sea breezes and Espy-Köppen effect, to be deduced from the foregoing observations, after the necessary reductions have been completed.

For the present we will deal with the results for the atmospheric layers above 4 km only.

Then it will at once appear from the graphs that the amplitude of the diurnal variation must be a minute one for both components, in any case too slight to be deduced with any certainty at all from the results obtained.

The semi-diurnal variation of the N. component is also a minute one, however, the scattering of the points of observation is much less and the curve drawn between these points deserves more confidence.

On the other hand, the amplitudes for the East component are much larger, whilst the scattering of the points is also slight.

According to this scattering one would expect mean errors of the

¹⁾ The expenses for this investigation have for the greater part been covered by funds put at the disposal of the Director of the K. Magn et Met. Observatorium on the occasion of the dissolution of the Nederl. Ind. Ver. voor Luchtvaart (Netherlands Indian Association for Aeronautics) with the purpose that these funds should be utilised for such aerological researches.

²⁾ According to the observations on Noordwachter during July—November 1916 the amplitudes of the diurnal variation of the E-W and N-S components are respectively 83 cm and 54 cm and, therefore are actually in inverse proportion to the distances to the Sumatra and Java coasts of respectively 68 km and 100 km seeing that $\frac{54}{83} = \frac{65}{100}$. The phases are respectively 249° and 204°, agreeing with the phase of the N. component above Batavia at 0.1 km i. e. 222°.

amplitudes smaller than those found for 4, 6.5—7 and 9—11 km, as may appear from the following summary.

Coefficients of the semi-diurnal oscillation, calculated and graphically deduced (in cm. pro sec.).

Height	N. S. Component						E. W. Component					
	x_2			y_2			x_2			y_2		
	calc. graph.	Δ		calc graph.	Δ		calc. graph.	Δ		calc. graph.	Δ	
4 km.	4 10	-6	0 0	0	0	-40 -45	5	43 30	13			
4.5—5 "	17 9	8	7 7	0	-43 -43	0	27 28	1				
5.5—6 "	-15 -1	-14	19 12	7	-31 -35	4	23 20	3				
6.5—7 "	-6 -9	3	1 8	-7	-34 -27	-7	2 2	0				
7.5—8.5 "	-27 -9	-18	-1 -1	0	-12 -9	-3	-26 -26	0				
9—11 "	9 -4	13	-21 -21	0	50 30	20	-23 -23	0				
Mean (absolute values)		10		2		7		3				
Mean error	4 km.	17		17		18		18				
	6.5—7 "	21		21		22		22				
	9—11 "	32		30		34		32				

Even if above 7 km the course of the curves may not be quite reliable and consequently the small deviations as assumed above be somewhat flattered, this is not the case below 7 km. Thus the fact that these deviations are so small must partly be explained by the circumstance that the values arrived at for successive levels are not independent of one another, because for the greater part they are based on observations obtained from the same couple of ascensions for a series of successive heights, and it is especially during undisturbed weather that the E-monsoon current exhibits a fairly amount of homogeneity between 4 and 11 km.

From the above may further be concluded that the course of the curves according to the heights possesses a certainty more approaching the above mentioned Δ 's, but that the curves as a whole may have a greater error, i. e. that they are drawn either too high or too low on the graph.

Therefore, if their course may be trusted, it can be taken as

fairly certain that, at least as regards the semi-diurnal East component, the values for x_2 and y_2 above 4 km. respectively increase and diminish, which comes to this that the phase runs from the second quadrant to the fourth through the third.

Considering the manner the curves are drawn on the graph, the following is arrived at for amplitude and phase.

Height	Semidiurnal variation.			
	North Component		East Component	
	Ampl.	Phase	Ampl.	Phase
4 km	10 cm.	0°	54 cm.	144°
5 "	13 "	51	48 "	147
6 "	13 "	108	38 "	152
7 "	12 "	150	22 "	181
8 "	10 "	280	24 "	243
9 "	13 "	230	28 "	287
10 "	20 "	259	38 "	317

As has been mentioned previously, the results obtained for the lower layers (below 4 km.) are strongly affected by land and sea breezes and the Espy-Koppen effect and only after final reduction of the observations above the Java Sea we may look forward to a better insight into the wind movement in these layers.

From the wind records of the Noordwachter lighthouse 50 m. above sea level, the following particulars have been derived for the semi-diurnal variation of the East component:

$$\begin{aligned} \text{July—November} & \quad 13 \sin (2t-160^\circ) \\ \text{July—September} & \quad 23 \sin (2t-176^\circ) \end{aligned}$$

This value will probably for the greater part be free from the Espy-Koppen effect, but not quite from the influence of land and sea breezes, as the amplitude for the diurnal term amounts to 0.84 m and undoubtedly it will be accompanied by a semi diurnal one, as has been discussed previously for the analogical case at Batavia.

The graphic, however, distinctly indicates the presumable course of the curves between 0 and 4 km and this course is opposite to the one above 4 km.

	Height	Ampl.	Phase
Semi-diurnal variation East-Comp.	0 km.	28 cm.	180°
	1 "	35 "	167
	2 "	44 "	159
	3 "	51 "	151

The surface value of the phase, i. e. 180°, given above, agrees

fairly well with the results for July—September obtained at Noordwachter, viz. 176° .

The principal results of the investigation as regards the East component therefore are:

From 0 up to 4 km, the amplitude increases and the phase decreases from about 180° — 144° , higher up to 7 km, both return to the bottom values.

On higher level until 10 the phase seems to increase greatly and the amplitude to increase again.

When calculating the air displacement (velocity \times density) we find:

Height	Ampl.	Air density	Air-displacement
0 km.	28 cm.	1.00	28
1 "	35 "	0.83	29
2 "	44 "	0.75	33
3 "	51 "	0.67	34
4 "	54 "	0.61	33
5 "	48 "	0.55	26
6 "	38 "	0.49	19
7 "	22 "	0.44	10
8 "	24 "	0.40	10
9 "	28 "	0.37	10
10 "	38 "	0.33	13

The foregoing points to a slight increase up to 4 km and a decrease from here upwards. The values above 7 km are too uncertain to warrant a fresh increase; a gradual decrease is more likely.

The original decrease of phase for the semi-diurnal oscillation of the East component in the lower parts of the atmosphere up to an altitude of 4 km corresponds with that for the semi-diurnal variation of the air pressure resulting from a comparison of the phases for Batavia and for the neighbouring Pangerango top.

	Height	Air pressure		Oscillation of the wind
		Ampl	Phase	Free atmosph Phase
Batavia	8 m.	1.00 mm.	160°	180°
Pangerango	3025 "	0.55 "	142°	151°

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However the variation of air pressure on Mount Pangerango will not be wholly equal to that in the free atmosphere.

The difference in phase for windcomponent and airpressure therefore is:

at 0 km. 20°
and „ 3 „ 9°

As regards greater heights in the equatorial zone only the observations on the Misti top (5840 m. lat. — 16°16')¹⁾ are available.

Here the phase for air pressure is 100° and for the wind 111° (presuming that the wind here blows principally from the W.) making a difference of 11°, i.e. quite in accordance with the value obtained for the Pangerango.

At the foot of the Misti the semi-diurnal variation of the air pressure has a phase of 164° (Mollende 24 m) and on the top of 114°, thus retarding 46° for a difference in height of 5.8 km. With regard to the Pangerango and Batavia this retardation amounts to 18° for a difference in height of 3.0 km., making per km. respectively:

$$\frac{46}{5.8} = 8^\circ \text{ and } \frac{18}{3} = 6^\circ$$

a little difference, seeing the uncertainty in phase for the two tops. The phase for the Misti has been calculated from one year's observations and the one for the Pangerango from three years', but only from two-hourly observations.

If one may go by the value set up for the Misti, one may fix the phase for airpressure above Java at 6 km. at 112°. This would, however make a difference with the phase of the windcomponent at 6 km. of 152°—112°=40°, going by which, we should arrive at: difference in phase of the semi-diurnal oscillation of wind and airpressure

0 km. 20°
3 „ 9
6 „ 40

and if still higher the phase of the air-pressure continues to decrease, the difference will increase to 180° at about 10 km.

This result therefore, gives no support to the reliability of our results as to the renewed increase of phase of the windvariation above 4 km.. in so far that the difference of phase between the variations of air-pressure and wind do not remain constant. On the other hand this support is supplied by the observations of the Ci-drift made at the Batavia Observatory during 1906—10.

¹⁾ HANN, Sitz. Berichte Wien. Bd 118.

When calculating the drift components, it was assumed that the height of the clouds was constant: 11.0 km. for Ci and 10.5 km. for Ci Cu. ¹⁾

For the East component has been found:

		Number of cases			Number of cases
6 ^h —7 a.m.	6.1 m.p.s.	114	0—1 p.m.	5.0 m.p.s.	28
7 —8 "	6.3 "	74	1—2 "	4.0 "	31
8 —9 "	6.9 "	35	2—3 "	5.2 "	55
9 —10 "	4.5 "	36	3—4 "	5.0 "	30
10 —11 "	5.8 "	28	4—5 "	7.3 "	38
11 —12 "	2.9 "	28	5—6 "	7.1 "	140
			6—7 "	6.1 "	34

and consequently for the semi-diurnal term $124 \text{ cm. } \sin(2t + 266^\circ)$. ²⁾

No doubt this result is pretty uncertain, but all the same it rather distinctly points to a high phase (266°), as did the results of the balloon observations (10 km. 317°), and it adds weight to the unexpected result that the phase after originally decreasing up to 4 km., would increase higher up, at first slowly and afterwards more quickly.

The question now arises, how do the results obtained agree with the theoretical ones?

MARGULES was the first to proffer a reasonable explanation of the phenomenon of the semi-diurnal barometrical oscillation, by demonstrating that the period of oscillation of an infinitely thin atmospheric shell comes near 12 hours, and consequently will be excited by the daily disturbance of the temperature. He therefore proceeds from the oscillation of the temperature and deduces barometer and wind oscillations, but by this process he finds the phases vastly different to those observed.

This is attributed by GOLD ³⁾ to the neglecting of the vertical velocities, as a consequence of dealing with an infinitely thin atmospheric shell, assumed in order to overcome the otherwise unsurmountable mathematical difficulties.

Hence GOLD proceeds on the contrary from the barometer variation and approximately solves the variations of temperature and wind (horizontal as well as vertical.)

¹⁾ FIGEE, Observations Batavia Observatory. Vol. XXX. App. II.

²⁾ By applying the "difference method" afterwards has been found $42 \sin(2t + 263^\circ)$

³⁾ Phil. Mag. Vol. 19.

In this case it is not necessary for him to proffer an explanation of the change of the phase with the height, as shown by the variation of the airpressure.

Of this he only says (p. 37): "This diminution is probably due in part to the greater resistance to motion near the earth's surface; it may be due in part also to a change in the phase of the semidiurnal temperature variation in the free atmosphere".

As regards the latter, there are, in effect, only two determinations available for the free atmosphere,¹⁾ i.e. at Lindenberg and at Batavia. No trustworthy results may be derived from mountain stations.

Phase of the semidiurnal variation.

Height	Lindenberg		Batavia	
	Temp.	Airpress.	Temp.	Airpress.
0 km.	61°	136°	63°	160°
½ "	33	—	92	—
1—2 "	57	—	146	—
3 "	—	113	—	142

At Batavia, therefore, the phases of temperature and pressure move in opposite direction and at Lindenberg there is no pronounced sense of change for the temperature.

On p. 39 GOLD writes: "The difference of phase (between temperature and pressure variation) ought to diminish only slowly with the height; for latit. 45° this decrease would only be 45° at a height of 10 km."

Lindenberg feebly agrees with the above, but at Batavia the diminution in difference of phase is too pronounced, the change in phase (with the height) of the airpressure agreeing indeed, although to a smaller degree.

Thus GOLD finds (see p. 38, note) from a graphical combination 38° diminution in phase for an increase in height of 3 km.; for Batavia-Pangérango (difference in height also 3 km.) 18° has been found.

Further from GOLD's results we find for the North and East components of the horizontal wind variation at the latitude of Batavia's (phase as compared to the one of the pressure variation)

¹⁾ See Observatory Batavia Verhandelingen 4, pg. XXXIX.

North comp.		East comp.	
Ampl.	Phase	Ampl.	Phase
5 cm.	20°	23 cm.	15°

whilst above from the balloon observations have been deduced 28 cm. and 20° as being the most probable values for the East component; a small value being found for amplitude of the North component.

Here, therefore, is a close agreement.

This agreement holds up to a height of 4 km., because the phase of the semi-diurnal variation of the East component follows the one of the air-pressure, and higher up the amplitude of the North component also remains considerably smaller than the one of the East component. E.g. at an average from 4-5 km. we deduce from our observations:

North component 11½ cm. East component 51 cm.

proportion $\frac{51}{11.5} = 4.5$, whereas GOLD finds on the surface of the earth 5 and 23 cm., i.e. a proportion of 4.6; but as to a reverse in the change of phase there is nothing to be found in GOLD's treatise.

However, are there any indications to explain a similar reverse?

In the first place we looked for them in the vertical motion of the air, as found by GOLD's theoretical investigation and have considered whether, as a consequence of the rising or descending of air, a returning flow in the upper layers may take place.

According to GOLD the maximum vertical velocity of the semi-diurnal motion occurs about the time of the greatest horizontal velocity viz. an upward motion in the case of Western motion; e.g. close to the equator at 5 km. he finds an amplitude of the vertical oscillation of 2 mm. pro sec. If in consequence of this we assume an average rise of 1 mm. pro sec. occurring over $\frac{1}{4}$ of the earth's surface or 10,000 km., then we may also surmise that this air would again have to flow off through a layer of a thickness of say 10 km. This would make an average velocity of 1 m. pro sec., i.e. actually a velocity of the order required and it may be accepted as probable that this velocity is in inverse direction to that near the earth's surface.

Also, that on account of the ever increasing outflow and inflow with increasing height, a gradual increase (up to inversion) of phase should occur.

Apparently a similar explanation would not seem illogical, but often such arguments are misleading when we are solving suchlike problems, so that we will only consider it as a hint in that direction.

Finally we examined the possibility that the inversion of phase

might have been occasioned by an accidental distribution of the errors of our observational results and in reality might not exist.

Let us take it that for the values found the real errors were the following ones:

East component.

Height ·k.m.	x_2			y_2			Phase
	Value calcul.	real error	real value	value calcul.	real error	real value	
6.5—7	-34	-9	-25	2	-18	20	142°
7.5—8.5	-12	-2	-10	-26	-41	15	124°
9—11	50	52	-2	-23	33	10	101°

According to the above the real values for amplitude and phase ought to be:

4	km.	59	cm.	133°
4.5—5	"	50	"	148
5.5—6	"	38	"	144
6.5—7	"	20	"	142
7.5—8.5	"	15	"	124
9—11	"	10	"	101

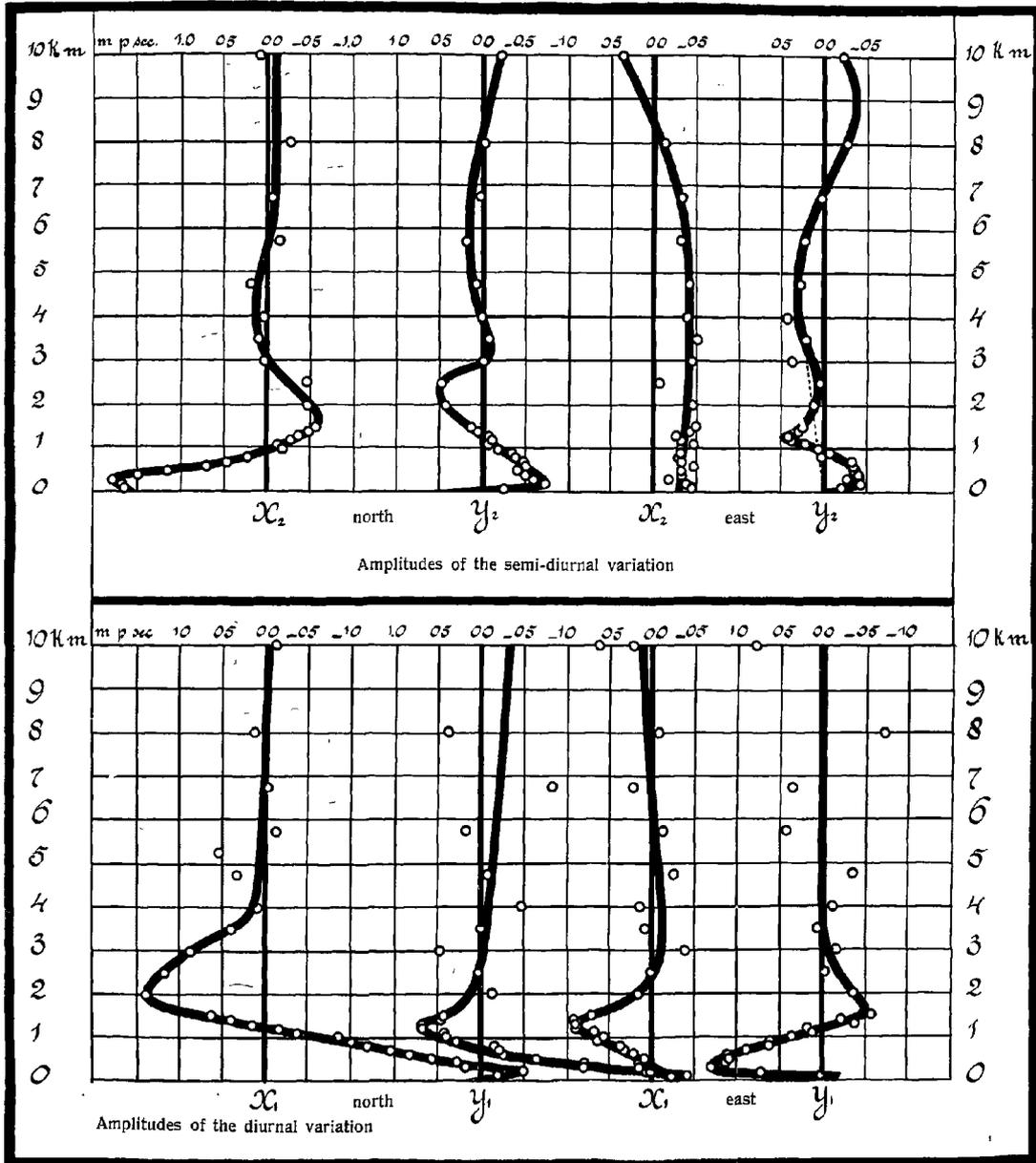
This would do away completely with the inversion and would carry on the original decrease of phase up to the highest heights observed, which should be accompanied by a rapid diminution of the amplitude.

If we observe the real errors, it strikes us that, though the ones for y_2 are one-sidedly negative, they are of about the same size as the mean errors.

	accepted error	mean error
6.5—7 km.	-18	18
7.5—8.5 "	-41	—
9—11 "	-33	32

But, as has been explained above and has been proved by the graph, the mean error is much larger than the one to be expected.

As regards x_2 the real errors accepted for 6.5—7 and 7.5—8.5 km. are small, but the ones for 9—11 km. are much larger than the mean error, already exaggerated, viz. 52 against 34.



This consideration and the support, afforded by the phase previously arrived at for the Ci-drift, therefore leads to the following conclusion: "Possible but not probable" by which is indicated at the same time the manner to arrive at a better insight, viz. more observations.

The ascensions made on the Java-sea, which supplied a number of observations up to about 11 km., have partly met the above requirement, and may conceivably be taken as valid for Batavia.

On the other part it has been decided to commence further ascensions; these are now taking place during the change of the monsoon, when the velocity of the wind (the non-periodical one) as well as 'accidental errors¹⁾ will be slight.

SUMMARY.

1. With a purpose of investigating the diurnal and semi-diurnal oscillation of the motion of the air in the free atmosphere up to high levels, a great number of pilot balloon ascensions took place at Batavia during various hours of the whole day.

2. For the first time some series of nocturnal ascensions of balloons carrying lights, were then performed up to great heights, following the device indicated by C. H. LEIJ²⁾ and as realized by him in some cases.

3. Afterwards will be published the various results for the lower layers of the atmosphere up to 4 km.

4. As regards the upper layers up to 10 km., it appears that the material of observations is insufficient for deducing a diurnal oscillation, on the other hand that for the semi-diurnal one leads up to positive results.

5. The amplitude of the semi-diurnal oscillation is larger for the East than for the North component, the phase of which remains uncertain.

6. In the lower layers the amplitude and phase seem to be in accordance with the theoretical results of GOLD (GOLD does not deal with the upper layers in that respect).

7. Up to 4 km. the phase of the semi-diurnal oscillation of the East component diminishes, in this respect following the corresponding phase of the oscillation of the air pressure.

8. Above 4 km. it is obviously probable that the phase again increases, thus effecting an inversion at a height of about 10 km.

¹⁾ Circumstances have prevented till now (May 1st) from doing so.

²⁾ Quart. Journal. R. Meteor. Soc. 1909.

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Physics. — “*On the Critical Temperature and Pressure of Mercury and Phosphorus.*” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of April 27, 1917).

A. Mercury.

1. In a previous paper¹⁾ I calculated the value 1260° abs. (987° C.) for the critical temperature of mercury, and 192 atm. for the critical pressure.

We namely calculated as most probable value from the densities of the compounds HgCl₂, HgBr₂ and HgI₂ (loc. cit. p. 7—8) for \bar{b}_k for mercury per Gr. atom the value $150 \cdot 10^{-5}$, and further for $\sqrt{a_k}$ from the values of T_k , found by ROTINJANZ (Z. f. ph. Ch. **87**, p. 153) for these compounds, the mean value (likewise per Gr. atom) $11,0 \cdot 10^{-2}$. (loc. cit. p. 8). With these values of $\sqrt{a_k}$ and \bar{b}_k we further calculate from the formulae

$$RT_k = \frac{8}{27} \lambda \frac{a_k}{\bar{b}_k} \times n \quad ; \quad p_k = \frac{1}{27} \lambda \frac{a_k}{\bar{b}_k^2},$$

with $R = 1 : 273,1$, $\lambda = \frac{27}{28} = 0,964$, $n = 2$, the values

$$T_k = 1260 \quad ; \quad p_k = 192 \text{ atm.}$$

All this on the supposition that (saturated) mercury vapour at T_k is bimolecular ($n = 2$); a supposition, to which the course of the vapour tensions between 0° and 500° C. leads us necessarily. (Cf. also loc. cit. p. 12—16).

2. Since then the vapour pressure observations of CAILLETET, COLARDEAU and RIVIÈRE (1900) have become known to me, which go up to 880° C. With

$$\log \frac{p_k}{p} = f \left(\frac{T_k}{T} - 1 \right), \quad \text{or} \quad f + \log p_k = \log p + \frac{fT_k}{T}$$

we calculate for fT_k the values 3004, 2979, 3233, 3107 (mean 3080) from the values 8,0, 22,3, 50, 102, 162 atm. at resp. 500°, 600°, 700°, 800°, and 880° C.; always from a corresponding couple of

¹⁾ On the Fundamental Values of the Quantities \bar{b} and \sqrt{a} etc. II. These Proc. of March 25, 1916, p. 4 and 9.

values of T and p . (f between two observations supposed to be constant). And for $f + \log p_k$ the values 4,789, 4,760, 5,022, 4,905; evidently the value 4,880 for $f + \log p_k$ corresponds with the mean value 3080 found just now for fT_k .

The correction quantity λ is represented (compare also loc. cit. p. 4) by the expression $\lambda = \frac{27}{8\gamma-1} \left(\frac{\gamma}{\gamma+1} \right)^2$. And as γ , the coefficient of direction of the straight connecting line between D_k and D_0 , is given by the approximative formula $2\gamma = 1 + 0,04\sqrt{T_k}$, we find, with about $\sqrt{T_k} = 34,5$, for 2γ the value 2,38 (which at the same time indicates the ratio $b_k : b_0$), i. e. 1,19 for γ . Therefore λ becomes = 0,936, i. e. somewhat smaller than we assumed formerly (0,964, see above).

If now x is the dissociation degree of the Hg_2 -molecules at T_k , there are on an average $n = 2 : (1 + x)$ atoms available per molecule (the association degree of Hg_1), and we have evidently:

$$\left. \begin{aligned} T_k &= 273 \times \frac{8}{27} \times 0,936 \times \frac{(11(1-x) + 36x)^2 \cdot 10^{-4}}{150 \cdot 10^{-5}} \times \frac{2}{1+x} \\ p_k &= \frac{1}{27} \times 0,936 \times \frac{(11(1-x) + 36x)^2 \cdot 10^{-4}}{(150)^2 \cdot 10^{-10}} \end{aligned} \right\}$$

because the quantity $\sqrt{a_k}$ is = $11 \cdot 10^{-2}$ per Gr. molecule for Hg molecules bound to Hg_2 ; much higher on the other hand for the free mercury atoms, viz. $36 \cdot 10^{-2}$ (cf. IV in These Proc. Vol. XIX, p. 317, where we found for bismuth, which stands in the same horizontal row as mercury, 35,6), so that $\sqrt{a_k}$ becomes on an average = $11(1-x) + 36x$ per Gr. atom.

Hence we find:

$$\left. \begin{aligned} T_k &= 10,10 \times \frac{(11(1-x) + 36x)^2}{1+x} \\ \log p_k &= 0,1877 + 2 \log (11(1-x) + 36x) \end{aligned} \right\}$$

with $fT_k = 3080$, $f + \log p_k = 4,880$ therefore (see above):

$$f = 4,692 - 2 \log (11(1-x) + 36x),$$

so that x can be found from

$$\frac{10,10(\quad)^2}{1+x} = \frac{3080}{4,692 - 2 \log(\quad)},$$

or from

$$[4,692 - 2 \log (11(1-x) + 36x)] \times (11(1-x) + 36x)^2 : (1+x) = 305.$$

If now $x = 0$ for T_k , i. e. everything bimolecular, this becomes with $10^2 \cdot \sqrt{a_k} = 11$:

$$316 = 305,$$

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which, considering the uncertainties in the values of b_k and $\sqrt{a_k}$ calculated from the halogen compounds, is already very fair agreement. With $\sqrt{a_k} = 10,8$ we should have found $306 = 305$.

With $x = 0,1$ we should find $393 = 305$ with $\sqrt{a_k} = 9,7 + 3,6 = 13,3$, which therefore does not agree at all. And for still higher values of x the difference would have become greater and greater.

The *least* dissociation of Hg_2 to Hg_1 for T_k is accordingly *quite excluded*, so that we must assume that the mercury is *perfectly bimolecular* there. The *liquid* mercury is *a fortiori* bimolecular, the saturated mercury *vapour* on the other hand will be Hg_1 only at *lower* temperatures (where the large volume prevails); at higher temperatures, however, in consequence of the decreasing volume, it will become Hg_2 in ever increasing degree (cf. also loc. cit. p. 3—4).

3. With the somewhat lower value for λ , viz. $\lambda = 0,936$, and with $b_k = 150 \cdot 10^{-5}$, $\sqrt{a_k} = 10,8 \cdot 10^{-2}$ we now find:

$$T_k = 10,10 \times 116,6 = 1178^\circ \text{ abs.} = 905^\circ \text{ C.}$$

It is therefore seen that at 880° CAILLETET c. s. have been *exceedingly near* the critical temperature of mercury, viz. $\pm 900^\circ$ C.; it lies possibly *scarcely* 20° *higher* than the highest temperature at which they have still carried out a vapour pressure determination (880° C.).

Would it not be desirable in virtue of this fact to determine the critical temperature of mercury at last experimentally? As it was possible to ROTINJANZ to determine those of the mercury halides, which lie resp. at 976° , 1011° and 1072° abs., it may also be possible to come to $\pm 1200^\circ$ abs. (at the melting point of silver, viz. 960° C., we are already far above the critical temperature of mercury).

The only scientist that calculated a fairly plausible value for T_k for Hg, was HAPPEL (Ann. der Ph. (4) 13, 351 (1904)), who gave 1370° abs., i. e. only 100° higher than was calculated by me in 1916 (1260° abs.). But the values of KÖNIGSBERGER (1912), viz. 1270° C. (1543 abs.) and of BENDER (1915), viz. $> 1500^\circ$ C. ($> 1773^\circ$ abs.) are very certainly too high. As $f T_k$ not far below T_k amounts only to $= 3080$ (this follows with absolute certainty from the vapour pressure observations, see above), the value of the factor f would at high temperatures be only $= 2$, or even $1,7$, instead of approaching $2,8$ (see below), whereas this factor is already about $2,7$ or $2,6$ between 0° and 100° C. — still apart from the fact that

then we should find quite improbable values for a_k and b_k ¹⁾.

We calculate for p_k :

$$\log p_k = 0,1877 + 2,0668 = 2,2545,$$

i. e.

$$p_k = 180 \text{ atm.}$$

In order to get somewhat more certainty concerning the values of T_k and p_k , and also of $\sqrt{a_k}$ and b_k , we can still make the following calculation.

From $f T_k = 3080$, $f + \log p_k = 4,880$ follows namely with f resp. = 2,5, 2,6 and 2,65:

$f = 2,50$	$T_k = 1232$	$\log p_k = 2,380$	$p_k = 240$
2,60	1185	2,280	191
2,65	1162	2,230	170

From $8n \cdot b_k = R T_k : p_k$ follows then with $n = 2$, $R = 1$: 273 for b_k (per Gr. atom) $b_k = T_k : 4370 p_k$, i. e. b_k resp. = 117, 142 and $156 \cdot 10^{-5}$.

With these values for b_k we get then a_k resp. = 95,2, 111,3, $119,6 \cdot 10^{-4}$, i. e. $\sqrt{a_k}$ (per Gr. atom) resp. = 9,76, 10,55 and $10,94 \cdot 10^{-2}$, from $T_k = 151,5 a_k : b_k$.

It appears from this most convincingly that — as b_k must lie in the neighbourhood of $150 \cdot 10^{-5}$, $\sqrt{a_k}$ in that of $11 \cdot 10^{-2}$ — the value 1232 abs. is pretty well excluded for T_k , and that we have therefore the choice between from 1185 to 1162. Retaining $b_k = 150 \cdot 10^{-5}$, we get $\sqrt{a_k} = 10,77 \cdot 10^{-2}$, as we assumed above (rounded off 10,8), and further:

$$\underline{T_k = 1172 \text{ abs.} = 899^\circ \text{ C.} \quad ; \quad \underline{p_k = 179 \text{ atm.}}$$

But it is also possible that T_k becomes somewhat higher, e. g. 1185° , to which corresponds $p_k = 191$ atm. Then the value of $\sqrt{a_k}$ would, however, be still lower than that which we calculated from Hg I₂, viz. $10,7 \cdot 10^{-2}$ (loc. cit. p. 8), and that of b_k would become $= 142 \cdot 10^{-5}$, i. e. equal to that which was calculated from this same compound. But these were the very lowest values. Those which were calculated from Hg Cl₂ and Hg Br₂, were both higher (loc. cit. p. 8).

¹⁾ With regard to the value of a , I have convinced myself that from the compressibility of mercury at 0° , 110° , and 192° C. follows about the same value of a as was calculated from the mercury halides for a_1 . And with regard to b_k , even on the supposition that Hg₂ for liquid mercury has the stoichiometric properties of mercurio compounds, a value would follow from the densities of Hg₂Cl₂ and Hg₂Br₂ for Hg (per Gr. atom) in Hg₂, which is only little less than was found for Hg in the *mercuri* compounds. (viz. about $140 \cdot 10^{-5}$ instead of $150 \cdot 10^{-5}$).

4. For the successive values of VAN DER WAAALS' vapour pressure factor f we now find between 0° and 880° C. from the following vapour pressure observations (at lower temperatures mean values)

	0°	100°	200°	300°	400°	500°	550°	600°	650°	700°
$p = 24 \cdot 10^{-5}$	0,2775	17,13	246	(mm.)	2,05	8,0	13,8	22,3	34	50
	750°	800°	850°	880° C.						
	72	102	137,5	162 (atm.)						

the following values.

$\log \frac{p_k}{p}$	8,7534	5,6903	3,8998	2,7427	1,9410	1,3497	1,1129
	0,9045	0,7213	0,5538	0,3955	0,2442	0,1145	0,0433
$\frac{T_k}{T} - 1$	3,2930	2,1421	1,4778	1,0454	0,7415	0,5162	0,4241
	0,3425	0,2698	0,2045	0,1457	0,0923	0,0436	0,0165
$f_{10} = 2,66$	2,66	2,66	2,64	2,62	2,62	2,61	2,62
						(min)	
	2,64	2,67	2,71	2,71	2,65	2,63	2,62
$f_e = 6,12$	6,12	6,12	6,08	6,04	6,03	6,02	6,04
	6,08	6,15	6,24	6,25	6,09	6,05	6,04

The value of p at 0° C. has probably been taken still somewhat too high; we assumed 0,00024 for it (HERTZ gave 0,00019, v. D. PLAATS 0,00047). And especially for the values at the higher temperatures the slightest error in the vapour pressure will make itself greatly felt in the calculated values of f ; the same thing holds with respect to only an minimum error in the calculated values of p_k and T_k . If we assume e. g. $p_k = 180$ atm. instead of 179 atm., $\log p_k$ becomes 24 units in the last decimal greater, which would cause the values of f at the highest three temperatures to rise immediately to 2,67, 2,68, and 2,77 (with nep. log.: 6,15, 6,17, 6,38). Then b_k would get the value $149 \cdot 10^{-5}$ instead of $150 \cdot 10^{-5}$, and $\sqrt{a_k}$ would become 10,74 instead of 10,77. But in any case the course of f is pretty regular; this quantity decreases from about 2,66 at 0° C. to 2,61 (the minimum value) at 500° C., after which it increases again to 2,7 or 2,8 at the critical temperature. The minimum lies at $T = 0,66 T_k$.

The value of f at the critical temperature might have been expected higher than 6,4 or 6,5 (nep. log.), since f_k is equal to 8γ according to our former considerations, when neither a nor b are functions of the temperature. Now γ is about $= 1,2$, hence 8γ would be $= 9,6$. But we should bear in mind that exactly in the case of mercury a would be a temperature function in a high degree. For only through the predominant influence of the volume does Hg become Hg_2 at higher temperatures, whereas if the temperature influence only could make itself felt, Hg_2 would dissociate to Hg_1 ,

which would cause \sqrt{a} to rise from about 11 to 36. The value of $\left(\frac{dn}{dt}\right)_v$ at T_k will, therefore, be very great positive, and this will lower the value of $\left(\frac{dp}{dt}\right)_v$ at the critical temperature considerably. Hence the value of $f_k = \left(\frac{T}{p} \frac{dp}{dt}\right)_k$ will also be considerably lower than the normal value. In our case the expected value is diminished from 9,6 to 6,5.

As T_k is now found = 1172° abs. instead of 1260° abs., as I calculated before, the ratios $T_k : T_s$ and $T_k : T_n$ will also be somewhat lower. For the former we find 1172 : 630 = 1,86, and for the latter 5,0. So high a value for the ratio $T_k : T_n$ is only found for He (5,2) and for Bismuth (5,5) of the elements calculated by us up to now. But we shall soon see (in a following paper), that $T_k : T_n$ is also = over 5 for tin, lead and the alkali metals. A pretty high value of $T_k : T_s$ (i. e. $> 1,7$) is also found for Argon, Krypton, Xenon, Niton (1,73—1,79), for the Halogenides (1,75 to 1,72), for O₂ (1,71), for P, Sb and Bi (1,75—1,77), but 1,86 was not reached yet. Among the compounds we mention HCl (1,71), HBr (1,78), HI (1,79), H₂O (1,71), H₂S and H₂Se (1,77), PH₃ (1,75), CS₂ (1,71), CH₄ (1,75), H. COH (1,97), while the three mercury halogenides, examined by ROTINJANZ, give 1,69 to 1,71.

5. In conclusion I will still point out that $b_k = 150 \times 10^{-5}$ does not only ensue from the densities of the mercury halogen compounds (see § 1), but also from the density of mercury itself. For it follows from DEWAR's determinations (1902), who found the value 14,382 for the density at 188° C., and those of MALLETT, who gave 14,193 for the density at -39°, that the limiting density D_0 at about -250° (below this no appreciable volume diminution takes place) will amount to 14,46. 200,6 Gr. of mercury then occupy a space of $200,6 : 14,46 = 13,87$ ccm., i. e. $= 13,87 : 22412 = 61,9 \cdot 10^{-5}$ in so called normal unities. This is, therefore, $b_0 = v_0$. Now according to one of our formulae $b_k : b_0 = 2\gamma$, hence $b_k = 61,9 : 10^{-5} \times 2,4 = = 149 \cdot 10^{-5}$, quite identical to the value which we found above (§ 4) with $p = 180$ atm. We may, therefore, put the value of b_k for mercury at $150 \cdot 10^{-5}$ with great certainty.

The value of D_k is found from the formula $D_k = D_0 : 2(1 + \gamma) = = 14,46 : 4,4 = 3,3$.

Recapitulating we probably have for mercury

$T_k = 1172^\circ$ abs. ($\pm 900^\circ$ C.) , $p_k = 180$ atm , $d_k = \pm 3,3$
 $b_k = 149 \cdot 10^{-5}$, $\sqrt{a_k} = 10,74 \cdot 10^{-2}$, $2\gamma = b_k b_0 = 2,4$; $f_k = \pm 6,4$
 $T_k : T_s = 1,86$; $T_k \cdot T_b = 5,0$.

These values are pretty certain, the critical temperature lies — taking the vapour pressure observations between 500° and 880° into consideration — almost as much as 100° lower than I had calculated in 1916, and *only* 20° higher than the highest temperature at which CALLETET c.s. have carried out their vapour pressure determinations.

That it *seems* at lower temperatures that the critical temperature of mercury lies much higher (as among others KONGSBERGER and BENDER supposed), is owing to this that the expansion of liquid mercury is *abnormally small* at those temperatures (0° — 300° C.). But this is to be attributed to still unknown disturbing circumstances (association e.g.). As little as we may conclude to entirely faulty critical values from the abnormal expansibility of water in the neighbourhood of 4° C. (and still far above it), or of Helium (where likewise a maximum density was observed), may we do so for mercury. We shall come back to this later on.

B. Phosphorus.

1. From the vapour pressures of liquid phosphorus, found by himself between 169° and 634° (These Proc of Oct. 17, 1914 and Jan. 18, 1915; Z. f. ph. Chem. **88** (1914), **91** (1916)), SMITS extrapolated the value 82,2 atm. for the critical pressure, on the assumption of the value 695° C., found by WAHL for the critical temperature of Phosphorus. It is easy to see that this value is *too low*. If from the vapour pressure formula

$\log \frac{p_k}{p} = f \left(\frac{T_k}{T} - 1 \right)$ with $T_k = 695 + 273,1 = 968,1$ we, namely, calculate the values of f at ten different temperatures, we find with $p_k = 80$, resp. 90 atm.:

$t =$	169°,0	210°,0	252°,0	298°,6	355°,7	409°,3	504°	550°	593°	634° C
$p =$	0,04	0,20	0,54	1,38	3,88	(7,36)	23,2	33,0	44,2	58,6 atm.
$\log \frac{p_k}{p} =$	3,3010	2,6021	2,1707	1,7632	1,3143	1,0362	0,5376	0,3846	0,2577	0,1352
	3,3522	2,6532	2,2218 ^s	1,8144	1,3654	1,0874	0,5887 ^s	0,4357	0,3088	0,1863
$\frac{T_k}{T} - 1 =$	1,1898	1,0039	0,8437	0,6934	0,5396	0,4187	0,2458	0,1762	0,1178	0,0672
$f =$	2,77	2,59	2,57	2,54	2,44	(2,47)	2,19	2,18	2,19	2,01
	2,82	2,64	2,63	2,62	2,53	(2,60)	2,40 (min)	2,47	2,62	2,77

From this it is evident that the first row of values (which correspond to $p_k = 80$ atm.) cannot be correct. For then f would *steadily* decrease from the value 2,77 at 169° up to the critical temperature, where the value would even become < 2 !, whereas it is known that f always passes through a *minimum* at $T =$ about 0,7 or 0,8 T_k , after which it *increases* again to T_k . It is easily seen that also with $p_k = 82$ atm. the decrease has not been checked up to T_k , and that not until 90 atm. is reached a suitable and *possible* course for f is obtained. A further calculation, about which presently more, has even taught me that the correct value of p_k is still somewhat higher, viz. about 95 atm. — at least when we continue to assume $T_k = 968,1$.

That SMITS extrapolated a too low value for p_k , is owing to this that he used an invalid formula for this extrapolation; a formula namely, which is only valid at temperatures that lie far from the critical temperature — and which can therefore not serve to extrapolate up to the critical temperature.

For in the well-known relation of CLAPEYRON

$$\frac{dp}{dt} = \frac{\lambda}{T\Delta v}$$

$\Delta v = v_2 - v_1$ can be replaced by v_2 only at *low* temperature, disregarding the liquid volume; and only at *low* temperatures $v_2 = RT/p$ may be put, on the assumption that the vapour follows the law of BOYLE — so that *only then* this formula becomes:

$$\frac{d \log p}{dt} = \frac{\lambda}{RT^2}$$

in which λ represents the (total) heat of evaporation. In imitation of so many other authors, who are still of opinion that this last formula is of general validity, because VAN 'T HOFF and others always used this *limiting* formula for researches where the above mentioned conditions are *fulfilled*, SMITS assumed that the formula with $d \log p$ would *continue to be valid up to the critical temperature*, when it was only assumed that λ decreases linearly with the temperature up to T_k . This now is certainly pretty accurately fulfilled at *lower* temperatures, but near T_k λ suddenly decreases rapidly and becomes $= 0$ at the critical temperature. On SMITS' assumption of linear decrease, however, λ would retain a large finite value still at T_k !

But we need not speak about this any longer, because, as we observed, the whole formula, the linear decrease of λ included, holds

only for *lower* temperatures. And this shows at the same time the incorrectness of the extrapolation carried out by SMITS.

At *all* temperatures, however, VAN DER WAALS' vapour pressure holds, which may be written in the form:

$$\log p = (f + \log p_k) - \frac{fT_k}{T}, \quad (a)$$

in which f is still a temperature function. When we compare this expression with the integrated formula $d \log p = \text{etc.}$, on the assumption of $\lambda = \lambda_0 - \varphi RT$, i. e. with

$$\log p = C - \frac{\lambda_0}{RT} - \varphi \log T = C - \frac{(\lambda_0 : R) + \varphi T \log T}{T}, \quad . (b)$$

it appears that in the formula used by SMITS, which — we repeat it — holds only for relatively low values, the constant C will be $= f_0 + \log p_k$, and that $\lambda_0 = f_0 RT_k$. But though the *form* of the last formula shows resemblance with VAN DER WAALS' formula, the numerator of the term with $1/T$ will be in no connection at all with λ at *higher* temperatures, as λ will approach 0 at T_k , while the numerator mentioned remains finite, and is virtually $= fT_k$, according to VAN DER WAALS' formula.

2. On the assumption of the quadratic relation

$$f = f_k - \alpha \frac{T_k - T}{T_k} + \beta \frac{(T_k - T)^2}{T_k^2}$$

for the portion of the vapour pressure curve between the minimum and the critical temperature, I calculated the values $\alpha = 11,71$, $\beta = 26,62$, $f_k = 3,77$, $p_k = 95,3$ for the four unknown quantities α , β , f_k , and p_k from the four vapour pressure observations at 504° , 550° , 593° , and 634° .

However — neither the values $T_k = 968,1$, $p_k = 95$, nor even with the somewhat lower pressure 90 atm., can satisfy us. It is namely almost sure that at 695° C., according to the determinations of the density of STOCK, GIBSON and STAMM (1912), the phosphorus vapour is still quite normal, i. e. $= P_4$, even at the low pressure of 75 m.m. And this will *à fortiori* be the case at a pressure of 80 à 90 atm. (i. e. at a *total* pressure, internal and external pressure combined, of $f_k \times 80$ or $90 = \pm 640$ or 720 atm.). The same thing follows also from PREUNER and BROCKMÖLLER's determinations (Z. f. ph. Chem. **81**, p. 159 (1912)).

From the formula $b_k = RT_k : 8p_k$ the value $465 \cdot 10^{-5}$ would now follow for b_k with $T_k = 968,1$, $p_k = 95,3$; and with $p_k = 90$ the value $492 \cdot 10^{-5}$. Both most probably too low, as $4 \times 140 = 560 \cdot 10^{-5}$ may be expected.

The only way out is that the critical temperature 695° C. determined by WAHL is about 20° or 25° too high, and that 675° or 670° C. is perhaps the correct temperature.

When the above given calculation (with $f = f_k - \alpha$ etc.) is now repeated for different values of T_k , we find e.g.

$T_k = 695^\circ \text{ C}$	$\alpha = 11,71$	$\beta = 26,62$	$f_k = 3,77$	$p_k = 95,3$	$b_k = 465$
680° "	10,31	25,80	3,48 ⁵	83,6	522
670° "	9,40	25,26	3,31	77,1	560

Only the last value of T_k , viz. 670°, gives a plausible value of b_k with the corresponding value of $p_k = 77,1$ atm. But as this value for phosphorus is not *perfectly certain*, it is also possible that an intermediary value, e.g. 675° C., must be assumed. The value of p_k would then become about 80 atm., and b_k a little more than $540 \cdot 10^{-5}$. With a value 2% lower, i.e. 948,7 abs. instead of 968,1 abs., or 675,6 C., and with $p_k = 80$ atm. we should find the following values for f for the same ten temperatures as in § 1.

$\log \frac{p_k}{p}$	3,3010	2,6021	2,1707	1,7632	1,3143	1,0362	0,5376	0,3846	0,2577	0,1352
$\frac{T_k}{T} - 1$	1,1460	0,9638	0,8068	0,6595	0,5088	0,3903	0,2209	0,1527	0,0954	0,0459
f	2,88	2,70	2,69	2,67	2,58	2,65	2,43 (min)	2,52	2,70	2,95

The value at 409°,3, still determined by SMITS with difficulty between the two series of observations, is rather divergent, as was to be expected. We find namely 2,65 instead of 2,50 about; but the other values all form actually one single series, so that the liquid white phosphorus can be considered with perfect certainty as the metastable continuation of the liquid red phosphorus below the triple point at 589°,5 — which has been proved irrefutably by SMITS.

We have, therefore, with some probability for the critical data of phosphorus:

$$T_k = \underline{\pm 948,1 \text{ abs.}} = \underline{\pm 675^\circ \text{ C.}}; \quad p_k = \underline{\pm 80 \text{ atm.}}$$

At T_k the value of f will then approach 3,4 (with nep. log. it will approach 7,8). For b_k we find $542 \cdot 10^{-5}$, i.e. $135 \cdot 10^{-5}$, per

Gr.atom¹⁾; and for $a_k = RT_k \times (27 : 8 \lambda) \times b_k$ the value 0,0665 with $\lambda = 0,955$ ($\gamma = 1,09$); cf. also IV, These Proc. of June 24, 1916, p. 307), so that $\sqrt{a_k}$ becomes $\approx 25,8$, i.e. $6,45 \cdot 10^{-2}$ per Gr.atom.

The value 7,8 found for f_k is somewhat lower than would follow from $f_k = 8 \gamma$, viz. 8,7, or 3,8 with ordinary log.

The minimum lies at $(T_k - T) : T_k = \alpha : 2\beta = 0,193$, i.e. at $T = 0,81 T_k$, or 183° lower than T_k , hence at 492° C., only slightly below 504° C. And this minimum value of f will evidently be $= f_k - (\alpha^2 : 4\beta) = 3,40 - (97,12 : 102,1) = 2,45$. We found above the slightly lower value 2,43 with the value of 80 atm. for p_k , which had been taken somewhat too low (80,7 atm. corresponds namely with $675^\circ,6$).

Fontanivent sur Clarens, March 1917.

¹⁾ From the critical data of PH_3 would even follow 131 with $H = 34$ (cf. I, These Proc. of Jan. 29, 1916, p. 1224). But these data are possibly not absolutely accurate either.

Physics. — “*Adiabatic Invariants of Mechanical Systems.*” I. By
 J. M. BURGERS. Supplement N^o. 41c to the Communications
 from the Physical Laboratory at Leiden. (Communicated by
 Prof. H. A. LORENTZ).

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Introduction.

During the past year¹⁾ the theory of quanta has made great progress by the study of a class of mechanical systems which are characterized by the following property: the integral of action:

$$W = \int 2 T . dt$$

(T : kinetic energy) separates into a sum of integrals each of which depends on one of the coordinates only:

$$W = \sum_k \int^{q_k} dq_k \sqrt{F_k(q_k)^2} \dots \dots \dots (1)$$

In general each coordinate can only move up and down within a certain interval (which is given by roots of the equation $F_k = 0$)²⁾.

From the formula given for W it follows that the momentum corresponding to the coordinate q_k is equal to:

$$p_k = \sqrt{F_k(q_k)},$$

hence:

$$\int dq_k \sqrt{F_k} = \int dq_k . p_k \dots \dots \dots (2)$$

For this class of systems EPSTEIN and other investigators use the following equation as the principle for the introduction of the quanta:

$$I_k = \int dq_k . p_k = n_k . h \dots \dots \dots (3)$$

¹⁾ K. SCHWARZSCHILD: Sitz. Ber. Berl. Akad. 1916, p. 548.

P. EPSTEIN: Ann. d. Physik 50 (1916) p. 490; 51 (1916) p. 168.

P. DEBIJE: Gött. Nachr. (1916) p. 142; Phys. Z. S. 17 (1916) p. 507, 512.

A. SOMMERFELD, Ann. d. Physik 51 (1916) p. 1; Phys. Z. S. 17 (1916) p. 491.

²⁾ The radical sign has been written in accordance with the most common cases; the function F_k then becomes a rational function.

³⁾ Comp. note 2 p. 150.

where during the integration q_k moves up and down once between its limits (n_k being an arbitrary integral number).

Now Prof. P. EHRENFEST¹⁾ has pointed out the great interest for the theory of quanta of the so-called *Adiabatic Invariants*, i.e. quantities the value of which does not change if the system is transformed in an adiabatic way (definition by EHRENFEST, l.c. and below § 1) from one state of motion to another. He has shown that for rigorously periodic systems the integral of action, extended over a full period $P = \frac{1}{\nu}$:

$$\int_0^P dt \cdot 2T = P \cdot \overline{2T} = \frac{2T}{\nu}$$

does not change its value during an adiabatic variation of the system; and also that both the quanta-formulae introduced by SOMMERFELD for the elliptic motion are related to adiabatic invariants. As Prof. EHRENFEST has already remarked it would be very interesting to inquire whether the above mentioned quantities I_k are also adiabatic invariants. In the following lines I will try to show that this is the case.

§ 1. General considerations about the adiabatic alteration of a system.

Suppose that the mechanical system under consideration possesses n degrees of freedom; the coordinates will be denoted by $q_1 \dots q_n$; the momenta by $p_1 \dots p_n$. H be the Hamiltonian function, expressed in terms of the q and p . For the present we will only suppose that no coordinate or momentum can increase indefinitely, but that all of them will remain between certain limiting values (to be deduced from the equations of motion) (*supposition A*).²⁾

In the function H besides the q and p certain *parameters* a occur: e.g. masses, electric charges, the intensity of a field of force. We may imagine that during a certain time these parameters are changed infinitely slowly. A *reversible adiabatic* variation of the system will

1) P. EHRENFEST, these Proceedings Vol. XIX (1), p. 576, 1917.

2) In the problems treated by EPSTEIN and others an azimuthal angle φ occurs, which can increase indefinitely. The configuration of the system, however, is periodic with respect to this coordinate; an increase of φ by 2π here takes the place of the up and down motion of the other coordinates. Apart from this the further treatment remains substantially the same. (It is also possible to introduce $q = \sin \varphi$ as a new variable — cf CHARLIER, Die Mechanik des Himmels I p. 112 — in order to return to the general case).

now be defined as consisting of a variation of the a , which is characterized by the following properties :

(I) The variation is infinitely slow as compared to the motions of the system; or more precisely: in a time during which every coordinate has moved up and down many times between its limiting values, the a have increased or decreased by an infinitely small quantity of the first order.

(II) $\frac{da}{dt}$ is approximately a constant.

(III) During the variation the Hamiltonian equations:

$$\frac{dq_k}{dt} = \frac{\partial H}{\partial p_k}; \quad \frac{dp_k}{dt} = -\frac{\partial H}{\partial q_k} \dots \dots \dots (4)$$

remain valid ¹⁾.

If the motion is transformed from a given state in which the a and the constants of integration of the equations of motion have certain values in an adiabatic way to another state, the values of these integration constants will change. For supposing:

$$c = f(q, p, a, t)$$

to be an integral, we have during the adiabatic process from (III)

$$\frac{dc}{dt} = \sum_s \frac{\partial c}{\partial a_s} \frac{da_s}{dt} \dots \dots \dots (5)$$

For simplicity it will be assumed that only one parameter is varied; then the total increase of c will be:

$$\delta c = \int \frac{\partial c}{\partial a} \frac{da}{dt} dt = \overline{\frac{\partial c}{\partial a}} \cdot \delta a \dots \dots \dots (6)$$

where the line over $\frac{\partial c}{\partial a}$ denotes an appropriately taken mean value ²⁾.

According to (II) we may take the mean with respect to the time, whereas on account of supposition (I) $\frac{\partial c}{\partial a}$ may be replaced by the

value of $\overline{\frac{\partial c}{\partial a}}$ for the *undisturbed* motion.

The increase of a function $g(c, a)$ of the integration constants and the parameters during the adiabatic change is given by the formula:

¹⁾ This is for instance always the case if only the a which occur in the function of forces are varied. — In a system possessing cyclic coordinates the cyclic momenta may appear as parameters; and the same holds for the cyclic velocities, if instead of H the function $R = H - \sum p \text{ cycl. } \dot{q} \text{ cycl.}$ is introduced.

²⁾ Supposition (A) was introduced in order to make possible the definition of a mean value of this kind.

$$\delta g = \sum \frac{\partial g}{\partial c} \delta c + \frac{\partial g}{\partial a} \delta a \dots \dots \dots (7)$$

If for such a function g : $\delta g = 0$, it will be defined as an *adiabatic invariant*¹⁾.

§ 2. If the equations of motion are completely integrated it is always possible to express the momenta $p_1 \dots p_n$ as functions of the q , the a and n constants of integration $\alpha' \dots \alpha^{n-2}$. In accordance with what was said in the introduction we shall specialize to systems where the expression of p_k contains only the coordinate q_k (together with the a and α):

$$p_k = \sqrt{F_k(q_k, \alpha' \dots \alpha^{n-2}, a)} \dots \dots \dots (8)$$

(Supposition B).

In connection with supposition (A) of § 1 the functions F_k are assumed to possess the following properties:

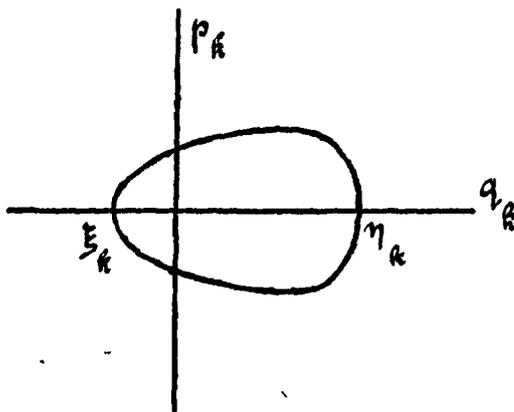
- (1) Each equation $F_k(q_k) = 0$ has (at least) two simple roots ξ_k and η_k ; for values of q_k between these roots $F_k > 0$.
- (2) At a certain instant q_k lies between ξ_k and η_k .

It can then be shown that q_k remains in this interval, and that it performs a so-called *libration*^{4) 5)} (Supposition A').

The following integrals will now be introduced, which will be called "phase-integrals":

$$I_k = \int dq_k \cdot p_k = \int dq_k \sqrt{F_k(q_k)} = I_k(\alpha' \dots \alpha^n a) \dots \dots (9)$$

¹⁾ Intégrals $c=f$ which are *independent* of the a are themselves adiabatic invariants (cf. form. 6). As an instance: in the motion under central forces the integral of the moment of momentum.



²⁾ This may be accomplished for instance by the integration of the partial differential equation of HAMILTON-JACOBI.

³⁾ Geometrical interpretation of this formula: If we draw a q p -diagram for the coordinate q_k , the point (q_k, p_k) describes a closed curve, the form of which is independent of the values of the other q .

⁴⁾ Cf. CHARLIER, Die Mechanik des Himmels, (Leipzig 1902) I, p 86, 100.

⁵⁾ Comp. note 2, page 150.

During the integration q_k moves up and down once between its limiting values ξ_k and η_k ; written explicitly:

$$I_k = 2 \int_{\xi_k}^{\eta_k} dq_k \sqrt{F_k(q_k)} \dots \dots \dots (9a)$$

If the system is varied adiabatically, the variation of I_k will be:

$$\delta I_k = \frac{\partial I_k}{\partial a} \delta a + \sum_m \frac{\partial I_k}{\partial \alpha^m} \delta \alpha^m = \delta a \cdot 2 \int_{\xi_k}^{\eta_k} dq_k \frac{\partial \sqrt{F_k}}{\partial a} + \sum_m \delta \alpha^m \cdot 2 \int_{\xi_k}^{\eta_k} dq_k \frac{\partial \sqrt{F_k}}{\partial \alpha^m} \quad (10)$$

It is thus necessary to calculate $\delta \alpha_m$. Solving the α from the equations (8) we obtain the system of n first integrals:

$$\alpha^m = H^m(q, p, a) \dots \dots \dots (11)$$

(One of the α , say α' is the total energy; then H' is the HAMILTONIAN function).

Hence according to equation (6) we have:

$$\delta \alpha^m = \frac{\partial H^m}{\partial a} \delta a \dots \dots \dots (12)$$

Now the quantities $\frac{\partial H^m}{\partial a}$ may be expressed by means of the $\frac{\partial \sqrt{F_k}}{\partial a}$.

If in equation (11) for the p 's the values (8) are introduced, it becomes an identity, thus:

$$\frac{\partial H^m}{\partial a} + \sum_l \frac{\partial H^m}{\partial p_l} \frac{\partial \sqrt{F_l}}{\partial a} = 0 \dots \dots \dots (13)$$

Further we put:

$$\frac{\partial \sqrt{F_l}}{\partial \alpha^m} = f_{lm}; \dots \dots \dots (14)$$

the determinant of the n^2 quantities f_{lm} will be called F ; its minors F^{lm} . From the properties of functional determinants it follows that:

$$\frac{\partial H^m}{\partial p_l} = \frac{F^{lm}}{F} \dots \dots \dots (15)$$

Equations (13) and (15) give:

$$\frac{\partial H^m}{\partial a} = - \sum_l \frac{F^{lm}}{F} \frac{\partial \sqrt{F_l}}{\partial a} \dots \dots \dots (16)$$

¹⁾ At the limits of the interval of integration the integrand $\sqrt{F_k} = 0$, hence it is unnecessary to take account of the variations of these limits.

²⁾ It may be noticed that:

- a) of the coordinates only q_l occurs in f_{lm} ;
- b) F^{lm} does not contain q_l but it contains the other q .

In order to find the mean of this quantity with respect to the time, it is necessary to study the properties of periodicity of the systems under consideration.

§ 3.

We introduce a set of n variables t_1, \dots, t_n defined by the equations:

$$t_i = \sum_k \int_{\xi_k}^{q_k} dq_k \cdot f_{ki} \dots \dots \dots (17)$$

During the motion of the system we have:

$$\frac{dq_k}{dt} = \frac{\partial H'}{\partial p_k} = \frac{F^k}{F} \dots \dots \dots (18)$$

(Comp. eq. 15).

From this equation it may be inferred that t_1, \dots, t_n are constants, whereas $t = t - t_0$. (The α and the t form a set of canonical integration constants¹⁾).

All the phases of the mechanical system can be characterized by the values of the q and p ; or by the q and α (cf. eq. 8); or by the t and α . We will consider the representation on each other of the following two n -dimensional spaces, obtained by taking the α constant:

(I) the q -space, limited by the surfaces $q_k = \xi_k, q_k = \eta_k$; (II) the t -space.

The representation of these spaces on each other is given by equations (17). The t are many-valued functions of the q with moduli of periodicity:

$$\omega_{ki} = 2 \int_{\xi_k}^{\eta_k} dq_k \cdot f_{ki}(q_k, \alpha' \dots \alpha^n, a) \dots \dots \dots (19)$$

($k, i = 1 \dots n$)

[ω_{ki} is the increase of t_i , if q_k moves once up and down between ξ_k and η_k , the other q remaining constant²⁾].

Hence the t -space can be divided into *period-cells*: similarly placed points of these cells correspond to the same point of the q -space. The representation of one period-cell on the q -space limited according to (I) is uniform; on the other hand every point of the q -space is

¹⁾ If the integral of action be W , we have:

$$t_i = \frac{\partial W}{\partial \alpha^i}$$

²⁾ These integrals obtain a simple meaning if q_k is considered as a complex variable (Cf. SOMMERFELD, Phys. Zeitschr. 17 (1916) p. 500).

represented in more than one point-of a period-cell, in such a way that the positive and negative values of $p_k = \sqrt{F_k}$ are separated.

The determinant of the ω_{ki} will be denoted by Ω ; it will be supposed that $\Omega \neq 0$. Its minors are Ω^{ki} ; we put:

$$\omega^{ki} = \frac{\Omega^{ki}}{\Omega}.$$

Ω is equal to the volume of one period-cell.

In the t -space the motion of the mechanical system is represented by a line parallel to the axis of t_1 , which passes through the cells. If every point of this line is replaced by the corresponding point in one of the cells, a set of points is obtained in this cell which is *everywhere dense*, if no relations of commensurability exist between the ω^{j1} (relations of the form:

$$\sum_j m_j \omega^{j1} = 0$$

the m_j being positive or negative *integral* numbers ¹⁾. (Supposition C).

We now replace the mean of a quantity z with respect to the time, - i.e. the mean value of z for all the states of the system represented by a great length of the t -line, by the mean value of z for all points of one period cell. ²⁾.

¹⁾ This theorem is due to STÄCKEL. It is founded upon theorems given by JACOBI and KRONECKER. Cf. KRONECKER, Werke 3, 1, p. 47.

Remark. We put:

$$\tau^j = \sum_i \omega^{ji} t_i.$$

The τ^j are SCHWARZSCHILD's "Winkelkoordinaten" (l.c.; comp. also EPSTEIN, Ann. d. Phys. 51 (1916) p. 176). If q_k moves up and down once between its limiting values ξ_k and η_k , while the other q remain constant, only τ^k increases by 1.

Taking the τ as a rectangular set of coordinates, the set of period cells becomes a system of hypercubes, bounded by the surfaces $\tau^k = \text{integral number}$, while the motion of the mechanical system is represented by the line

$$\tau^j = \omega^{j1} t + \text{constant}.$$

The ω^{j1} are the *mean motions*.

²⁾ That these methods of calculating the mean value come to the same may be demonstrated as follows (for the sake of simplicity we limit ourselves to a system of two degrees of freedom): The quantity z may be written as a function of the "angular variables" τ^1, τ^2 , which is periodic with respect to both these variables with periods equal to 1. If we suppose (which certainly is allowed) that

$\frac{\partial^2 z}{\partial \tau^1 \partial \tau^2}$ exists and is continuous everywhere in the region $0 < j < 1$, this function

may be expanded in a double Fourier series in τ^1 and τ^2 (Cf. on multiple Fourier series for instance BORN, Dynamik der Krystallgitter, Anhang (Leipzig, Teubner 1915)). Hence:

$$z = A_0 + \sum A_{rs} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} \left(r \cdot \frac{\tau^1}{2\pi} + s \cdot \frac{\tau^2}{2\pi} \right)$$

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Hence :

$$\bar{z} = \frac{1}{\Omega} \int \dots \int dt_1 \dots dt_n \cdot z \dots \dots \dots (20)$$

where the integration is extended over the volume of one period cell.

Written as a function of the q :

$$\begin{aligned} \bar{z} &= \frac{1}{\Omega} \int \dots \int dq_1 \dots dq_n \frac{\partial(t_1 \dots dt_n)}{\partial(q_1 \dots q_n)} \cdot z = \\ &= \frac{1}{\Omega} \int \dots \int dq_1 \dots dq_n \cdot F \cdot z \dots \dots \dots (20a) \end{aligned}$$

During the integration every q moves up and down once between its limits.

We use this to calculate $\frac{\partial \bar{H}^m}{\partial a}$ (comp. formula 16):

$$\begin{aligned} \frac{\partial \bar{H}^m}{\partial a} &= - \sum_l \left(\frac{F^{lm}}{F} \cdot \frac{\partial \sqrt{F_l}}{\partial a} \right) = \\ &= - \frac{1}{\Omega} \sum_l \int \dots \int dq_1 \dots dq_n \cdot F^{lm} \frac{\partial \sqrt{F_l}}{\partial a} \dots \dots \dots (21) \end{aligned}$$

By means of the relation :

$$\int \dots \int dq_1 \dots dq_{l-1} dq_{l+1} \dots dq_n \cdot F^{lm} = \Omega^{lm}$$

it can easily be verified that form. (21) reduces to :

$$\frac{\partial \bar{H}^m}{\partial a} = - \sum_l \omega^{lm} \cdot 2 \int_{\xi_l}^{\eta_l} dq_l \frac{\partial \sqrt{F_l}}{\partial a} \dots \dots \dots (22)$$

Now from form. (10), (12), (14) and (19) we have :

where:

$$A_0 = \int_0^1 \int_0^1 d\tau^1 d\tau^2 \cdot z.$$

This series converges uniformly and can be integrated term by term. If we now put: $\tau_j = \omega^j \cdot t + const.$, and calculate the form:

$$\bar{z} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{t_0}^{t_0 + T} dt \cdot z$$

it is found — as none of the factors $r\omega^{11} + s\omega^{21}$ is equal to zero — to reduce to :

$$\bar{z} = A_0 = \int_0^1 \int_0^1 d\tau^1 \cdot d\tau^2 \cdot z.$$

$$dI_k = d\alpha \left[2 \int_{\xi_k}^{\eta_k} dq_k \frac{\partial V_{F_k}}{\partial \alpha} + \sum_m \omega_{km} \frac{\partial \overline{H^m}}{\partial \alpha} \right] . \quad (23)$$

Substituting for $\frac{\partial \overline{H^m}}{\partial \alpha}$ its value according to (22), it is immediately found that :

$$\underline{dI_k = 0,}$$

hence I_k is an adiabatic invariant.

SUMMARY.

If a mechanical system possesses the following properties :

1. every momentum p_k can be expressed as a function of the corresponding coordinate q_k (supposition B) ;
 2. the motion of every coordinate q_k is a *libration* (supposition A') ;
 3. no relations of commensurability exist between the mean motions ω^1 of the "angular variables" (supposition C) ;
- then the "phase integrals"

$$I_k = 2 \int_{\xi_k}^{\eta_k} dq_k \cdot p_k$$

are *invariant* against an *adiabatic disturbance* of the system.

Remark. Those cases of degeneration in which supposition C is not satisfied will be treated separately in a subsequent communication.

Physics. — “*Adiabatic Invariants of Mechanical Systems*”. II. By J. M. BURGERS. Supplement N^o. 41*d* to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of December 21, 1916).

Systems between the mean motions of which relations of commensurability exist.

In the 1st part of this paper¹⁾ it was shown that for mechanical systems, possessing the following properties:

1. each momentum p_k can be expressed as a function of the form:

$$p_k = \sqrt{F_k(q_k, \alpha' \dots \alpha^n, a)}$$

2. the motion of each coordinate is a libration;
the n phase-integrals:

$$I_k = \int p_k dq_k$$

are all of them adiabatic invariants, provided no relations of commensurability exist between the mean motions ω_i of the “angular variables” α . As remarked in the paper quoted, this supposition was necessary in order that the system might pass consecutively through all the states which are represented by the points of a period-cell, so that an integral with respect to the time might be replaced by an integral over the volume of a period-cell.

In this section we shall consider the case that relations of commensurability do exist between the mean motions, and it will be shown that if the adiabatic disturbances are limited to such *as do not violate these relations*, at least certain definite linear combinations of the I_k (with integral coefficients) are invariants. If the system is rigorously periodic, so that the mean motions are all equal, the only combination of this character is found to be the sum of all the phase-integrals (in other words: the integral of action, extended over a full period of the system), the invariancy of which has already been demonstrated by EHRENFEST²⁾.

We shall describe the motion of the mechanical system in the

¹⁾ These Proceedings. p. 149.

²⁾ P. EHRENFEST, *ibidem* XIX (1) p. 576, 1917.

system of coordinates of the angular variables τ , which are related to the canonical variables t by the formulae:

$$\tau^j = \sum_i \omega^i \cdot t_i \dots \dots \dots (1)$$

In the t -space the boundary "surfaces" of the period-cells are given by

$$\sum_i \omega^i \cdot t_i = \text{integral number};$$

hence the τ -space will be divided into "cubes" with side = 1. As $t_2 \dots t_n$ are constant during the motion of the system, whereas $t_1 = t - t_0$, the orbit of the system is represented in the τ -space by the straight line:

$$\tau = \omega^1 \cdot t + \text{const.} \dots \dots \dots (2)$$

In order to simplify our formulae we will assume the t to be determined in such a way that the constants are equal to zero.

We will now suppose that between the mean motions ω^i relations of the form:

$$\sum_j m_j^\mu \cdot \omega^j = 0 \dots \dots \dots (3)$$

($\mu = 1 \dots \lambda$; the m_j^μ being *integral numbers*).

exist.

If each point of the t -line is replaced by the corresponding point in the first cell, the points thus obtained will *not* fill up this cell; they only fill the $(n-\lambda)$ -dimensional regions determined by the equations:

$$\sum_j m_j^\mu \cdot \tau^j = \text{integral number. } (\mu = 1 \dots \lambda) \dots \dots (4)$$

Let us consider the region which contains the t -line itself, for this:

$$\sum_j m_j^\mu \cdot \tau^j = 0 \quad (\mu = 1 \dots \lambda) \dots \dots \dots (5)$$

In this region we may construct a *period-lattice* in the following way: the points of the net are the *integral solutions* of the equations (5). These solutions can all of them be expressed as *linear integral combinations* of a "primitive" set of $n-\lambda$ independent solutions:

$$\tau = r_s^j \quad (s = 1 \dots n-\lambda) \dots \dots \dots (6)$$

Such a primitive set gives the angles of a *primitive period-cell*.

In the region (G) defined by equations (5) we shall introduce a system of $n-\lambda$ coordinates ϑ^s , so that:

$$\tau = \sum_s r_s^j \cdot \vartheta^s \dots \dots \dots (7)$$

Then the period-cells in this region are bounded by the "hyper-surfaces"

$$\vartheta^s = \text{integral number.}$$

In a way analogous to the one used in the general case it can be shown that the mean value of a function taken for all points of the t -line may be replaced by the mean value for all points of an $(n-\lambda)$ -dimensional period-cell in the region G . From this it follows that the mean of a quantity Z with respect to the time is equal to:

$$\bar{Z} = \int_0^1 \dots \int_0^1 d\vartheta^1 \dots d\vartheta^{n-\lambda} \cdot Z \dots \dots \dots (8)$$

In the case considered this formula has to be used instead of eq. (20) of the previous paper in computing the quantities: $\frac{\overline{\partial H^m}}{\partial a}$.

If now we put:

$$Y_s = \sum_k r_s^k \cdot I_k \quad (s = 1 \dots n - \lambda) \dots \dots (9)$$

we can show that the quantities Y_s are invariants for such adiabatic disturbances as do not violate the relations (3).

Scheme of the calculation.

Making use of the expression obtained in the first part (eq. 23) as the value of $\frac{\delta I_k}{\delta a}$, it is found that:

$$\frac{\delta Y_s}{\delta a} = \sum_k r_s^k \cdot \frac{\delta I_k}{\delta a} = \sum_k r_s^k \cdot 2 \int_{\xi^k}^{\eta^k} dq_k \frac{\partial V F_k}{\partial a} - \sum_{klm} r_s^k \cdot \omega_{km} \cdot f^{lm} \frac{\overline{\partial V F_l}}{\partial a} \dots (10)$$

The second part of this expression is equal to:

$$- \sum_l \int_0^1 \dots \int_0^1 d\vartheta^1 \dots d\vartheta^{n-\lambda} \sum_{km} r_s^k \cdot \omega_{km} \cdot f^{lm} \cdot \frac{\partial V F_l}{\partial a} \dots \dots (11)$$

(the quantities r_s^k , ω_{km} being constants, they may be taken under the sign of integration). We will now transform the term of the sum which bears the index l from the variables $\vartheta^1 \dots \vartheta^s \dots \vartheta^{n-\lambda}$ to the variables: $\vartheta^1 \dots \vartheta^{s-1} q_l \vartheta^{s+1} \dots \vartheta^{n-\lambda}$. The Jacobian of this transformation is:

$$\frac{\partial(\vartheta^1 \dots \vartheta^s \dots \vartheta^{n-1})}{\partial(\vartheta^1 \dots q_l \dots \vartheta^{n-1})} = \frac{1}{\frac{\partial q_l}{\partial \vartheta^s}} = \frac{1}{\sum_{km} f^{lm} \cdot \omega_{km} \cdot r_s^k} \dots \quad (12)^1$$

Hence (11) changes into :

$$- \sum_l \int_0^1 \dots \int_0^1 d\vartheta^1 \dots d\vartheta^{s-1} d\vartheta^{s+1} \dots d\vartheta^{n-1} \int dq_l \frac{\partial V/F_l}{\partial a} \dots \quad (13)$$

If ϑ^s changes from 0 to 1, τ^l increases by r_s^l ; hence q_l describes r_s^l full periods²⁾. The expression (13) now becomes :

$$- \sum_l r_s^l \cdot 2 \int_{\xi_l}^{\eta_l} dq_l \cdot \frac{\partial V/F_l}{\partial a} \dots \dots \dots \quad (14)$$

If this is introduced into eq. (10), it is found that: $\sigma Y_s = 0$; it has thus been shown that Y_s is an invariant for the adiabatic disturbances considered.

Remarks.

1. It has been pointed out by SCHWARZSCHILD and EPSTEIN³⁾ that the total energy α^1 of the system, when expressed as a function of the I_k , depends only on the linear integral combinations \mathbf{Y}_k of the \mathbf{I}_k ; this is a consequence of the equations (3). From this it follows that it is always possible to fix the value of the energy by "quantizing" the adiabatic invariants (i.e. by equating the adiab. inv. to integral multiples of PLANCK'S constant).

2. In the equations: $Y_s = \sum r_s^k \cdot I_k =$ adiabatic invariant, an arbitrary primitive system of solutions of eq. (5) may be chosen for the system of coefficients: $r_s^1 \dots r_s^n$ ($s = 1 \dots n - \lambda$). All such systems are connected together by linear integral substitutions, the determinant of which is equal to ± 1 . Hence the same holds for the sets of $n - \lambda$ independent Y_k : if $Y_1^1 \dots Y_{n-\lambda}^1$ and $Y_1^2 \dots Y_{n-\lambda}^2$ be two of these sets, we have:

¹⁾ This follows from the equation:

$$dq_l = \sum_m f^{lm} dt_m = \sum_{mk} f^{lm} \cdot \omega_{km} \cdot d\tau^k = \sum_{mks} f^{lm} \cdot \omega_{km} \cdot r_s^k \cdot d\vartheta^s.$$

²⁾ In the diagram of complex values of q_l (cf. A. SOMMERFELD, Phys. Zeitschr. 17, p. 500, 1916) the path of integration goes r_s^l times round the branch points $q_l = \xi_l, q_l = \eta_l$ of the function $p_l = \sqrt{F_l(q_l)}$.

³⁾ K. SCHWARZSCHILD, Sitz. Ber. Berl. Akad. p. 550, 1916.

P. EPSTEIN, Ann. d. Phys. 51 p. 180, 1916.

$$Y_{s'}^2 = \sum_s c_{s'}^s \cdot Y_s^1$$

$$\text{and } Y_s^1 = \sum_{s'} \gamma_s^{s'} Y_{s'}^2$$

where the $c_{s'}^s$ like the $\gamma_s^{s'}$ are *integral* numbers. If Y_s is put equal to $n_s \cdot h$, where n_s takes all positive and negative integral values, the $Y_{s'}^2$ also pass through all positive and negative integral multiples of h . In like manner the same set of values is obtained for the total energy α^1 of the system, whether expressed as a function of the Y_s^1 , or of the $Y_{s'}^2$.

3. The question arises whether the quantities Y_s found above are the only adiabatic invariants of these systems.

Physics. — “*Adiabatic Invariants of Mechanical Systems. III*”.

By J. M. BURGERS. Supplement N^o. 41e to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

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In the two preceding papers ¹⁾ on this subject the question was investigated as to what quantities possess the property of being adiabatic invariants for those mechanical systems in which the variables can be separated, i.e. where the momenta can be expressed by formulae of the form:

$$p_k = \sqrt{F_k(q_k, \alpha^1 \dots \alpha^n, a)}$$

The result obtained was that the “phase-integrals”: $I_k = \int dq_k p_k$ do not change during an adiabatic disturbance of the system; this conclusion is closely connected with the quantum formulae as introduced by EPSTEIN, DEBYE and SOMMERFELD, who put these integrals equal to integral multiples of PLANCK’S constant. SCHWARZSCHILD²⁾, however, has put the quantum formulae into another form, which is far more general. He supposes that by means of certain transformations it is possible to express the original coördinates and momenta (q, p) as functions of a new system (Q, P), possessing the following properties:

1. The Q are *linear* functions of the time;
2. the P are constants;
3. the q and p are periodic functions of the Q with a period 2π ; hence for instance:

$$q(Q_1 + 2l_1\pi, \dots \quad Q_n + 2l_n\pi) = q(Q_1, \dots \quad Q_n).$$

These variables Q are the so-called “angular variables” (“Winkelkoordinaten”). He then introduces the quantum formulae:

$$\int_0^{2\pi} dQ_k \cdot P_k = 2\pi P_k = n_k \cdot h + \text{constant} \quad \dots \quad (A).$$

If the character of the system is such that the variables can be

¹⁾ These Proceedings p. 149 and 158.

²⁾ K. SCHWARZSCHILD, Sitz. Ber. Berl. Akad. p. 548, 1916.

separated, it is always possible to introduce angular variables; in that case the formulae of SCHWARZSCHILD and those of EPSTEIN coincide¹⁾. In this paper, however, it will be shown without making use of the separation of the variables, that — provided certain conditions mentioned below are fulfilled — it is always possible to choose the quantities P_k in such a way that they are adiabatic invariants. This is of importance as the possibility of introducing angular variables is not limited to those systems.

§ 1. We consider a mechanical system possessing solutions of the following form: the coordinates and momenta q and p can be expanded into trigonometric series (multiple Fourier series) proceeding according to sines and cosines of multiples of n variables $Q_1 \dots Q_n$:

$$\left. \begin{aligned} q_k &= \sum_{-\infty}^{\infty} A_{m_1 \dots m_n}^k \begin{cases} \cos \\ \sin \end{cases} (m_1 Q_1 + \dots + m_n Q_n) \\ p_k &= \sum_{-\infty}^{\infty} B_{m_1 \dots m_n}^k \begin{cases} \cos \\ \sin \end{cases} (m_1 Q_1 + \dots + m_n Q_n) \end{aligned} \right\} \dots (1)$$

These variables are *linear* functions of the time:

$$Q_i = \omega_i t + \varepsilon_i; \dots \dots \dots (2)$$

we limit ourselves to the case that the *mean motions* ω_i are all *incommensurable*. $\varepsilon_1 \dots \varepsilon_n$ are n constants of integration; the ω_i and the coefficients of the trigonometric series are functions of the parameters a occurring in the equations of the system (masses, intensity of a field of force, &c.) and of n other integration constants $P_1 \dots P_n$, chosen in such a way that together with the Q they form a system of canonical variables; the transformation of the q and p into the new variables Q and P is a *contact-transformation*²⁾.

We suppose that for a given domain of values of the P the series considered are uniformly convergent, independent of the value of t .

A method of obtaining solutions of this kind is treated in the last chapter of WHITTAKER'S *Analytical Dynamics* (Cambridge 1904³⁾): *Integration by Trigonometric Series*. — If the Hamiltonian function is a quadratic function of the original variables q and p , the angular variables Q are immediately related to the normal coordinates or principal vibrations of the system⁴⁾; the series then reduce to:

1) Cf. for instance P. S. EPSTEIN, Ann. d. Phys. (4) 51 (1916) pg. 176.

2) Cf. f. i. E. T. WHITTAKER, Anal. Dynamics, p. 282. (Cambr. 1904).

3) A 2nd edition has appeared in 1917 (note added in the English translation).

4) WHITTAKER, l. c. p. 399.

$$q_k = q_{k_0} + \sum \alpha_i^k \cos Q_i + \sum \beta_i^k \sin Q_i \dots \dots \dots (3)$$

with analogous expressions for the p_k .

§ 2. Adiabatic disturbances of the system.

As before we shall assume that during the infinitely slow change of the parameters the HAMILTONIAN equations for the original coordinates and momenta q and p remain valid (see, however, below, remark 4, a). In order to investigate how the variables Q and P behave during such a process, it is simplest to consider into what expression the differential form:

$$\sum p dq - H(q, p, a) dt \dots \dots \dots (4)$$

changes by the transformation from the q, p to the Q, P ¹⁾. As remarked above this transformation is a *contact-transformation*; hence as long as the a are not varied we have:

$$\sum p dq = \sum P dQ + dW \dots \dots \dots (5)$$

dW being the complete differential of a function of the Q and P , which may also contain the a . During the variation the a are explicitly given functions of the time; the formula (5) has then to be replaced by

$$\sum p dq = \sum P dQ + F \cdot \frac{da}{dt} dt + DW \dots \dots \dots (6)$$

where:

$$DW = \sum \frac{\partial W}{\partial Q} dQ + \sum \frac{\partial W}{\partial P} dP + \frac{\partial W}{\partial a} \frac{da}{dt} dt^2) \dots \dots (7)$$

F is a function of Q, P and a , which — if the P have been properly chosen — contains the Q only in the form of trigonometric functions:

$$F = \sum C_{m_1 \dots m_n} \begin{cases} \cos \\ \sin \end{cases} (m_1 Q_1 + \dots m_n Q_n) \dots \dots (8)$$

The proof of this proposition is given in § 3.

Hence the differential expression (4) changes into:

$$\sum P dQ - \{H^*(Q, P, a) - F \cdot \dot{a}\} dt + DW \dots \dots (9)$$

$H^*(Q, P, a)$ is obtained from $H(q, p, a)$ by replacing the q and p by their expansions in trigonometric series. Now the characteristic property of the angular variables is that H^* does not contain the Q :

$$H^* = H^*(P, a)^2) \dots \dots \dots (10)$$

The equations of motion for the Q and P are the canonical equations derived from a HAMILTONIAN function, which is equal to the coefficient of dt in the differential expression (9).¹⁾

¹⁾ WHITTAKER, l. c. p. 297.

²⁾ In order to simplify the formulae it is assumed that only one parameter a is varied.

³⁾ WHITTAKER, l. c. p. 407.

Hence we have for P_k :

$$\frac{dP_k}{dt} = \frac{\partial F}{\partial Q_k} \dot{a} = \dot{a} \left[\sum' \pm m_k \cdot C_{m_1 \dots m_n} \left\{ \begin{matrix} \sin \\ \cos \end{matrix} \right\} (m_1 Q_1 + \dots + m_n Q_n) \right] \quad (11)^1$$

If no relations of commensurability exist between the mean motions ω_i of the Q_i — as is assumed in § 1 — the mean of this expression with respect to the time is *zero*: hence during the variational process P_k remains unchanged²⁾. We have thus proved that the expressions which are “quantized” by SCHWARZSCHILD are invariants for an adiabatic disturbance of the system.

As according to formula (10) the total energy $E = H^*(P, a)$ only depends on the P and on the parameters, it is always possible to fix the value of the energy by quantizing the P .³⁾ 4)

1) The meaning of Σ' is: summation over all + and — values of the m , with the exception of simultaneous zero values of all the m .

2) This may be formulated more exactly as follows:

For the sake of simplicity suppose $\frac{da}{dt}$ to be constant: then by integrating eq. (11) term by term (which is allowed on account of the uniform convergence):

$$\delta P_k = a \left[\sum' \Gamma_{m_1 \dots m_n}^k \left\{ \begin{matrix} \cos \\ \sin \end{matrix} \right\} (m_1 Q_1 + \dots + m_n Q_n) \right]_{t_0}^{t_0 + T}$$

Independently of the value of t the value of the term between [] always remains below a finite limit g . Hence:

$$|\delta P_k| < 2\dot{a} \cdot g$$

On the other hand:

$$\delta a = \dot{a} \cdot T$$

We thus have:

$$\lim_{T \rightarrow \infty} \frac{\delta P_k}{\delta a} = 0$$

This reasoning also applies to the demonstration given in the 1st part of this paper (These Proceedings, p. 149).

3) If the original HAMILTONIAN function $H(q, p, a)$ is a quadratic function of the q and p , $H^*(P, a)$ will be found to be of the form:

$$\sum \omega_k \cdot P_k + \text{constant.}$$

Hence if P_k is put equal to $n_k \frac{h}{2\pi}$ the total energy of the system is:

$$E = \frac{h}{2\pi} \sum \omega_k \cdot n_k + \text{constant.}$$

4) It can be shown that $-\frac{\partial H^*(P, a)}{\partial a}$ is equal to the mean with respect to the time of the force exerted by the system “in the direction of the parameter a ”.

§ 3. Proof of formula (8).

In the expression $\sum p_k dq_k$ q and p are replaced by their expansions (1); in differentiating the Q , P , and t are regarded as independent variables, the parameter a being an explicitly given function of t . This gives:

$$\sum p_k \cdot dq_k = \sum f_1^k \cdot dQ_k + \sum f_2^k \cdot dP_k + f_3 \cdot \frac{da}{dt} \cdot dt$$

f_1^k , f_2^k , f_3 are FOURIER series with respect to the Q .

As for $a = \text{constant}$ this substitution is a contact transformation, we must have:

$$\sum f_1^k \cdot dQ_k + \sum f_2^k \cdot dP_k = \sum P_k dQ_k + \sum \frac{\partial W}{\partial Q_k} dQ_k + \sum \frac{\partial W}{\partial P_k} dP_k \quad (12)$$

Hence:

$$\frac{\partial W}{\partial Q_k} = -P_k + f_1^k = -P_k + \gamma_0^k(P, a) + \sum' \gamma_{m_1 \dots m_n}^k \left\{ \begin{matrix} \cos \\ \sin \end{matrix} \right\} (m_1 Q_1 + \dots m_n Q_n)$$

and:

$$W = \sum (-P_k + \gamma_0^k) Q_k + \sum \delta_{m_1 \dots m_n} \left\{ \begin{matrix} \cos \\ \sin \end{matrix} \right\} (m_1 Q_1 + \dots m_n Q_n)$$

Furthermore we have:

$$\frac{\partial W}{\partial P_k} = f_2^k = -Q_k + \sum \frac{\partial \gamma_0^k}{\partial P_k} Q_l + \sum \frac{\partial \delta_{m_1 \dots m_n}}{\partial P_k} \left\{ \begin{matrix} \cos \\ \sin \end{matrix} \right\} (m_1 Q_1 + \dots m_n Q_n)$$

In f_2^k the Q occur only under sines and cosines; from this it follows that the coefficient of Q_k on the second side of the equation must be zero, and hence:

$$\gamma_0^k = P_k + \pi_k(a).$$

As the condition (12) determines the P and Q all but the additive constants, it is always possible to include the $\pi_k(a)$ in the P . If we suppose this to be the case, we get:

$$\gamma_0^k = P_k,$$

hence:

$$W = \sum \delta_{m_1 \dots m_n} \left\{ \begin{matrix} \cos \\ \sin \end{matrix} \right\} (m_1 Q_1 + \dots m_n Q_n) \dots \dots \quad (13)$$

It follows that:

$$F = f_3 - \frac{\partial W}{\partial a}$$

is a FOURIER series with respect to the Q , and thus the proposition has been proved.

Remarks.

1. If $\pi_k(a)$ is not made equal to zero by a proper choice of the additive constant of P_k , it will be found that:

$$P_k + \pi_k(a) = \text{adiabatic invariant.}$$

2. In many cases the P_k can immediately be introduced in such a way that the quantities $\pi_k(a)$ are zero. As examples we may mention:

a. systems the HAMILTONIAN function of which can be expanded according to ascending powers of the q and p , and which are to be treated by a method given by WHITTAKER¹⁾;

b. systems in which the variables can be separated; the P are then determined by the formulae:

$$2\pi P_k = I_k = \text{phase-integral corresponding to the coordinate } q_k = \int_{\xi_k}^{\eta_k} p_k \cdot dq_k.$$

3. Suppose the P to be determined as assumed above, so that W is a periodic function of the Q (form. 13). If the parameters are not varied:

$$\sum_l p_l \cdot dq_l = \sum_k P_k \cdot dQ_k + dW.$$

Integrating this expression from $Q_k = 0$ to $Q_k = 2\pi$ ($Q_1 \dots Q_{k-1} \dots Q_{k+1} \dots Q_n, P_1 \dots P_n$ being kept constant), we find:

$$\int_{Q_k=0}^{Q_k=2\pi} \sum p dq = 2\pi P_k = \text{adiabatic invariant.}$$

[If the $\pi_k(a)$ have not been included in the P , it is found that:

$$\int_{Q_k=0}^{Q_k=2\pi} \sum p dq = 2\pi (P_k + \pi_k) = \text{adiab. inv. according to remark 1].$$

ERSTEIN has given the quantum formulae in a form which is equivalent to:

¹⁾ WHITTAKER, l.c. p. 398 - 408.

²⁾ The constants ϵ_k which occur in SCHWARZSCHILD's formulae (l. c. p. 549, 551; see also higher up, form. A), and which are determined by the limits of the phase-space, are probably connected with the quantities π_k introduced here; but I have not been able so far to find a general proof.

$$\int_{Q_k=0}^{Q_k=2\pi} \Sigma p dq = n_k \cdot h \text{ } ^1)$$

and is therefore in agreement with the above.

4. The following points have still to be mentioned:

a. Probably it will be found sufficient that in passing from $a =$ constant to $a =$ a given function of the time, the Hamiltonian equations remain unchanged only if we neglect terms of the 2nd and higher orders in \dot{a} . This has yet to be investigated.

b. In the present paper it has been supposed that the mean motions ω_i are all incommensurable. The ω_i are, however, functions of the parameters. Hence if the a are varied, the ω_i change too, and their ratios pass through rational values. It has still to be investigated, whether this may give rise to difficulties. (This applies also to the demonstrations given in the preceding papers).

S U M M A R Y.

If a mechanical system of n degrees of freedom possesses solutions which can be expressed by means of multiple trigonometric series, proceeding by the sines and cosines of n angular variables, between the mean motions of which no relations of commensurability exist, it is possible to determine the canonical momenta corresponding to these angular variables in such a way that they are *adiabatic invariants* for an infinitely slow change of the parameters of the system. — (The fact that during an adiabatic disturbance the mean motions change and that their ratios pass through rational values has to be further inquired into.)

¹⁾ P. S. EPSTEIN, Verh. d. D. Physik. Ges. 18 (1916) p. 411.

Physics. — “*The spectrum of a rotating molecule according to the theory of quanta.*” By J. M. BURGERS. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 26, 1917).

§ 1. *Introduction.*

N. BJERRUM has drawn attention to the fact that if a molecule which carries a vibrating resonator, rotates, this rotation exerts an influence upon the frequency of the light emitted ¹⁾. If the frequency of the resonator is ν_0 ²⁾, the angular velocity of the molecule being $\omega = 2\pi\nu'$, the frequencies: ν_0 , $\nu_0 + \nu'$, $\nu_0 - \nu'$ will be found in the light emitted by the system. Molecules of this kind will also absorb the frequencies ν_0 , $\nu_0 + \nu'$, $\nu_0 - \nu'$ from radiation which falls upon them. Starting from this principle BJERRUM has explained the structure of the bands which are found in the infra-red absorption spectra of certain gases. It was assumed that the velocity of rotation of the molecule is determined by a condition taken from the theory of quanta, so that ω can only have values which are an integral multiple of a certain quantity ω_0 . In the spectrum of such a gas a line of the frequency ν_0 will be accompanied by a set of equidistant satellites, given by the general formula:

$$\nu_l = \nu_0 + n \frac{\omega_0}{2\pi}.$$

The bands observed in the absorption spectra of water vapour and other gases actually have a structure that may be described by this formula ³⁾.

On the principles of the theory of quanta, however, one will be inclined to assume that a given spectral line is not emitted by a vibrating electron, but that it is emitted when the electron passes from a certain definite state of motion *discontinuously* to another

¹⁾ N. BJERRUM, Nernst-Festschrift p. 93 (1912). — Lord RAYLEIGH was the first to point out this influence of the rotation (Scientific Papers, IV, p. 17). — Compare also: W. C. MANDERSLOOT, De breedte van spektraallijnen (Diss. Utrecht 1914).

²⁾ In this paper “frequency” will always denote the number of vibrations per second.

³⁾ Cf. for instance: EVA VON BAHR, Verh. Deutsch.Phys. Ges. 15, p. 710, 1150, (1913); H. RUBENS & G. HETTNER, Sitz. Ber. Berl. Akad. p. 167, 1916.

definite state. If in the first state the energy of the electron is: α' , in the second state: α'' , then according to BOHR's hypothesis the difference $\alpha' - \alpha''$ will be emitted as light of the frequency:

$$\nu = \frac{\alpha' - \alpha''}{h}$$

On the other hand the electron can absorb light of the same frequency if it passes back from the second state to the first.

Now the following question arises: Suppose the electron to move in the field of a rotating molecule; does the rotation of the molecule exert an influence of the same kind on the frequency of the light emitted, as it does in BJERRUM's theory? The object of this communication is to show that following the lines of the theory of quanta, it is possible to deduce at least for certain rotating systems spectral formulae which show the same character as the one given by BJERRUM.

§ 2. General formulae for the motion of an electron in the field of a rotating molecule.

It will be assumed that the molecule has an unvariable form, and that it can rotate about an axis fixed in space. The position of the molecule is determined by the angle of rotation φ_2 . In the field of the molecule an electron moves; its position will be given by polar coordinates r, ϑ, φ_1 (the axis of the polar system of coordinates coincides with the axis of the molecule).

The potential energy of the system V is a function of the relative positions of the electron and the molecule, hence it depends on r, ϑ and $\varphi_1 - \varphi_2$ ¹⁾. If m be the mass of the electron, I the moment of inertia of the molecule about the axis of rotation, the Lagrangian function for the system is:

$$L = \frac{m}{2} (\dot{r}^2 + r^2 \dot{\vartheta}^2 + r^2 \sin^2 \vartheta \dot{\varphi}_1^2) + \frac{I}{2} \dot{\varphi}_2^2 - V(r, \vartheta, \varphi_1 - \varphi_2). \quad (1)$$

In this formula we shall put:

$$\varphi_1 - \varphi_2 = \psi_1; \quad \varphi_2 = \psi_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the momenta corresponding to the coordinates $r, \vartheta, \psi_1, \psi_2$ are calculated, the Hamiltonian function will be found to be:

$$H = \frac{1}{2m} \left(R^2 + \frac{\Theta^2}{r^2} + \frac{\Psi_1^2}{r^2 \sin^2 \vartheta} \right) + \frac{(\Psi_2 - \Psi_1)^2}{2I} + V(r, \vartheta, \psi_1). \quad (3)$$

ψ_2 being a cyclic coordinate, Ψ_2 is constant. Ψ_1 represents the

¹⁾ In V $\varphi_1 - \varphi_2$ necessarily occurs: otherwise the rotation of the molecule cannot exert any influence upon the motion of the electron. (This applies also to the theory of RAYLEIGH and BJERRUM, cf. W. C. MANDERSLOOT, l. c. II, § 3).

total moment of momentum of electron and molecule together; it determines the rotation of the system as a whole.

If $\Psi_2 = 0$, the motion of the electron is determined by the function:

$$H_0 = \frac{1}{2m} \left(R^2 + \frac{\Theta^2}{r^2} + \frac{\Psi_1^2}{r^2 \sin^2 \vartheta} \right) + \frac{\Psi_1^2}{2I} + V(r, \vartheta, \psi_1) \quad (4)$$

It will now be assumed that it is possible to find solutions of the problem characterized by the Ham. function (4) (in this problem there is no disturbing influence of the rotation), and that these solutions are of the following form: the coordinates and momenta can be expressed as periodic functions (with period 2π) of three variables q_1, q_2, q_3 , which depend linearly on the time (so-called "angular variables")¹⁾. If the canonical momenta p_1, p_2, p_3 , corresponding to these variables, are introduced²⁾, the original coordinates and momenta $r, \vartheta, \psi_1, R, \Theta, \Psi_1$ can be expressed as functions of $q_1, q_2, q_3, p_1, p_2, p_3$. This transformation of the variables possesses the property of conserving the canonical (HAMILTONIAN) form of the equations of motion.³⁾

To find solutions of the problem given by (3) ($\Psi_2 \neq 0$), it may be considered as a problem of disturbed motion, and instead of the original coordinates and momenta the p and q may be introduced as new variables. The equations of motion of the q and p then are the HAMILTONIAN equations, derived from the function $K(q, p)$, which is obtained if in (3) the original coordinates and momenta are replaced by their expressions as functions of the q and p . This function has the form:

$$\begin{aligned} K(q, p) &= H_0 - \frac{\Psi_1 \Psi_2}{I} + \frac{\Psi_2^2}{2I} = \\ &= A_0(p_1, p_2, p_3) + \frac{\Psi_2^2}{2I} - \frac{\Psi_{10}(p_1, p_2, p_3) \cdot \Psi_2}{I} - \\ &\quad - \frac{\Psi_2}{I} \sum' \left[\beta_{m_1 m_2 m_3}(p_1, p_2, p_3) \cdot \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (m_1 q_1 + m_2 q_2 + m_3 q_3) \right] \quad (5) \end{aligned}$$

¹⁾ Solutions of this kind are — as is known — of frequent use in Astronomy, especially for the treatment of problems of disturbed motion. In the most common cases they have the form of trigonometric expansions according to sines and cosines of combinations of the q . — (The expression found for ψ_1 has a slightly different form, as this variable can increase indefinitely; for instance ψ_1 may be found to be equal to q_3 plus a periodic function of q_1, q_2, q_3).

In the theory of quanta K. SCHWARZSCHILD was the first to introduce solutions of that nature (Sitz. Ber. Berl. Akad. p. 548, 1916) Compare also J. M. BURGERS, these Proceedings p. 163.

²⁾ These momenta p_1, p_2, p_3 are constant.

³⁾ Comp. WHITTAKER, Anal. Dynamics (Cambridge 1904) p. 297, 396.

⁴⁾ Σ' denotes a summation over all positive and negative values of the m , with the exception of simultaneous zero values.

(where Ψ_{10} represents the mean value of Ψ_1 (the moment of momentum of the electron).

It will be assumed :

1. that in $A_0(p_1, p_2, p_3)$ all the p occur, in such a way that between the three differential quotients $\partial A_0/\partial p_1$, $\partial A_0/\partial p_2$, $\partial A_0/\partial p_3$ there do not exist any rational relations;

2. that I is very large, and that the quantity Ψ_2/I is small as compared to the mean angular velocity of the electron, so that the second and higher powers of this quantity may be neglected.

It is then very easy to find solutions of the problem considered, following a method given by DELAUNAY and WHITTAKER¹⁾; if these solutions are restricted to the terms which contain Ψ_2/I to the powers 0 and 1, they are of the form :

$$\begin{aligned} p_1 &= P_1 + \frac{\Psi_2}{I} \cdot \sum' \left[\gamma_{m_1 m_2 m_3}(P_1, P_2, P_3) \cdot \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (m_1 Q_1 + m_2 Q_2 + m_3 Q_3) \right] \\ q_1 &= Q_1 + \frac{\Psi_2}{I} \cdot \sum' \left[\delta_{m_1 m_2 m_3}(P_1, P_2, P_3) \cdot \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (m_1 Q_1 + m_2 Q_2 + m_3 Q_3) \right] \end{aligned} \quad (6)$$

Here Q_1, Q_2, Q_3 are new angular variables; P_1, P_2, P_3 are the canonical momenta, corresponding to them.

The total energy of the system is found to be (to the same degree of approximation):

$$\alpha = A_0(P_1, P_2, P_3) - \frac{\Psi_2}{I} \cdot \Psi_{10}(P_1, P_2, P_3) + \frac{\Psi_2^2}{2I} \dots \quad (7)$$

§ 3. The Quantum formulae.

Following the ideas developed by SCHWARZSCHILD²⁾, the quantum formulae for the system may be introduced as follows :

the quantities P_1, P_2, P_3, Ψ_2 are put equal to integral multiples of $\frac{h}{2\pi}$:

$$P_1 = n_1 \frac{h}{2\pi}; \quad P_2 = n_2 \frac{h}{2\pi}; \quad P_3 = n_3 \frac{h}{2\pi}; \quad \Psi_2 = n_4 \frac{h}{2\pi} \quad \dots \quad (8)$$

The energy, when expressed as a function of the quantum numbers n_1, n_2, n_3, n_4 , becomes:

$$\alpha = \alpha_0(n_1, n_2, n_3) - n_4 \cdot \frac{\alpha_1(n_1, n_2, n_3) \cdot h}{2\pi I} + n_4^2 \frac{h^2}{8\pi^2 I} \quad \dots \quad (9)$$

¹⁾ Cf. WHITTAKER, l. c. p. 404.

²⁾ The three terms of this equation may be interpreted approximately as follows: A_0 is the energy of the electron; $\Psi_2^2/2I$ is the energy of rotation of the molecule; the term $-\frac{\Psi_2 \cdot \Psi_{10}}{I}$ is related to the CORIOLIS-reaction generated by the rotation.

³⁾ K. SCHWARZSCHILD, l. c.

If the electron passes from a state of motion characterized by the numbers $n_1' n_2' n_3' n_4'$ to another, characterized by $n_1'' n_2'' n_3'' n_4''$, the energy decreasing from α' to α'' , according to BOHR's hypothesis the system emits light of the frequency:

$$\nu = \frac{\alpha' - \alpha''}{h} \dots \dots \dots (10)$$

Hence the spectrum lines of the molecule under consideration are given by the formula:

$$\nu = \frac{\alpha_0' - \alpha_0''}{h} - \frac{n_4' \cdot \alpha_1' - n_4'' \cdot \alpha_1''}{2\pi I} + (n_4'^2 - n_4''^2) \frac{h}{8\pi^2 I} \dots \dots (11)$$

With the aid of this expression it is possible to show the influence of the rotation on the spectrum.

§ 4. Discussion of the spectrum.

The spectrum lines given by formula (11), which are characterized by 8 numbers, may be grouped in different ways. In order to show the influence of the rotation of the molecule as clearly as possible we will consider a definite change $n_1' n_2' n_3' \rightarrow n_1'' n_2'' n_3''$ (hence the values of $\alpha_0' \alpha_0'' \alpha_1' \alpha_1''$ are fixed); then by giving different values to the numbers n_4', n_4'' , different systems of lines are obtained.

A. First consider the case $n_4' = n_4'' = 0$ (in both states of motion the rotation of the molecule as a whole is zero); then the frequency is:

$$\nu_0 = \frac{\alpha_0' - \alpha_0''}{h} \dots \dots \dots (12)$$

B. If n_4' and n_4'' are equal, and different from zero, the frequency will be found to be:

$$\nu_I = \nu_0 - n_4' \frac{\alpha_1' - \alpha_1''}{2\pi I} \dots \dots \dots (13)$$

Hence the original line ν_0 appears to be accompanied on both sides by equidistant satellites, in the same way as in BJERRUM's theory. The distance of the satellites is equal to:

$$\Delta \nu = \frac{\alpha_1' - \alpha_1''}{2\pi I} \dots \dots \dots (14)$$

In general the value given by (14) is not the same as that given by BJERRUM's theory which is:

$$\Delta \nu = \frac{h}{4\pi^2 I} \dots \dots \dots (14a)$$

The expressions (14) and (14a) may give the same value if for

instance $\alpha_1 = n_3 \frac{h}{2\pi}$; for certain systems this may be approximately the case ¹⁾).

C. If $n_4' \neq n_4''$, so that the general formula (11) has to be retained, each line ν_0 appears to possess a double infinite system of satellites, the distances of which are given by a quadratic formula. This formula is of the same type as the one given by DESLANDRES and others for the band spectra ²⁾. A formula of this kind has been derived from the theory of quanta for the first time by SCHWARZSCHILD ³⁾; SCHWARZSCHILD has also pointed out that if the moment of inertia I is calculated from the coefficient of the term of the second degree, the values obtained are of the proper order of magnitude.

Other groups of lines.

D. If n_1', n_2', n_3' are equal to n_1'', n_2'', n_3'' , respectively, so that only n_4 changes in the transition from the first state of motion to the second, a set of lines is obtained, which may be denoted by the name of "rotation spectrum":

$$\nu_r = - (n_4' - n_4'') \frac{\alpha_1}{2\pi I} + (n_4'^2 - n_4''^2) \frac{h}{8\pi^2 I} \dots (15)$$

From the order of magnitude of the coefficients it may be inferred that these lines are to be found in the infra-red (they stretch out as far as $\nu = \infty$, $\lambda = \infty$).

E. RUBENS and HETTNER ⁴⁾ have observed in the absorption spectrum

¹⁾ The difference between formula (14) and (14a) becomes of importance if it is desired to calculate the value of the moment of inertia from the distance of the lines. (In BJERRUM's theory $\frac{h}{2\pi^2 I}$ is sometimes given for $\Delta\nu$ instead of the value (14a); cf. H. RUBENS and G. HETTNER, l. c. p. 168).

A more important difference between formula (14) and BJERRUM's theory is that the value given by (14) depends on $\alpha_1' - \alpha_1''$, and hence on the numbers $n_1' n_2' n_3' n_1'' n_2'' n_3''$. This makes the value of $\Delta\nu$ in general different for different lines ν_0 , whereas on BJERRUM's theory $\Delta\nu$ is independent of ν_0 .

Compare also the example given in § 5.

²⁾ Cf. H. M. KONEN, *Das Leuchten der Gase und Dämpfe*, (BRAUNSCHWEIG, 1913), p. 214, seq.

³⁾ K. SCHWARZSCHILD, l. c. p. 566. — SCHWARZSCHILD supposes that the rotation of the molecule and the motion of the electron do not exert any influence upon each other; the opposite supposition is essential to the theory given above. This is the cause of the term which is linear in n_4 and n_4'' being absent in SCHWARZSCHILD's formula.

⁴⁾ H. RUBENS and G. HETTNER, l. c.

of water vapour a system of lines which are related to the series given by (13) by the formula :

$$\nu_{II} = \nu_I - \nu_0 \quad (16)$$

These investigators, who explain the system ν_I on BJERRUM's theory ascribe the lines ν_{II} to the emission or absorption of the rotating molecules themselves¹⁾. The interpretation of the lines on the theory given above is more difficult, and less general. They may occur in special cases, if it is possible to find transitions $n_1' n_2' n_3' \rightarrow n_1'' n_2'' n_3''$, for which α_0 does *not* change, while the value of α_1 changes by the same amount as is given by the formula (13)²⁾. In general it will thus not be possible to find a system ν_{II} corresponding to each system of lines ν_0, ν_I . Compare also the example given in § 5³⁾.

§ 5. Example.

An illustration of the preceding theory is afforded by considering a system, which is characterized by the following expression for the potential energy of the electron in the field of the molecule :

$$V = -\frac{Ee}{r} \pm \frac{a}{r^2} + \frac{b + c \cos(\varphi_1 - \varphi_2)}{r^2 \sin^2 \vartheta} \quad (17)$$

(The form of V has been chosen in this way in order to make possible the integration of the equations of motion by means of the method of separation of the variables; cf. P. STACKEL, C.R. **116**, p. 485, 1893; **121**, p. 489, 1895).

The energy of the permissible motions of the electron, when expressed as a function of the quantum numbers, is found to be :

$$\begin{aligned} a &= -\frac{2\pi^2 m e^2 E^2}{h^2} \left(\frac{1}{n_1^2} - \frac{8\pi^2 m \cdot a}{n_1^3 n_2 h^2} - \frac{8\pi^2 m \cdot b}{n_1^3 \cdot |n_2| h^2} \right) + \frac{(n_3 - n_4)^2 \cdot h^2}{8\pi^2 I} \\ &= \alpha_0 - \frac{n_3 n_4 h^2}{4\pi^2 I} + \frac{n_4^2 h^2}{8\pi^2 I} \quad (18) \end{aligned}$$

(in this formula terms of the 2nd and higher orders in a, b, c have been neglected).

The mean value Ψ_{10} of the moment of momentum of the electron is equal to :

¹⁾ Compare in connection with this: M. PLANCK, Ann. d. Phys. **52**, p. 491, 1917.

²⁾ In every case changes $n_1' n_2' n_3' \rightarrow n_1'' n_2'' n_3''$ must be possible for which only the sign of the moment of momentum of the electron changes (and hence the sign of α_1); α_0 then retains the same value. Cf. § 5.

³⁾ It may be remarked that formula (15) can also give a system of equidistant lines in the infra red, if $n_1' = -n_4''$ (the moment of momentum of the molecule changes sign, while the direction of rotation of the electron remains the same); the distance of the lines is equal to: $\alpha_1/I\pi$.

$$\nu_{10} = n_3 \frac{h}{2\pi} + \dots$$

n_3 may be positive or negative; this depends on the direction of motion of the electron.

In the principal part α_0 of α only the absolute value $|n_3|$ occurs.

From (18) the spectral formula may be deduced in the same way as above. The following groups of lines (corresponding to those called **B** and **E** in § 4) are of special interest:

a). Take: $n_3' = -n_3'' = -n_3$; $n_4' = n_4'' = n_4$; the values of n_1, n_2 change in an arbitrary manner. The frequencies emitted then are.

$$\nu_I = \frac{2\pi^2 m e^2 E^2}{h^3} \left(\frac{1}{n_1''^2} - \frac{1}{n_1'^2} + \dots \text{etc.} \right) + \frac{2n_3 n_4 h}{4\pi^2 I} = \nu_0 + \frac{2n_3 n_4 h}{4\pi^2 I} \quad (I)$$

If n_3 has always the same value, different positive and negative values of n_4 give a set of equidistant lines, accompanying the line ν_0 ; the distance of two consecutive satellites will be:

$$\Delta \nu = \frac{2n_3 \cdot h}{4\pi^2 I}$$

b). Take: $n_3' = -n_3'' = -n_3$; $n_4' = n_4'' = n_4$ (as was done above under a); while the values of n_1 and n_2 do not change. In this case:

$$\alpha_0(n_1', n_2', n_3') = \alpha_0(n_1'', n_2'', n_3'');$$

hence the frequency emitted becomes:

$$\nu_{II} = + \frac{2n_3 n_4 \cdot h}{4\pi^2 I} = \nu_I - \nu_0 \dots \dots \dots (II)$$

The structure of these systems is in some respects analogous to that of the absorption bands of water vapour; (I) corresponds to the band observed near: $\lambda = 6,26\mu$; (II) to the lines in the far distant infra-red.

It must not be forgotten, however, that this example has been chosen arbitrarily, so that no great value can be attached to the absolute magnitude of $\Delta \nu$.

Summary.

An attempt is made to show that it is possible to deduce from the theory of quanta spectral formulae for rotating systems, which may explain the structure of the bands, observed in the infra-red absorption spectra of certain gases.

At the same time a formula has been found which might be useful in the explanation of the band spectra and which is an extension of one already given by SCHWARZSCHILD.

In order to simplify the problem it has been assumed that the system rotates about a fixed axis, hence the question arises whether it is not possible to give a more general treatment, in which account is taken of the precessional motion of the molecule.

Physics. — “*Isothermals of di-atomic substances and their binary mixtures. XIX. A preliminary determination of the critical point of hydrogen*”. By H. KAMERLINGH ONNES, C. A. CROMMELIN and P. G. CATH (Communication N°. 151c from the Physical Laboratory at Leiden).

(Communicated in the meeting of June 24, 1916).

1. *Introduction. Apparatus and method.*

The results so far obtained by different observers in the determination of the critical data for hydrogen show a wide divergence. DEWAR ¹⁾ found $T_k = 29^\circ \text{K}$, 30°K and 32°K respectively, $p_k = 15$ atm., OLZEWSKI's ²⁾ latest values were $T_k = 32^\circ.3 \text{K}$ and $p_k = 13$ atm., BULLE ³⁾ found $T_k = 31^\circ.4 \text{K}$ and $p_k = 11$ atm. It will appear from this communication that all these results differ very considerably ⁴⁾ from those which we consider to be the correct ones, viz. $T_k = 33^\circ.2 \text{K}$, $p_k = 12.8$ atm. In view of the great difficulty of the problem this is not to be wondered at.

We ourselves had repeatedly been compelled to defer the accurate investigation regarding the critical condition of hydrogen, because we were unable to get over the difficulty of keeping temperatures such as those, at which the experiments had to be carried out, sufficiently constant. As soon as this difficulty had been conquered by the construction of our hydrogen-vapour cryostat ⁵⁾ we were enabled to avail ourselves of this material improvement in order to arrive at a first determination of the critical temperature of neon ⁶⁾ and also a more accurate measurement of the critical data of hydrogen.

¹⁾ J. DEWAR. Inaug. Adress Brit. Ass. Adv. Sc Belfast 1902.

²⁾ K. OLSZEWSKI, Ann. d. Phys. (4) 17 (1905) pg. 986, Ann. de chimie et de phys 8 (1906) pg. 193.

³⁾ F. BULLE, Physik. ZS. 14 (1913) pg. 860.

BULLE's results differ a good deal more from ours than OLSZEWSKI's much earlier results.

⁴⁾ With the exception of DEWAR's p_k and ours (Note added in the translation). In fact the weaker point in OLSZEWSKI's work will have been probably the determination of the temperature.

⁵⁾ H. KAMERLINGH ONNES, Proc. XIX (2) p. 1049. Comm. N°. 151a.

⁶⁾ H. KAMERLINGH ONNES, C. A. CROMMELIN and P. G. CATH, Proc. XIX (2) p. 1058. 1917. Comm. N°. 151b.

On the whole the same apparatus were used for both substances; as regards these we may therefore refer to the communication on neon just quoted. Only the pressures were measured in a different way. The readings on the closed manometer M_{60} , which was used in the case of neon, do not begin before 20 atm. and the critical pressure of hydrogen being smaller than that, we had to use the open standard-gauge of the laboratory ¹⁾ for the purpose.

The hydrogen which had been purified by distillation was free from all admixture as shown by the heterogeneous parts of the isothermals in the pressure-density diagram being straight lines running parallel to the density-axis (comp. fig. 1). At the same time we wish our results to be considered as preliminary ones. In the first place because a larger number of observations than we have made (comp. fig. 1) will be needed to smooth out certain small irregularities which our observations still show and thus draw with sufficient certainty the set of isothermals which have to serve the purpose of settling in a perfectly satisfactory manner physical constants of so fundamental a character as the critical data of hydrogen. But even more because in our opinion it is necessary for definite determinations to be able to follow the critical phenomena by eye which we have not been able to do as yet, no more than in the

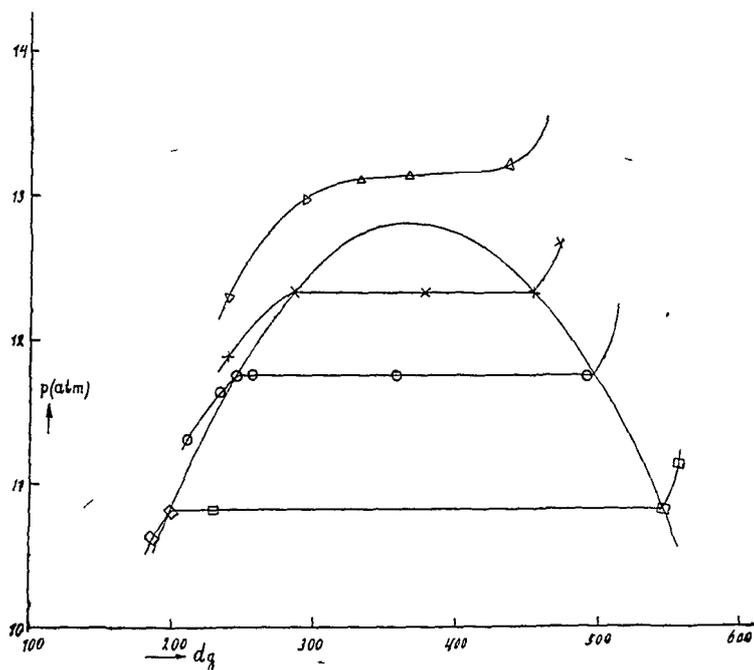


Fig. 1.

¹⁾ H. KAMERLINGH ONNES, Proc. I p. 213. Comm. N^o. 44.

case of neon, although we hope before long to be in a position to carry out this purpose.¹⁾

As regards the method of deducing the critical data from the observations we have in our Communication on the critical condition of neon referred to the similar case of hydrogen, which is the subject of our present communication. In this case we are able to illustrate our method of procedure by means of a suitable diagram²⁾.

This figure gives the main features of the pressure-density diagram, drawn during the observations to keep a graphical record of the results already obtained, in order to guide us, as we went along, in the choice of the conditions under which the next observations had to be made.

In representing an observation we used as abscissa the quantity of gas³⁾ that was at that moment present in the part of the vapour-pressure apparatus which was at the temperature of the observation⁴⁾.

The observations relating to one isothermal are each time indicated by one and the same of the signs \square , \circ , \times and Δ . The determination of the points of beginning and completed condensation had been preceded by tentative readings in the neighbourhood of the observations recorded in the diagram. The fact that the heterogeneous

¹⁾ Compare, besides the paper already quoted on the hydrogen-vapour cryostat (151a), particularly H. KAMERLINGH ONNES, Proc. XVIII. pg. 507. Comm N^o. 147c, where a cryostat is discussed working with neon boiling under enhanced pressure to be used amongst others for this object.

²⁾ The corresponding diagram of neon being somewhat modified owing to impurities would necessitate an elaborate discussion.

³⁾ The quantity is given in cc. of gas measured in the normal condition.

⁴⁾ The volume of this part is approximately 1.0J cc. Our apparatus, being a simple vapour-pressure apparatus, was not suitable either for the accurate measurement of this volume or of the quantity of substance which enters this volume. In consequence of this the uncertainty as regards the accurate value of the volume which is at the observational temperature as also the value of the temperature of certain other parts of the apparatus whose volume cannot be neglected is such that the accuracy of the density-determinations cannot be guaranteed beyond a limit of a few percentagés.

Owing to the uncertainty of the correction for the "waste" space, the figure may deviate in a systematic manner from the correct pressure-density diagram to the same degree: in order to obtain the correct figure the chords of the boundary curve i. e. the heterogeneous parts of the isothermals will have to be shifted without any change in length, each by an amount about proportional to the pressure; the uncertainty about the part of the volume which has the low observational temperature causes the value of the unit of density which is assumed in setting off the density on the axis of abscissae in fig. 1 to be only approximately known.

parts of the isothermals are accurately parallel to the axis of abscissae proves on the one hand that the hydrogen was absolutely pure and on the other that the temperature could be kept constant to .01 of a degree¹⁾. It proved possible to connect the points which give the beginning and the completion of the liquefaction by means of an ordinary parabola. The pressure corresponding to the top of this parabola was taken as the critical pressure. The temperature corresponding to the critical pressure thus found was obtained by extrapolation from the measurements of the vapour-pressure at the temperatures immediately below the critical temperatures.

Beside the observations just mentioned on the isothermals which show a heterogeneous part, an isothermal will be found plotted in the figure which was determined at a slightly higher temperature and where a similar part parallel to the density-axis (heterogeneous condition) is no longer found. The tangent to the point of inflexion is inclined to the axis of densities and this isothermal thus appears to belong to a temperature higher than the critical temperature. It is clear, that by means of this figure an upper and a lower limit may be fixed for the critical pressure and a probable value of the critical pressure may be established, from which in their turn follow an upper and a lower limit and a probable value of the critical temperature. The degree of certainty with which the latter determination may be effected is fairly satisfactory. For hydrogen the two limiting values just mentioned as regards the temperature differ by less than .4 of a degree. The figure further shows that in the manner described the temperature itself may be considered to be determinable with a certainty of .1 of a degree.

§ 2. Results.

In the following table of vapour-pressures the absolute temperature as well as that on the centigrade scale have been corrected to the KELVIN-scale by means of the table of corrections published on former occasions²⁾.

The pressure is given in international³⁾ cms mercury and in

¹⁾ To make this result possible the distribution of the temperature must also have been a very uniform one throughout the experimental space. We are glad to express once more our thanks to Mr. J. M. BURGERS, phil. cand. for his careful assistance in the regulation of the temperatures.

²⁾ H. KAMERLINGH ONNES, Proc. X, p. 589. Comm. N^o. 102*b*, and H. KAMERLINGH ONNES and G. HOLST, Proc. XVII, 1, pg. 501. Comm. N^o. 141*a*.

³⁾ In the original paper the pressures were given in local cms mercury and in international atmospheres. [Note added in the translation].

international atmospheres, the international atmosphere being taken equal to a mercury column of 75.9488 cms at Leiden.

T	θ	$p_{koex.}$ (int. cm.)	$p_{koex.}$ (int. atm.)
32.02° K.	- 241.07° C.	822.7	10.825
32.60	- 240.49	893.2	11.752
32.93	- 240.16	936.5	12.322

Above θ_k the following point was measured :

T	θ	p (int. cm.)	p (int. atm.)
33.28° K	- 239.81° C.	999.5	13.151

The critical quantities derived from the above figures are as follows :

T_k	θ_k	p_k (int. cm.)	p_k (int. atm.)
33.18° K.	- 239.91° C.	973	12.80

The deviation of BULLÉ's result from ours may, as we think, be partly explained from his having used a resistance-thermometer which was only calibrated by means of hydrogen- and oxygen-temperatures and on the other hand perhaps also from the arrangement of his apparatus. Possibly owing to the rapidity with which he had to conduct the experiment the flask in which the hydrogen was compressed had not yet assumed the temperature of the resistance-thermometer when the measurement was made.

§ 3. Estimation of the critical density.

By means of the above value of the critical temperature, of the

liquid-densities ¹⁾ and vapour-pressures ²⁾ published on former occasions and finally of the values of the constant B ³⁾, it is now possible to make a calculation of the critical density of hydrogen assuming the diameter of CALLETET and MATHIAS to be a straight line for hydrogen; there is all the more reason for the latter supposition as according to the figure the inclination of the diameter in the neighbourhood of the critical point cannot deviate much from that at the lower temperatures where the expansion of the liquid has been determined.

For this purpose, using the vapour-pressures and the value of B , by means of the relation ⁴⁾ $d_A = \frac{p}{A_A} \left\{ 1 - \frac{B_A}{A_A^2} p \right\}$ the vapour densities are calculated at the same temperatures at which the density of the liquid has been measured. The constant A_{A_0} is taken equal to .99939.

In this manner the ordinates of the diameter are obtained and by means of these the equation of the diameter. In the following table $\rho_{\Gamma vap}$ and $\rho_{\Gamma liq}$ denote the densities of the saturated vapour and the liquid respectively in gr. per cm³ and y the ordinate of the diameter. The two points through which the diameter is laid are indicated by an asterisk.

θ .	$\rho_{\Gamma liq}$	$\rho_{\Gamma vap}$.	y (W).	y (R).	W-R
- 252.68	.07081	.00135	.03608	.03604	+ .00004
- 253.24	7137	116	3627	3626	+ 1
* - 253.76	7192	101	3647	3647	0
- 255.19	7344	0.00064	3704	3704	0
- 255.99	7421	49	3736	3735	+ 1
* - 256.75	7494	38	3766	3766	0
- 257.23	7538	31	3784	3785	- 1
- 258.27	7631	20	3826	3826	0

¹⁾ H. KAMERLINGH ONNES and C. A. CROMMELIN, Proc. XVI, 1, pg. 245, Comm. No. 137a.

²⁾ H. KAMERLINGH ONNES and W. H. KEESOM, Proc. XVI, 1, pg. 440, Comm. No. 137d.

³⁾ H. KAMERLINGH ONNES and W. J. DE HAAS, Proc. XV, 1, p. 405, Comm. No. 127c. The values of B were smoothed in the manner as given in this paper.

⁴⁾ B_A was found by graphical interpolation; C_A does not come into account.

The equation of the diameter becomes

$$y = - .06453 - .000398 \theta.$$

or in the more usual form

$$y = + .04416 - .000398 T.$$

Substituting in this equation our value for the critical temperature $\theta = - 239.91^\circ \text{C}$. the critical density is found to be

$$\rho_{\Gamma_k} = .0310.$$

In 1904 DEWAR¹⁾ published an estimate of the density viz. .033, calculated from a couple of liquid densities as determined by himself.²⁾

¹⁾ J. DEWAR, Proc. R. S. 73 (1904) pg. 251.

²⁾ If the critical density is derived using the quantities d_q in the small flask as read from fig. 1, the weight of a cc. of hydrogen measured under normal conditions and the volume of the flask as given in note 4 on page 180 the result is $\rho_{\Gamma_k} = .033$. If the diameter is truly a straight line and thus $\rho_{\Gamma_k} = .031$ as given in the text, a comparison of ρ' from the figure and ρ from the diameter would provide a means of correcting fig. 1 for the systematic deviation (see the note mentioned) from the true pressure density diagram. It is found that the direction of the diameter in the neighbourhood of the critical point in the corrected figure still coincides within the limits of accuracy with the direction holding for lower temperatures according to the above table.

Chemistry. — "*Amygdalin as nutriment for Fusarium.*" By Dr.
H. I. WATERMAN. (Communicated by Prof. Dr. J. BÖESEKEN).

(Communicated in the meeting of May 26, 1917).

A solution of amygdalin in tapwater which at the same time contained inorganic salts as NH_4NO_3 , KH_2PO_4 , and MgSO_4 remained in the laboratory for some time at the ordinary temperature. After 18 days spontaneous infection was observed. On the liquid a white flocky mass of mycelium had appeared, under which a rose-coloured underground.

From this mycelium something was transferred to a plate of malt agar and cultivated at the ordinary temperature. After 24 hours some growth could already be observed, after 2×24 hours a flocky mycelium had been formed, whilst 24 hours later a very vigorous development was observed. A white flocky mass of mycelium was visible then, the plate had obtained on some spots a yellow and on other spots a red colour. The red colour was especially concentrated in those places of the nutrient plate which in transferring had been in contact with the platinum-wire.

The following day (after 4×24 hours) the whole glass-box was filled up with white mycelium.

The microscopy of the thus isolated species of mould and especially the presence of sickle-shaped spores divided into several cells pointed to *Fusarium*.

This species of *Fusarium* developed well on nutrient-soils of the composition: tapwater whether or not coagulated with agar and containing 2% amygdalin, 0.15% NH_4NO_3 , 0.15% KH_2PO_4 , 0.10% magnesiumsulfate (crystallised). From the means of isolation this could be expected.

On amygdalin-agar *Fusarium* developed as white flocky mycelium, whilst this nutrient plate was for the greater part coloured yellow.

Especially on this nutrient soil the formation of sickle-shaped spores came to the front.

Some days later the yellow colour had for the greater part become red, whilst the mycelium had shrivelled. Besides, on malt agar this shrivelling after a prolonged cultivation was observed too.

The formed red colour of the amygdalin plate did not dissolve

in boiling water. With hydrochloric acid the colour became yellow, with sodium hydroxide, ammonia or soda violet and otherwise. So the colour acted as indicator.

Furthermore I observed that the infection with *Fusarium* occurred too with solutions of amygdalin, on which *Aspergillus niger* had developed first (temperature 34°).

Twelve days after inoculation with *Aspergillus niger* I delivered the solutions in question containing amygdalin from the mould layer; the clear solutions were kept at ordinary temperature in tumblers covered with watch-glasses. Not all amygdalin was used, a part had remained.

Miss Prof. Dr. JOH. WESTERDIJK was kind enough to determine the isolated *Fusarium*. The found species was *Fusarium discolor var. triseptatum*¹⁾.

This organism was found first by SHERBAKOFF on rotting potatoes.

It was possible that in my case the descent would be the same, because a few years consecutively I had experimented on potatoes in the same laboratory.

With the isolated species of mould I made almost the same researches as some time ago with *Aspergillus niger*.²⁾

TABLE I. (*Fusarium*).

Glucose as exclusive organic food.			Amygdalin as exclusive organic food.	
Composition of the culture liquid 50 cm ³ of tapwater, in which dissolved 0.15 % NH ₄ NO ₃ , 0.15 % KH ₂ PO ₄ , 0.1 % magnesiumsulfate (crystallised). Ordinary temperature.				
A. 2 % glucose: 1000 milligr.			B. 2 % amygdalin: 1000 milligr.	
Assimilated glucose (milligr.)	Obtained dry weight of mould (mgr.)	Number of days after inoculation.	Assimilated amygdalin (milligr.)	Obtained dry weight of mould (milligr.)
1000	322	12	600	274
		15	not determined.	347
1000	297	73		
1000	300	220	not determined.	235
		230	not determined.	299

¹⁾ C. D. SHERBAKOFF, *Fusaria* of potatoes. Memoir N^o. 6. Cornell University Agricultural Experiment Station, May 1915. p. 239.

²⁾ Amygdalin as nutriment for *Aspergillus niger*, These Proceedings Vol. XIX, p. 922 (1917).

TABLE II a. (*Fusarium*).

Retarding influence of benzaldehyde and hydrogen cyanide.

Culture liquid: 50 cm³. tapwater, in which dissolved 0.15 % NH₄NO₃, 0.15 % KH₂PO₄, 0.1 % MgSO₄ · 7 H₂O and 2 % glucose. Ordinary temperature.

No.	Added.	Development after				Obtained dry weight of mould (Mgr.) after 73 days.
		4	7	21	37 days.	
1	—	++	++++	+++++	+++++	297 ²⁾
2	1 drop of benzaldehyde.	—	?	+ ¹⁾	++++	324 ²⁾
3	3 drops of benzaldehyde.	—	—	—	— ¹⁾	
4	5 drops of benzaldehyde.	—	—	—	— ¹⁾	
5	1 cm ³ P	++	++++	+++++	+++++	277 ²⁾
6	3 cm ³ P	+	++	+++++	+++++	282 ²⁾
7	5 cm ³ P	+	++	+++++	+++++	238 ²⁾
8	5 cm ³ Q	++	++++	+++++	+++++	

The solution P was prepared as follows: 50 milligr. KCN was dissolved in distilled water and filled up to 100 cm³. Added 10 cm³ of $0,98 \times \frac{1}{10}$ Normal sulfuric acid. The solution Q was obtained by adding to 100 cm³ of H₂O 10 cm³ of $0,98 \times \frac{1}{10}$ Normal sulfuric acid.

TABLE II b. (*Fusarium*)50 cm³. of tapwater, in which dissolved 0.15 % NH₄NO₃, 0.15 % KH₂PO₄, 0.1 % MgSO₄ · 7 H₂O. Ordinary temperature.

No.	Added.	Development after		
		4	6	11 days
1,2	2 % glucose	++++	+++++	+++++
3,4	2 % glucose + 0,04 % emulsin	++	+++++	+++++
5,6	2 % amygdalin	++, +++	+++++	+++++
7,8	2 % amygdalin + 0.04 % emulsin	— ³⁾	— ³⁾	— ³⁾

The results obtained with *Fusarium* were almost quite analogous with *Aspergillus niger*.

¹⁾ Sweet smell of benzaldehyde could be stated.

²⁾ All glucose was used.

³⁾ The smell of benzaldehyde or (and) HCN was stated.

So it was proved:

1 Amygdalin is assimilated by *Fusarium* whilst young mycelium is formed at the expense of the assimilated amygdalin. (Table I).

2. Compared with glucose amygdalin is not an inferior nutriment at least with regard to the dry weight of mould obtained. (Table I).

3. Benzaldehyde and to a small degree HCN hinder the development of *Fusarium* in liquids containing glucose (Table II^a), whilst the addition of emulsin to liquids containing amygdalin prevents growth entirely. The same emulsin has practically no retarding influence on the development of *Fusarium* in glucose containing solutions (Table II^b).

Therefore it is impossible that when amygdalin as only source of carbon is assimilated by *Fusarium* this glucoside is dissociated to an important degree into glucose, benzaldehyde and HCN out of the cell.

Dordrecht, May 1917.

Physiology. — “*On the behaviour of the Uranium-heart towards Electric Stimulation, as investigated by Mr. M. DEN BOER.*
By Prof. Dr. H. ZWAARDEMAKER.

(Communicated in the meeting of May 26, 1917).

When an isolated Kroneckered frog's heart, after being freed from circulation-potassium, is fed with a uranium-containing fluid (15 mgrms of uranyl-nitrate ¹⁾, 100 mgrms of calcium-chloride, 200 mgrms of sodium-bicarbonate, 7 grms of sodium-chloride per Litre) it will soon recover its automatical pulsations and also its mechanic excitability in a most perfect way. If to such a heart we apply during the diastole, electric stimuli in the form of opening induction shocks of moderate force, the usual extrasystoles will be produced when the flow of uranium begins. Later on when the uranium-circulation has continued, say, 15 minutes, and when the uranium-salt has penetrated into all lacunae and cell-walls, a short pause will still be observable after a stimulus given at the right moment, but ultimately no manner of action will be seen any more. When the uranium condition of the heart is complete, the ventricle has become electrically inexcitable. Mechanical excitability continues, though slightly diminished ²⁾.

If the single induction shocks be replaced by a series of “making” and “breaking” shocks, strong enough to produce extrasystoles, something very striking takes place. We procured the said periodic stimuli by causing the teeth of a rotating disc to be dipped into a little mercury, the disc being so driven by a small electromotor that the time of closure of a current (from an accumulator of 2 volts) is equal to the time of opening. In this way we effectuated 500 closures and 500 openings per minute, affording in all 1000 stimuli per minute. When they were sent in some direction or other through the normally pulsating uranium-heart, a standstill in diastole ensued in typical cases almost without a latent period. On discontinuing the stimulation the heart resumes its beats suddenly with normal rhythm and with perfectly regular systoles, perhaps after a short after-effect.

¹⁾ Winter-frogs require 25 mgrms, summer-frogs from 1 to 5; in this case we took an average quantity.

²⁾ Cf. H. ZWAARDEMAKER Potassium-ion and automaticity of the Heart. Ned. Tijdsch. v. Geneesk. 1917, I, p. 1174.

A totally different result will be observed when a ventricle, brought to a complete standstill by removing the potassium, is acted upon by the electric disc with quite the same force. Then the isolated heart will pulsate normally and with a rhythm about equal to that which occurred before with Ringer-circulation. On discontinuing the stimulation of the toothed disc the systoles will also cease.

So there is a marked contrast. Whereas the motionless heart, freed from circulation-potassium, will for some time resume its normal contractility through stimulation with the toothed disc, the normal action of the uranium-heart will cease altogether when acted upon in the same way and with the same force. In both cases this holds good as long as the stimulus lasts or only for a slightly longer duration and in both cases the tonus remains unaltered.

Under similar circumstances the usual Ringerheart is brought into a condition of tonicity and undulation.

The alternating current just described was obtained through sudden closures and openings of a primary current. We also used instead of it a sinusoidal current of about 1000 complete periods per minute. It goes without saying that a considerably stronger battery had to be inserted in the primary circuit with changes of greater slope. Mostly, however, 8 or 10 volts proved sufficient to achieve similar results. We made use of platinum-electrodes.¹⁾

The Ringer-heart did not present anything particular while the alternating current was passing, at the most an increase of tonicity, which rendered the pulsations somewhat more incomplete.

The motionless heart freed from circulation-potassium, recommenced its regular beats while the sinusoidal current was passing, its systole-form, rhythm and tonicity being equal to that of the Ringer-heart. A latent period and an after-effect were often distinctly manifest, mostly, however, they were scarcely visible with a stimulus of about a minute's duration.

The uranium-heart behaves quite differently. When for instance the same hearts that during a standstill had been experimented upon with sinusoidal stimuli, were restored to action by a uranium-containing circulating fluid, a sudden standstill was seen at making the alternating current, which, when the sinusoidal stimulus was discontinued after a minute, would as suddenly make room for the normal rhythm. There is often hardly a latent period or an after-effect.

¹⁾ According to S. RINGER (J. of Phys Vol 4 p. 372) an excessive dosis of potassium or rubidium yields the same effect by faradization as has been described here for the uranium-heart,

Still, it sometimes occurs that a latent period of in maximo 1 minute appears and an after-effect that will occasionally persist for 2 or 3 minutes. Then we are in a position to see that, during such an after-standstill, the mechanic excitability has been maintained.

Whereas the RINGER-heart and the heart, fed with a potassium-free fluid, generally stand the faint sinusoidal stimuli very well, the uranium-heart does not. In most cases the minute-stimuli can be applied only three times even with intervals of five minutes or more. After that the heart is irrevocably lost (permanent standstill).

So with the sinusoidal current we also observe: a short recurrence of the pulsations in the motionless heart freed from circulation-potassium, arrest of the pulsations of the heart beating under the influence of uranium. Analogous experiments may be made with the constant current.

A normally beating RINGER-heart is only slightly affected by weak currents transmitted with nonpolarizable electrodes. If the force of the current be raised to about 3 m.A., the tonus is markedly increased while the current passes and a series of rapid undulations reveal themselves in the constantly contracted heart. After breaking the current the heart suddenly relaxes and a pause appears that outwardly bears a resemblance to a compensatory pause after extrasystole.

A heart that is arrested through deprivation of circulation-potassium resumes its beats at once under the influence of a constant current of from 1 to 3 m.A., while it as suddenly comes to a standstill when the current is broken.

If the heart, either fresh or stimulated in the way described, is deprived of potassium and is made to pulsate again perfectly by uranium-containing RINGER's mixture so long that, with fairly strong stimuli no more extrasystoles are produced, a gradual transmission of from $\frac{1}{2}$ to 3 m.A. will bring about a complete standstill with relaxation. Again normal systoles will recur after breaking the current. Only in the case of superexcitation increase of tonicity is noted. In order to observe the very remarkable arrest of the pulsations without further by-effect it is, therefore, necessary: 1 to wait till induction-shocks of moderate force are no longer succeeded by extrasystoles; 2 not to apply stronger currents than are just necessary for the individual heart.

The direction of the current is of no consequence, the result being the same whether it flows from base to point or conversely. Frequent stimuli or such as are too strong or last too long destroy the heart.

The pulsations become smaller and less frequent, the mechanic excitability slackens and disappears.

This then is the fourth time that we find a contrast between the condition produced by potassium-free circulation and the uranium condition; recovery of pulsation through electrification with the one and inhibition of the normal systoles with the other.

In a previous paper¹⁾ I demonstrated an antagonism between potassium and uranium, viz. that the two elements compensate each other's action when acting simultaneously in a circulating fluid. This antagonism obtained for the heart, the vascular endothelium, the curarised muscle²⁾, the kidney³⁾. As for the automaticity of the heart radium-, respectively mesothorium-radiation (through glass or mica) also appeared to be antagonistic to uranium. So it appears after all that electricity in impulsive, sinusoidal periodical or continuous form also counteracts uranium contained in a circulating fluid. Electricity annihilates the favourable effect of uranium. On the other hand electrification acts on the heart fed with a potassium-free circulating fluid like potassium and like radiation. Potassium-radiation with β -rays (and γ -rays) and prolonged electric stimulation in any form appear, therefore, in many respects to act physiologically in the same way.

The physiological actions I have in mind are:

A heart without circulation-potassium resumes its beats.

1. with potassium⁴⁾
2. with radiation, so far investigated only in a form in which negative charges are given to the tissue⁵⁾,
3. with electrification.

A normally beating uranium-heart is arrested:

1. with potassium,
2. with radiation⁶⁾,

¹⁾ H. ZWAARDEMAKER. K. Akad. v. Wet. Amst. Proceedings 24. Febr. 1917. Vol. 25. p. 1096.

²⁾ I. GUNZBURG. Congress April 1917. The Hague.

³⁾ H. I. HAMBURGER (by word of mouth). Cf. also HAMBURGER and BRINKMAN. K. Ak. Amst. Proc. 27 Jan. 1917, in which the substitution of potassium by uranium was demonstrated with regard to the permeability of the kidney.

⁴⁾ Also with other radio-active elements. H. ZWAARDEMAKER and T. P. FEENSTRA. K. Akad. Amst. Proc. 30 Sept 1916, Vol. 25, p. 517.

⁵⁾ H. ZWAARDEMAKER, C. E. BENJAMINS and T. P. FEENSTRA, Ned. Tijdsch. v. Geneesk. 1916, II, p. 1923.

⁶⁾ H. ZWAARDEMAKER, Congress. The Hague. April 1917.

3. with electrification.

Antagonistic to uranium, provided that the dosage of both factors be cautiously measured ¹⁾ are.

1. potassium,
2. radiation,
3. electrification.

For vagus-influences in all these cases see an article in Arch. néerl. de physiol. ²⁾. Probably they do not play a part in what has been described in this paper:

¹⁾ H. ZWAARDEMAKER, K. Akad. Amst. Proc. March 1917.

²⁾ H. ZWAARDEMAKER and J. W. LELY Arch. néerl. de physiol. Part I, p. 745, 1917.

Neurobiology. — “*A hypothesis concerning the mutual relation between some hereditary abnormalities that occur combined*”.
By Dr. N. VOORHOEVE. (Communicated by Prof. Dr. I. K. A. WERTHEIM SALOMONSON).

(Communicated in the meeting of May 26, 1917).

In the following lines I intend:

1. to explain the grounds on which my hypothesis rests *that a hereditary inferiority of the mesenchyme occurs,*
2. to elucidate the significance and the scope of this hypothesis.

I. I was induced *to state this hypothesis* in consequence of considerations concerning the results of an examination of three patients, whilst an examination of the family relations afforded *strong proofs for the validity* of this hypothesis.

It appeared, that a father and his two daughters were troubled with *blue sclerotics and brittle bones*, a combination which, though very rare, has already several times been described, and the heredity of which has been proved.

The father was moreover suffering from *haemophily*, an abnormality, which is likewise exceedingly hereditary.

If we account for the *anatomical substratum* of these abnormalities, then it appears:

a. that the blue colour of the sclerotics is caused by their congenital excessive thinness;

b. that the brittle bones which in my cases proved to be the consequence of osteopsathyrosis infantilis, is a consequence of an *inferiority of the ossificating elements*;

c. that so much may be stated with certainty concerning haemophily, though its pathogenesis may not yet be perfectly clear, that it is a consequence of an *inferiority of blood resp. bloodvessels*.

Consequently there existed in these individuals a hereditary inferiority of 3 systems of organs: sclerotics, skeleton and blood resp. bloodvessels. Their hereditary transmission pointed to an endogenous cause, or in other words, to a defect in design.

The abnormalities found here belong in fact to the rarities, and it was obvious that the combined occurrence of these abnormalities, which in themselves are already rare, could not be regarded as merely accidental. Consequently not 3 abnormalities existing beside and independently of each other, but 3 consequences of one and the same germinal defect. If this were indeed the case, there should be one point in the embryonal development from which these three systems of organs differentiate. And now embryology teaches us that this is indeed the case, and that they are all three products of the mesenchyme. We have now therefore put forward the hypothesis, *that we have here to do with an hereditary inferiority of the mesenchyme.*

The foregoing hypothesis is now supported:

A. By the results of a closer examination of the 3 patients.

It appeared namely that in these patients still other products of the mesenchyme showed abnormalities, which were either congenital, or consequences of an inferiority revealing itself in abnormally early wastage of the respective organs.

So we find in the father (at the age of 54 years):

on both sides *a very strong arcus senilis corneae;*

a rather strong sclerosis of the bloodvessels, though there were no propitiating causes at work as lues, intoxications (lead, alcohol, tobacco) or nephritis;

a rectangular position of the two auricles with regard to the skull.

In the elder girl *the two little fingers were in radial adduction in the metacarpophalangeal joint.*

B. By the examination of the other members of the family.

I could obtain information about 244 members of the family extending over 5 generations (children that died very young, are not included). Only the branch of my patient's father has been included in the scheme. Of these 59 children I myself could interrogate and examine superficially 40. It appeared now that already from my patient's grand-parents haemophily occurred in this family, and that there were several cases of blue sclerotics and also of haemophily among the 59 individuals whom I included in the scheme. Moreover there was one case of *congenital defect of the heart,* one of *split palate with harelip,* one of *rachischisis.*

This is of course the minimum of the existing abnormalities for I could only make a thorough examination of a few of the 40 individuals whom I saw myself. Two cases of *very severe rickets*

are likewise indicated in the scheme, in the first place, because it is possible that some other, perhaps hereditary, abnormality of the skeleton was present, and in the second place, because perhaps the occurrence of severe rachitis point to an hereditary inferiority of the skeleton

Now it appears that all the congenital defects in this family relate to products of the mesenchyme. There are however some mesenchyme-derivations, where about we did not yet speak. These are the spleen, the lymph-glands and -vessels, the conjunctive cellular tissue and the involuntary muscles. Were these groups of organs perhaps not defect in design? In order to find an answer to this question we must consider the following:

We still know so little about the physiology of the spleen that we cannot be astonished, if an inferiority of this organ, which we can miss entirely even without any disturbance worth mentioning, does not come to expression in a clinical respect. But moreover and especially, it is very doubtful whether the spleen originates in the mesenchyme.

As to the *lymph-glands* and *-vessels* we are struck by the fact that so much lymph-gland-tuberculosis occurs in this family, whereas the relation of frequency between tuberculosis of the lymph-glands on the one hand and that of other organs on the other hand is very large. Perhaps we may see in this fact a proof of inferiority expressing itself in a diminished resistance of the lymph-apparatus against infection with the bacilli of tuberculosis.

With regard to the three latter groups: *conjunctive cellular tissue*, *ligaments* and *involuntary muscles* it must be born in mind, that the physiological signification of this tissues, hidden in the body, is only of a secondary vital interest. And if we consider now, that the blue sclerotics are only recognised as such, thanks to their superficial situation, we need not be astonished that a less strong design and a decreased power of resistance of these tissues needs not come to expression in a clinical respect. We still remark moreover that many women of this family and even men showed the type of the "*habitus atonicus sive asthenicus*"; I leave undecided however, whether this should be considered as a proof of a congenital inferiority of the ligaments.

Taking all in all it is not doubtful, but the results of the *scrutinous examination* of these three patients and of the other members of the family form a *strong support* for the *hypothesis* stated above.

There is however more. Whilst the three patients showed us an

entirely developed inferiority of the mesenchyme, the examination of the other members of the family enables us *to follow the development of all the phases of our disease and to observe the precursors of the outbreak.*

Indeed the inferiority of the bloodvessels is not seen exclusively in the presence of haemophily, a congenital defect of the heart shows in what a labile equilibrium the constitution of this organic system is found. Osteopsathyrosis does not yet occur, but the skeleton already shows signs here and there of abnormal design, the rachischisis and the split palate are there to prove it. Blue sclerotics, although less intensive than in my patients are already found in several individuals, and one of them shows moreover a congenital cornea-abnormality (embryotoxon).

The catastrophe first take place in the person of my patient and his daughters; what had been threatening for some generations is realised: the mesenchyme shows its insufficient design in an unmistakable inferiority.

II. The *significance of this hypothesis* is of for greater general scope than to explain the origin of these abnormalities in my patients.

In this family we had to do with a hereditary inferiority in design of one of the 4 great groups into which the embryonal cells are differentiated in the very first phase of the development of the germ. It seems to me that it is of great interest for the doctrine of hereditary abnormalities that it is possible that germinal defects exist affecting the individual already at so early a stage, and set their stamp upon him.

Do such inferiorities of the whole mesenchyme or of the greater part of it occur more? Can they likewise be restricted to the exclusion of the mesenchyme and of the two other germinal layers to one germinal layer? Do they likewise occur hereditarily? Numerous facts indeed seem to point that way. Innumerable are the questions rising with regard to this hypothesis. It is really *a working hypothesis*. And it seems to me that it is a very important undertaking to examine, guided by this hypothesis, the combinations of hereditary abnormalities in connection with other degenerations in one and the same family. For what is known of these combinations or correlations is, almost without any exception, limited to the mere statement of the facts as such, and a dominant idea, if there was one, in the explanation of these correlations, has not been successful.

One question be still mentioned here, because I had to put it already when studying this family:

How far can the degeneration of the mesenchyme proceed in a family before one or more of the other germinal layers also begin to degenerate? It is obvious, that precisely families with a defective mesenchyme are the most suited to give an answer to this question, in view of the comparatively less important functions of most of the mesenchyme-organs.

I was able to have two members of this family and two of my patients examined otologically (Prof. BURGER). All four of them, though they had no complaints worth mentioning, proved to be suffering from a *labyrinth deafness*, an hereditary disease par excellence. But an affection of an ectodermal organ.

On the contrary VAN DER HOEVE and DE KLEYN found in their patients who suffered from blue sclerotics and brittle bones, otosclerosis (mesenchyme), although they could state with one patient a combination of otosclerosis and labyrinth deafness. I doubted however immediately, whether the affection of the organ of CORTI in my patients was a primary or a secondary one. For according to the investigations of QUIX and VAN LENNEP the atrophy of the organ of CORTI, is most probably caused in some cases of hereditary labyrinth-deafness (in casu the dancing-mouse) by a primary affection of the stria vascularis. Now the latter is a product of the mesenchyme.

And so at any rate the possibility is present that the affection of the labyrinth in this family is a further proof of an inferior mesenchyme, and the occurrence of this abnormality need not lead to the conclusion that the inferiority in this family is not restricted to the mesenchyme.

Physics. — “*In what way does it become manifest in the fundamental laws of physics that space has three dimensions?*”
 By Prof. Dr. P. EHRENFEST. (Communicated by Prof. Dr. H. A. LORENTZ).

(Communicated in the meeting of May 26, 1917).

Introduction.

“Why has our space just three dimensions?” or in other words: “By which singular characteristics do geometrics and physics in R_3 distinguish themselves from those in the other R_n 's?” When put in this way the questions have perhaps no sense. Surely they are exposed to justified criticism. For does space “exist”? Is it three-dimensional? And then the question “why”? What is meant by “physics” of R_4 or R_7 ?

I will not try to find a better form for these questions. Perhaps others will succeed in indicating some more singular properties of R_n and then it will become clear to what are the “justified” questions to which our considerations are fit answers.

§ 1. **Gravitation and planetary motion.**

As to the planetary motion, we shall see, that there is a difference between R_3 and R_2 as well as between R_3 and the higher R_n 's with respect to the stability of the circular trajectories. In R_3 a small disturbance leaves the trajectory finite if the energy is not too great; in R_2 on the contrary this is the case for all values of the energy. In R_n for $n > 3$ the planet falls on the attracting centre or flies away infinitely. In R_n for $n > 3$ there do not exist motions comparable with the elliptic motion in R_3 , — all trajectories have the character of spirals.

For the attraction under the influence of which a planet circulates in the space R_n , we put $\alpha \frac{Mm}{r^{n-1}}$; to this corresponds for $n > 2$ a potential energy:

$$V(r) = -\alpha \frac{Mm}{(n-2)r^{n-2}} \dots \dots \dots (1)$$

We deduce this law of attraction from the differential equation of LAPLACE—POISSON The means: we assume the force to be

directed towards the centre and to be a function of r only, so that it can be derived from a potential and we shall apply GAUSS' theorem for the integral of the normal component of the force over a closed surface (force-current).

The equations of motion thus have the form

$$m \frac{d^2 x_h}{dt^2} = -\alpha \frac{Mm}{r^{n-1}} \frac{x_h}{r} = -\frac{\partial V}{\partial x_h} \quad (h = 1, \dots, n)$$

The motion takes place in a plane. In this plane we introduce polar coordinates. Then the two first integrals can be written down at once

$$\begin{aligned} \frac{m}{2} (\dot{r}^2 + r^2 \dot{\varphi}^2) + V(r) &= E, \\ m r^2 \dot{\varphi} &= \Theta. \end{aligned}$$

By elimination of $\dot{\varphi}$ we find for \dot{r}

$$\begin{aligned} \dot{r} &= \sqrt{\frac{2E}{m} - \frac{2V}{m} - \frac{\Theta^2}{m^2 r^2}}, \\ \dot{r} &= \frac{1}{r} \sqrt{Ar^2 + Br^{4-n} - C^2} \dots \dots \dots (2) \end{aligned}$$

That r may oscillate along the trajectory between positive values, \dot{r} must have real and alternately positive and negative values. Therefore the quantity from which the root has to be taken must always be positive, between two values of r for which it is zero. The discussion of the latter cases is to be found in appendix (I). There we shall also consider the case $n = 2$ for which (1) has to be replaced by

$$V = \alpha Mm \log r$$

and (2) therefore by

$$\dot{r} = \frac{1}{r} \sqrt{ar^2 - \beta r^2 \log r - \gamma^2}, \dots \dots \dots (2^*)$$

where

$$a = \frac{2E}{m}, \quad \beta = 2\alpha M, \quad \gamma^2 = \frac{\Theta^2}{m^2}.$$

The result of this discussion is

n	Circular trajectories	Motions between two positive values of r	Motion to the infinite
4 5...	instable	impossible!	possible
3	stable	possible (moreover closed)	possible
2	stable	possible (not closed)	impossible!

Remarks:

1st. In this connexion we may remind of the following theorem of BERTRAND ¹⁾: The trajectories of a material point described under the influence of a force which is directed towards a fixed centre and a function of the distance to that centre are only then closed when the force is proportional to that distance or inversely proportional to its square.

2nd. It is remarkable that also in a non-euclidian three-dimensional space the planetary trajectories corresponding to the elliptic ones prove to be closed, if the changes in the gravitation law and in the equations of mechanics corresponding to the curvature of the space are introduced. (Comp. LIEBMANN ²⁾).

3^d. We may put the question: what does of BOHR's deduction of the series in the spectra in R_n become, if $n \neq 3$. Let us change in this deduction the law of electric attraction in the same way as that of gravitation, and like BOHR quantize the moment of momentum. From the preceding it is clear that for $n > 3$ only circular trajectories can occur. For $n > 4$ we find infinite series and for $n = 4$ a singular case which is particularly remarkable with respect to the theory of quanta. (See appendix II).

§ 2. **Translation—rotation, force—pair of forces, electric field—magnetic field.**

In R_3 there is dualism between rotation and translation, in so far as both are defined by three characterizing numbers. This is closely connected to the fact that the number of planes through the pairs of axes of coordinates equals the number of axes themselves.

In every other R_n these two numbers are not equal. The number of axes of coordinates is n . Taking two of these at a time we can draw through them $\frac{n(n-1)}{2}$ planes. Evidently $\frac{n(n-1)}{2} > n$ for $n > 3$, while $n > \frac{n(n-1)}{2}$ for $n < 3$ e.g.:

for $n = 2$ we have only one rotation and two translations,

for $n = 4$ we have 6 rotations and 4 translations.

This corresponds to the dualism which exists only for $n = 3$ between the three components of the force and the three components of a pair of forces which together can replace an arbitrary system of forces.

¹⁾ J. BERTRAND, Comptes Rendus. T. 77, 1873, p. 849.

²⁾ H. LIEBMANN, Nicht-euklidische Geometrie. 2e Aufl. 1912, p. 207.

Starting from the formulae of the theory of relativity we easily see that also the dualism between the electric and magnetic quantities is restricted to R_3 .

In R_n the electric field is determined by n components, the magnetic one by $\frac{n(n-1)}{2}$ numbers.

The space-coordinates in the $(n+1)$ -dimensional "world" will be denoted by $x_1 \dots x_n$ and t will be replaced by $x_0 = ict$. The electric and magnetic forces can be deduced from an $(n+1)$ -fold potential (corresponding to the four-fold retarded potential in R_3): $\varphi_0, \varphi_1, \dots, \varphi_n$.

The $\frac{n(n-1)}{2}$ components of its rotation

$$\frac{\partial \varphi_h}{\partial x_k} - \frac{\partial \varphi_k}{\partial x_h} \quad \left(\begin{array}{l} h \text{ and } k = 1, \dots, n \\ \neq 0 \end{array} \right)$$

give the magnetic field and the n components of the rotation:

$$\frac{\partial \varphi_h}{\partial x_0} - \frac{\partial \varphi_0}{\partial x_h} \quad (h = 1, \dots, n)$$

the electric field.

§ 3. Integrals of the equation of vibration in R_n .

(Generalization of the retarded potentials).

The integrals of the equation:

$$\frac{1}{c^2} \frac{\partial^2 \varphi}{\partial t^2} - \Delta \varphi = 0,$$

have the following properties in R_3 : If at the time $t=0$ we have everywhere $\varphi = 0$ and $\frac{\partial \varphi}{\partial t} = 0$ except in a small domain γ , then we have at an arbitrary later moment t (if only t is taken large enough) still everywhere $\varphi = 0$, $\frac{\partial \varphi}{\partial t} = 0$, except in a thin layer between two surfaces (fig. A), which in the limit, when γ becomes small enough, become spherical surfaces with the centre at γ .

In R_2 we have something else: here we have except a disturbance of equilibrium between two concentric lines round γ still an asymptotically diminishing disturbance of equilibrium in the whole extension (III) enclosed by the inner line.

In this respect all R_{2n+1} 's behave like R_3 , all R_{2n} 's like R_2 (see appendix III).

But among the R_{2n+1} 's R_3 is characterized by a particularity

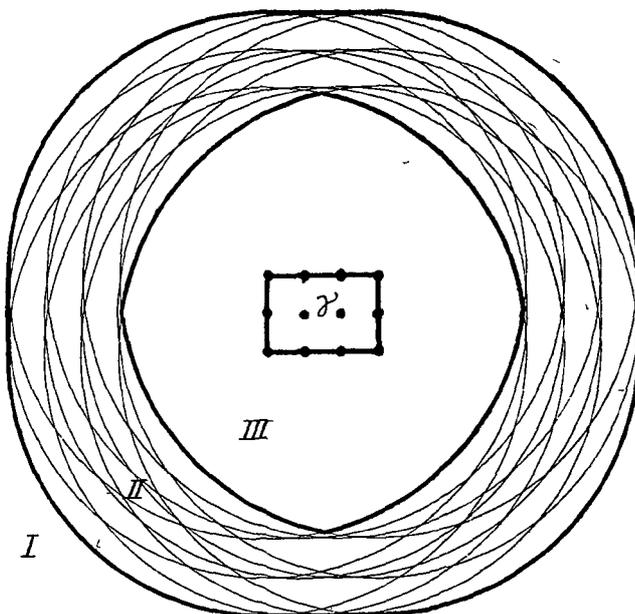


Fig. A.

which becomes evident when the retarded potentials i.e. the integrals of the differential equation

$$\frac{1}{c^2} \frac{\partial^2 \varphi}{\partial t^2} - \Delta \varphi = \rho$$

for R_3 are compared with those for the higher R_{2n+1} 's.

For R_3 :

$$\varphi = \frac{1}{C_3} \iiint d\omega \frac{[\rho]}{r},$$

For R_5 :

$$\varphi = \frac{1}{3C_5} \iiint \iiint d\omega \left\{ \frac{[\rho]}{r^3} + \frac{1}{c} \left[\frac{\partial \rho}{\partial t} \right] \frac{1}{r^2} \right\},$$

For R_7 :

$$\varphi = \frac{1}{5C_7} \int \dots \int d\omega \left\{ \frac{[\rho]}{r^5} + \frac{1}{c} \left[\frac{\partial \rho}{\partial t} \right] \frac{1}{r^4} + \frac{1}{c^2} \left[\frac{\partial^2 \rho}{\partial t^2} \right] \frac{1}{r^3} \right\}.$$

(see appendix IV).

Here $C_3 = 4\pi$, $C_5 = \frac{8}{3}\pi^2$, $C_7 = \frac{11}{15}\pi^3$, are the areas of spheres with a radius equal to unity in R_3 , R_5 , R_7 respectively. The symbol

$[\rho]$, $\left[\frac{\partial \rho}{\partial t} \right]$, $\left[\frac{\partial^2 \rho}{\partial t^2} \right]$ expresses that the values must be taken at the

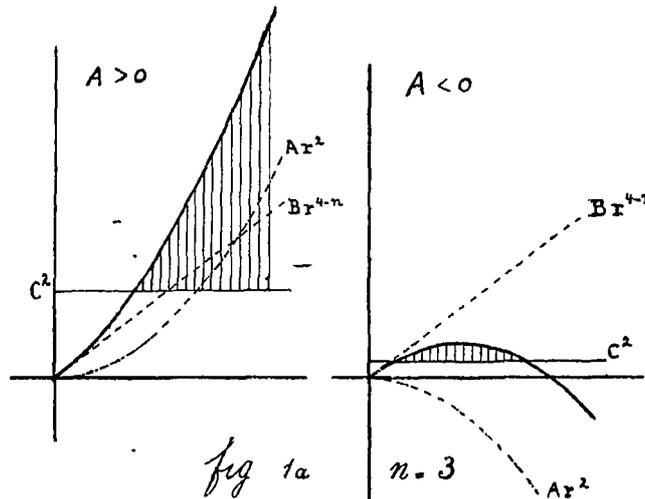
time $t - \frac{r}{c}$ (the "retarded values"). While in R_6 the retarded potentials depend on ϱ only, we see that in R_6, R_7 etc. they are functions of the differential coefficients of ϱ with respect to the time too.

It must be remarked here that for high values of r (which in radiation problems are the only ones we are concerned with) the highest differential coefficient is the most important because here the lowest power of r occurs in the denominator. An electron with sharply bounded charge causes therefore by its motion high singularities.

Appendix.

I. The discussion mentioned in § 1 may be illustrated by fig. 1, where the dotted lines give the terms $A r^2$ and $B r^{4-n}$ as functions of r , while the full curve represents their sum and the horizontal line the part C^2 to be subtracted. In this graphical representation the condition is that the horizontal line cuts the full curve in two points between which the line lies below the curve so that the difference $(A r^2 + B r^{4-n}) - C^2$ is here positive.

For $n = 2$ we have added fig. 2 of analogous structure; the lines represent: $\alpha r^2 - \beta r^2 \log r$, ¹⁾ their sum and γ^2 . Then the condition is satisfied.



¹⁾ $-A$ divided by $\frac{2}{m}$ is the energy a planet must have in order to be brought

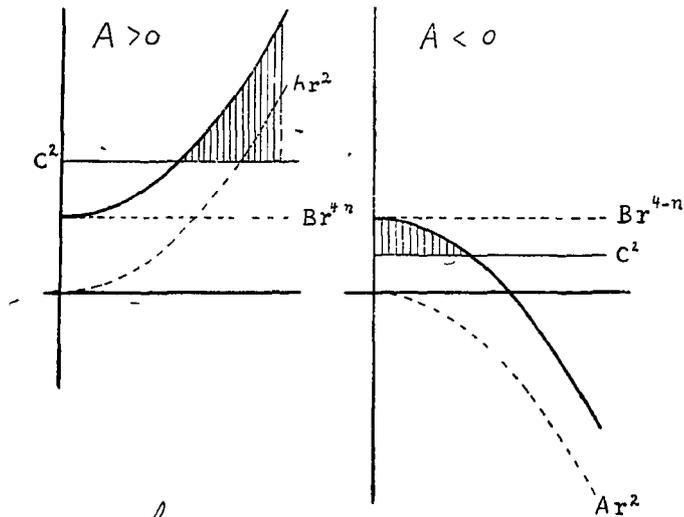


fig 1b $n = 4$

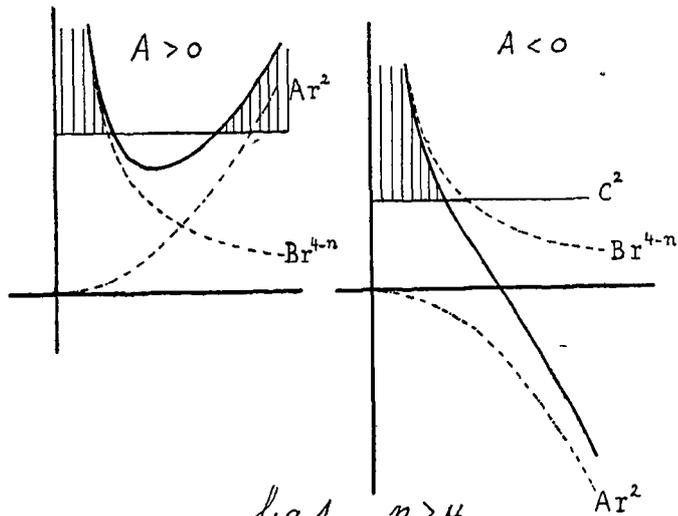


fig 1c $n > 4$

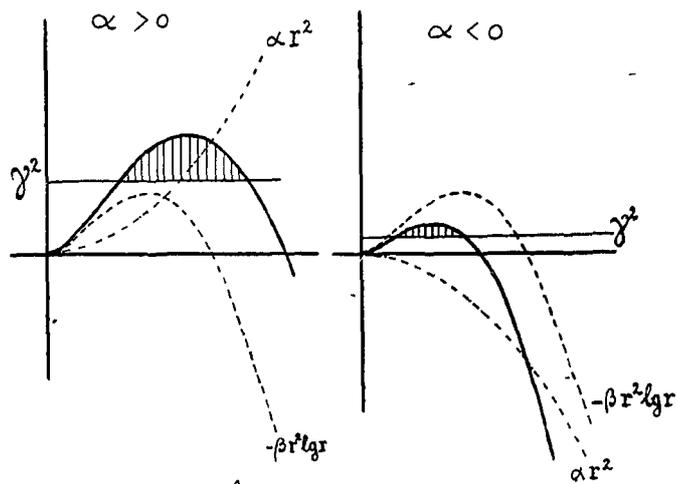


fig 2 $n = 2$

II. That the electric attraction gives the centripetal force for the circular motion is expressed by the equation

$$mr\dot{\varphi}^2 = \frac{e^2}{r^{n-1}}. \quad (A)$$

Bohr's condition for the stationary circular paths gives

$$mr^2\dot{\varphi} = \frac{\tau h}{2\pi}$$

where τ is a whole number.

For the τ^{th} circle the energy is therefore

$$E_\tau = \tau^{-\frac{2(n-2)}{4-n}} \left(\frac{4\tau^2 m}{h^2} \right)^{\frac{(n-2)}{4-n}} e^{\frac{4}{4-n}} \frac{n-4}{2(n-2)},$$

where $n > 2$.

For R_n too we suppose the radiated frequencies to be calculable from

$$\nu_{\sigma, \tau} = \frac{E_\sigma - E_\tau}{h}$$

For $n = 4$ we have a singular case. Equation (A) becomes then

$$r^4 \varphi^2 = \frac{e^2}{m}$$

so that

$$mr^2 \dot{\varphi} = e \sqrt{m}.$$

The moment of momentum can thus have only one perfectly defined value: $e\sqrt{m}$, so that the coefficient of attraction must be connected with h if the quantum condition (necessarily with only one value of τ) remains. For $n > 4$ we find

$$\nu_{\sigma, \tau} = \nu_0 (\sigma^\alpha - \tau^\alpha),$$

where α is a positive fraction in general. Thus we obtain series in the spectrum which for constant τ and increasing σ contain lines in the ultraviolet which become more and more distant from one another.

III. The solution of the equation of vibration for a membrane can be derived from that for a three-dimensional body by supposing in the latter case the disturbances of equilibrium to be in the beginning independent of one of the rectangular coordinates e.g. of

to an infinite distance without velocity, — α divided by $\frac{2}{m}$ on the other hand the energy required to carry it without velocity to the distance 1 from the centre,

z. Then spheres with a radius $r = ct$ are continually cutting the domain of the original disturbance of equilibrium. Working out the calculation we find that the number of integrations to be executed if one of the coordinates does not occur is still the same as when it occurs.¹⁾ That is the reason why in R_n a disturbance of equilibrium never vanishes there where it once appeared. In an analogous way we can pass from a solution for R_{2n+1} to one for R_{2n} . In this way it becomes clear that the continuation of a disturbance of equilibrium is a common property of all R_{2n} 's.

IV. The easiest way to find these solutions is by means of KIRCHHOFF'S method.²⁾ A special solution χ of the equation without right-hand side is then used. This χ is a function of t and of the distance r to a fixed centre P only so that the equation which is satisfied by χ , becomes in R_n

$$\frac{1}{c^2} \frac{\partial^2 \chi}{\partial t^2} - \frac{n-1}{r} \frac{\partial \chi}{\partial r} - \frac{\partial^2 \chi}{\partial r^2} = 0.$$

Applying the operation $D = \frac{1}{r} \frac{\partial}{\partial r}$ to a special solution of this equation we find a solution of the same equation for $n+2$ instead of for n . For odd values of n the special solution is

$$\chi = D^{\frac{n-1}{2}} \left\{ G \left(t + \frac{r}{c} \right) \right\},$$

viz. for $n = 1$:

$$G \left(t + \frac{r}{c} \right),$$

where G is an arbitrary function;

for $n = 3$:

$$\frac{1}{r} \frac{\partial G}{\partial r} \text{ or also } = \frac{1}{r} F \left(t + \frac{r}{c} \right)$$

(F an arbitrary function);

for $n = 5$:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(\frac{1}{r} F \left(t + \frac{r}{c} \right) \right) = -\frac{1}{r^2} F \left(t + \frac{r}{c} \right) + \frac{1}{r^2 c} F' \left(t + \frac{r}{c} \right)$$

etc.

Applying GREEN'S identity to the required solution ψ and this χ (e.g. for $n = 5$) in the whole space ω outside a small sphere with radius R round P we find

¹⁾ Comp. e.g. H. A. LORENTZ: The theory of electrons. Note 4, p. 233.

²⁾ See e.g. RAYLEIGH, Theory of Sound, Ch. XIV, § 275.

$$\begin{aligned}
-\iiint d\Sigma \left(\psi \frac{\partial \chi}{\partial N} - \chi \frac{\partial \psi}{\partial N} \right) &= \\
&= \frac{d}{dt} \iiint d\omega \left(\chi \frac{\partial \psi}{\partial t} - \psi \frac{\partial \chi}{\partial t} \right) + \iiint d\omega \chi \varrho.
\end{aligned}$$

where Σ represents the area of the sphere and N its normal drawn towards ω .

Now we must integrate with respect to t from a high negative value t_1 to a high positive one t_2 ¹⁾. For the arbitrary function F occurring in χ we take a function which is zero for all values of the argument except for those very near zero (there we must pass to the limit) in this way however that for zero the integral of F over that small domain has just the value 1. By interchanging the passage to the limit and the integration²⁾ and by contraction of the sphere the identity becomes

$$-3C_s \psi_{P,(t=0)} = - \int_{t_1}^{t_2} dt \iiint d\omega \varrho \left\{ -\frac{1}{r^3} F\left(t + \frac{r}{c}\right) + \frac{1}{r^2 c} F'\left(t + \frac{r}{c}\right) \right\},$$

or after a partial integration

$$\psi_{P,(t=0)} = \frac{1}{3C_s} \left\{ \int d\omega \frac{(\varrho)_{t=-\frac{r}{c}}}{r^3} + \int d\omega \frac{\left(\frac{\partial \varrho}{\partial t}\right)_{t=-\frac{r}{c}}}{r^2 c} \right\}.$$

A translation of the point $t=0$ then gives the result we want.

¹⁾ If we want to be accurate the extension must also be delimited at the outside. For the largest value of r which occurs $t_1 + \frac{r}{c}$ must still be negative.

Only afterwards we pass to the limit of an infinite extension.

²⁾ This interchange which is not further justified will be known to be characteristic of KIRCHHOFF's method. Here we shall simply borrow it from KIRCHHOFF. If we want to execute the integration rigorously, we shall have to avail ourselves of a method given by J. HADAMARD: Acta Math. 31 (1908) p. 333; especially § 22 Comp. for further literature J. HADAMARD, Journ. de Phys. 1906.

Physics. — “*Contribution to the research of liquid crystals. II. The influence of the temperature on the extinction; further experiments upon the influence of the magnetic field.*” By Dr. W. J. H. MOLL and Prof. Dr. L. S. ORNSTEIN. (Communicated by Prof. JULIUS).

(Communicated in the meeting of February 24, 1917).

In the further research of the liquid crystals, the results of which we intend to communicate hereafter, the same method as described in a former communication was used again. (These Proc. XIX p. 1315). The method was improved in a few respects only, the principal change being that a copper-disk with a central hole of about three millimeter diameter takes the place of the glass-pieces in the oven. The substance is put between two object-glasses, which lie on the disk. In this way we get the advantage that the matter does not come into contact with the copper, and that it is possible to examine several substances successively with the same oven. Though the narrow hole in the copper diminishes the intensity of the image on the thermo-pile it secures an absolutely homogeneous heating of the very small part of the matter under observation.

§ 1. *The influence of the temperature on the extinction.*

The extinction in its dependence on the temperature was measured in the following way. The matter that has been melted before between two glasses and congealed afterwards, is put on the oven the temperature of which is below the melting-point. Then such a value is given to the heating current, that in the long the melting to isotropic-liquid will be reached. Then if after some time the substance has been molten, the current of heating is put off (or diminished) so that the substance gets liquid crystalline again and congeales afterwards. In the method described before the extinction is registered during this rising and falling of temperature. There were examined p-azoxy-anisol, p-azoxy-phenetol, anisaldazine and p-azoxy-benzoeacid-aethylester. In fig. 1 and 2 the curves of extinction are reproduced of two of these substances ¹⁾.

¹⁾ p azoxy-phenetol and anisaldazine produced melting curves of the same character as p azoxy-anisol.

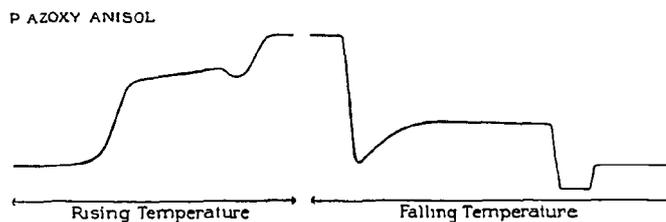


Fig. 1.

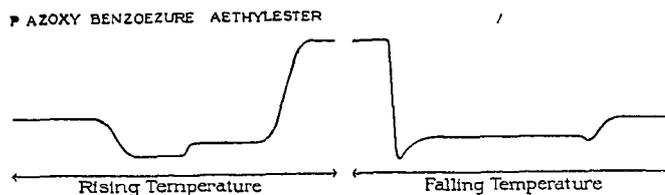


Fig. 2

When we consider these curves of extinction, the fact is obvious that the extinction in the liquid-crystalline condition, proceeding from melting of the solid phase ("ex-solid") is different from the liquid-crystalline condition formed by cooling of the isotropic liquid ("ex-liquid"). This different extinction is accompanied by an absolutely different aspect.

These differences are mostly conspicuous in the case of p-azoxybenzoic-acid-aethylester. With this substance the ex-solid condition is milky-opalescent, the ex-liquid grainy-opalescent, and when the preparation is heated the first condition always changes into the other at the same temperature. In the curve that transition appears by a leap-wise increase of the extinction. In the cooling-branch of the extinction-curve we only found an indication that at the sudden transition from liquid into liquid-crystal during a short period the ex-solid state might inconstantly have existed as instable, however by cooling very quickly we succeeded in obtaining durably the ex-solid condition from the liquid state.

With the three other substances examined, also a very obvious difference in extinction between the ex-liquid state and the ex-solid state (vid. fig. 1) shows itself, but contrary to p-azoxybenzoic-acid-aethylester, with these three substances of both liquid-crystal conditions the ex-liquid one is the most opaque.

Another particularity of the extinction-curves are the different bag-shaped drops.

The drops at the transition from liquid-crystal into isotropic-liquid and the reverse are not real, i.e. they have no meaning for the extinction as such. They are caused by the melting (resp. the getting turbid) not occurring simultaneously in all parts of the substance.

By the great difference in index of refraction of the isotropic and of the crystalline liquid, phenomena of refraction occur at the limit, and therefore the image of the NERNST-burner is broadened, deformed or shifted. A temporary weakening of the thermo-current, therefore a drop of the extinction-curve will be the consequence of this.

In our opinion the slow rise of the extinction-curve when the liquid-crystalline phase has proceeded from the isotropic-liquid phase (the continuation of the bag-shaped drop) can be explained by the fact that at the sudden turbidity a very disorientated state appears, on which only very slowly the directing influence of the glass makes itself felt.

Sometimes the extinction-curve of *p*-azoxy-anisol showed a peculiar drop at the transition from liquid-crystalline into solid. In fig. 1 this drop is represented. It occurred especially when the preparation had been examined in a very thin layer and was then strongly undercooled. At macroscopic examination it appeared to us that under these conditions greenish-yellow crystals were formed, which we soon could identify with the meta-stable solid phase already described by LEHMANN in 1890.¹⁾

Finally from our curves the dependence on the temperature of the extinction can be read. If we define ourselves to *p*-azoxy-anisol (fig. 1) then a strong dependence on the temperature may be stated in the ex-solid condition, in such a way that at rising temperature the extinction decreases. Also the reverse effect, increase of the extinction at falling temperature, could be established with certainty for the ex-solid condition. In the ex-liquid condition the dependence on the temperature is very much less evident, without any doubt it exists however in the same sense as in the case of the ex-solid state. Already in 1902 SCHENCK has performed measurements on this question with the aid of the spectrophotometer of GLAN, and has only reached a negative result. But he examined the extinction for yellow light, whereas our method gives the extinction for a mixture of rays in which ultra-red dominates.

So we thought it useful to examine the dependence on the temperature also in another range of wave-lengths. We chose as such the photographically active rays. The image of the NERNST-burner was for that purpose formed instead of on the vertical slit of the thermopile on the horizontal slit of a photographical registration-

¹⁾ Perhaps it is well to remark that we succeeded in establishing the reversible melting-point of this greenish-yellow phase at 108°. VORLÄNDER as well as SCHENCK doubt the validity of an analogous result of LEHMANN.

apparatus. The line thus registered on the sensitive paper enables us at once to judge by its breadth and blackness of the extinction of the substance:

As well with ex-solid as with ex-liquid the temperature appeared to exercise a plainly perceptible influence on the extinction, but the direction of the effect is for the photographically active rays just the reverse as for the ultra-red rays, i.e. for the short waves at rising temperature the extinction increases. So, as the effect of the temperature in the case of strongly differing wave-lengths has a right to a different sign, the apparent contradiction between the result of SCHENCK and that which follows from our extinction-curves is explained.

§ 2. *The influence of a magnetic field on the extinction.*

The fact that there appeared to exist two liquid-crystalline states, made it desirable to extend our research on the influence of magnetic field to the second states. Besides the magnetic effect on the three remaining substances we disposed of, had to be examined.¹⁾

With p-benzoë-acid azoxy aethylester no influence could be established, not even with the strongest fields we could excite, (ca. 1100 GAUSS). An examination with still stronger magnetic field is being prepared now. Anisaldazine experiences a strong influence as well in ex-solid as in ex-liquid state. With p-azoxy-phenetol the influence is much weaker, but could still be observed by us with certainty in both states. The character of the effect is for both substances principally the same as for p-azoxy-anisol.

The magnetic effect of p-azoxy-anisol in the ex-solid condition is represented by the figures 3 and 4. For sake of comparison we

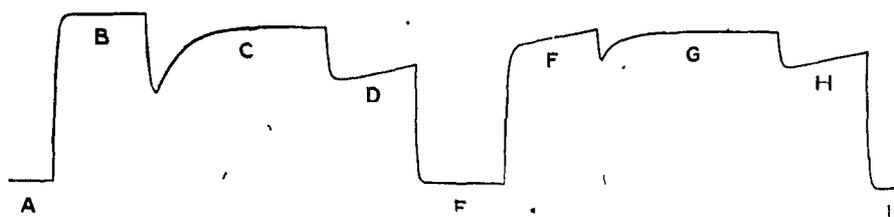


Fig. 3. P-azoxy-anisol ex-solid vertical field (1100 Gauss).

¹⁾ In our first communication we mentioned the preponderating influence the nature of the adjacent surface has on the magnetic effect. In order to examine this influence more closely we have registered the magnetic effect, for substances of different thickness, put between glass whether or no chemically cleaned, or enclosed between mica. The differences found, however, were only of quantitative character.

reprint from our first communication the figures 5 and 6, which represent the effect of equally strong magnetic fields on the ex-liquid state.¹⁾

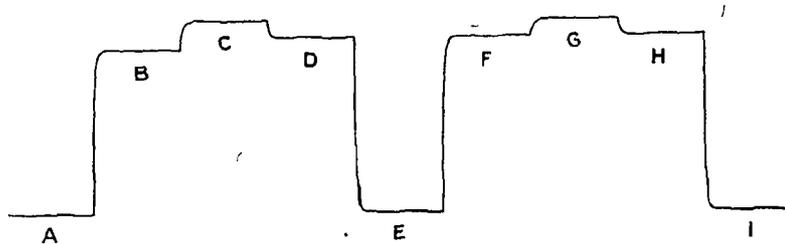


Fig. 4. P-azoxy-anisol ex-solid horizontal field (1100 Gauss).

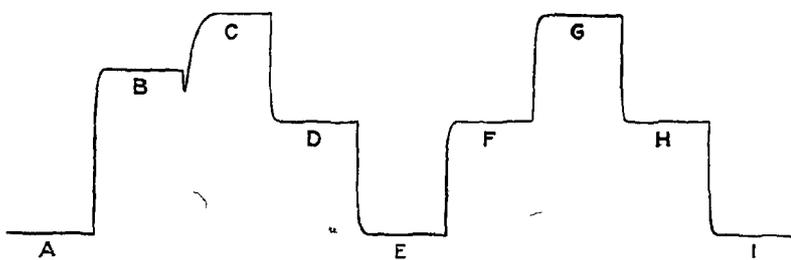


Fig. 5 P-azoxy-anisol ex-liquid vertical field (1100 Gauss)

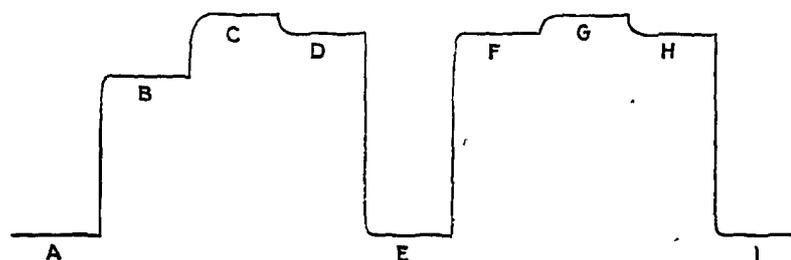


Fig. 6. P-azoxy-antsol ex-liquid horizontal field (1100 Gauss).

A comparison between figures 3 and 5 and also between figures 4 and 6 shows that the magnetic effect for ex-solid indeed differs from that for ex-liquid. That however the difference is greatly quantitative appears when fig. 3 is compared to fig. 7. This figure too is reproduced from our former communication and represents the influence of a *weak* vertical field on the ex-liquid state.

¹⁾ For the meaning of these figures and the method of registration we refer to our first communication.

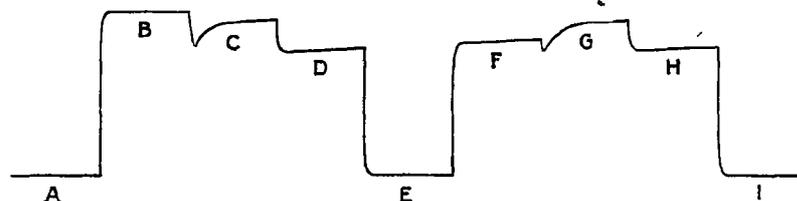


Fig 7. P-azoxy-anisol ex-liquid vertical field (300 Gauss).

The different magnetic effect in the two states consequently can be described as follows: a strong field acts analogously on ex-solid as a weak field on ex-liquid.

Finally we shall mention a magnetic effect of a particular kind. A horizontal field causes *lasting* clearing up as well in the ex-solid as in the ex-liquid state. In our former communication we explained this diminishing of the extinction by the fact that the particles are directed to a high degree. Now it seemed to us of importance to examine how a vertical field would *disturb* this order. Figures 8 and 9 show this disorientating influence of a vertical field on ex-liquid and ex-solid, when the substance has first been exposed to the effect of a horizontal field.

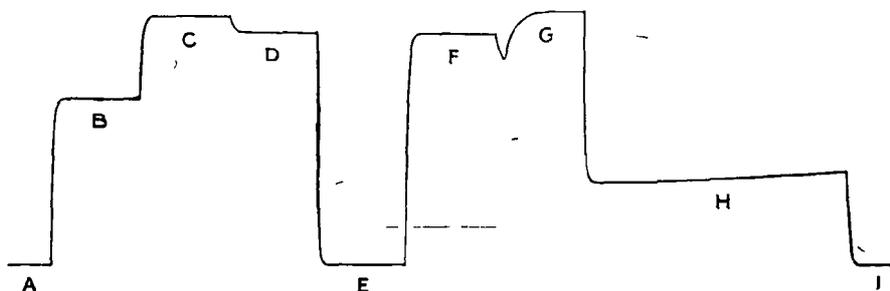


Fig 8. P-azoxy-anisol ex-liquid first horizontal field, then vertical field.

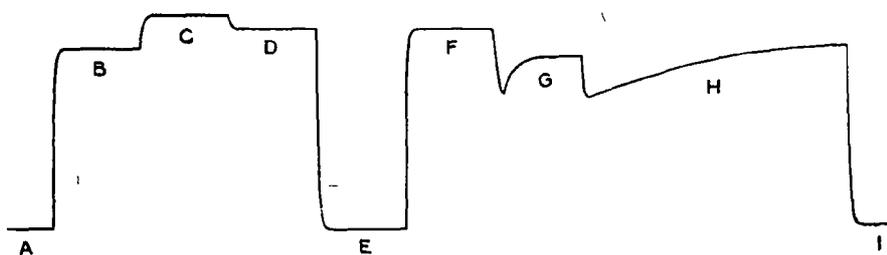


Fig. 7. P-azoxy-anisol ex solid first horizontal, then vertical field.

The explication we gave in our first communication of the magnetic effect, can be transmitted unchanged to the phenomena described above. The different degree of extinction in ex-liquid and ex-solid and the different influence thereupon of a magnetic field, we are inclined to ascribe to the fact that the little parts have a *different directability* in the ex-liquid state and in the ex-solid state.

S U M M A R Y.

The extinction of p-azoxy-anisol, p-azoxy-phenetal, anisaldazine and p-azoxy-benzoë-acid-aethylester is examined in its dependence on the temperature.

It appears that two different liquid-crystalline states exist ("ex-solid" and "ex-liquid") which possess each a different extinction, and which undergo in a different degree the influence of a magnetic field.

The coefficient of temperature of the extinction appears to be negative for ultra-red and positive for ultra-violet.

Utrecht, Februari 1917.

*Physical Laboratory
Institute for Theoretical Physics.*

Zoology. — “*The Fore-brain of Synbranchidae*”. By Dr. C. J. V. D. HORST, Amsterdam. (Communicated by Prof. MAX WEBER).

(Communicated in the meeting of May 26, 1917).

The Synbranchidae are distinguished from all other Teleosts by a secondary coalescence of the two halves of their fore-brain.

In the rich collection of the Central Institute for Brain Research at Amsterdam, which includes almost all the suborders of the Teleostei, I found several representatives of other suborders of Teleosts in which the hemispheres of the fore-brain are pressed together, but where no coalescence has occurred.

In only one of the three series of Hippocampus in the Institute the two hemispheres partially have grown together in the midline, dorsal from the commissura anterior. This, however, must be regarded rather as an abnormality in this specimen caused by the presence of parasites in the brain cavity, whereby the fore brain has become totally changed in form.

Of the suborder of Synbranchii, I was able to examine the brains of *Monopterus albus* (Zuiew) received from Dr. SUNIER of Batavia, and of *Synbranchus marmoratus* Bl., which I obtained from the Aquarium of the Royal Zoological Society “*Natura Artis Magistra*” at Amsterdam. The brains of these fishes were cut in series of sections 20μ thick, treated by the WEIGERT-PAL method and contrasted with paracarmine.

Monopterus and *Synbranchus* are exactly alike as regards the formation of the brain, as I have pointed out in a previous paper (2). The coalescence of the two hemispheres is therefore not an abnormality here as in the above-mentioned specimen of *Hippocampus*, but is a typical characteristic of the family of Synbranchidae, and, if it also occurred in Amphipnous, even of the whole order of Synbranchii.

The outer form of the fore-brain.

The fila olfactoria are collected in a short nervus olfactorius which forms a fairly sharp boundary with the bulb.

As in most of the Teleostei the bulbi olfactorii in *Monopterus* and *Synbranchus* are sedentary; an elongated tractus olfactorius is not found here.

Further back the bulbi, which in comparison with the fore-brain are considerably big, decrease in size according as the fore-brain becomes larger. On the median side they are separated by a deep groove. Whereas in most Teleosts with sedentary bulbi, this groove extends over the dorsal and lateral side of the bulbus, so that the front point of the fore-brain projects in the ventricular cavity above the bulbi; this is not the case in the Synbranchidae; the foremost point of the telencephalon has already united with the bulb.

On this boundary between the bulb and the fore-brain the ependyma, which forms the roof of the fore-brain, is attached to the dorsal and lateral sides of the olfactory bulb, while on the medial side the place of attachment lies on the bulb rather before this boundary (see fig. 2). Except for a small fold on the front, the membranous roof lies flat over the whole fore-brain. To the ventro-lateral side of the hemispheres in the fissura endorhinalis (not lateral from it, as in many other Teleosts), the tela choroidea is attached and the ependyma passes over into the subventricular ependyma, which even extends over the hemispheres themselves.

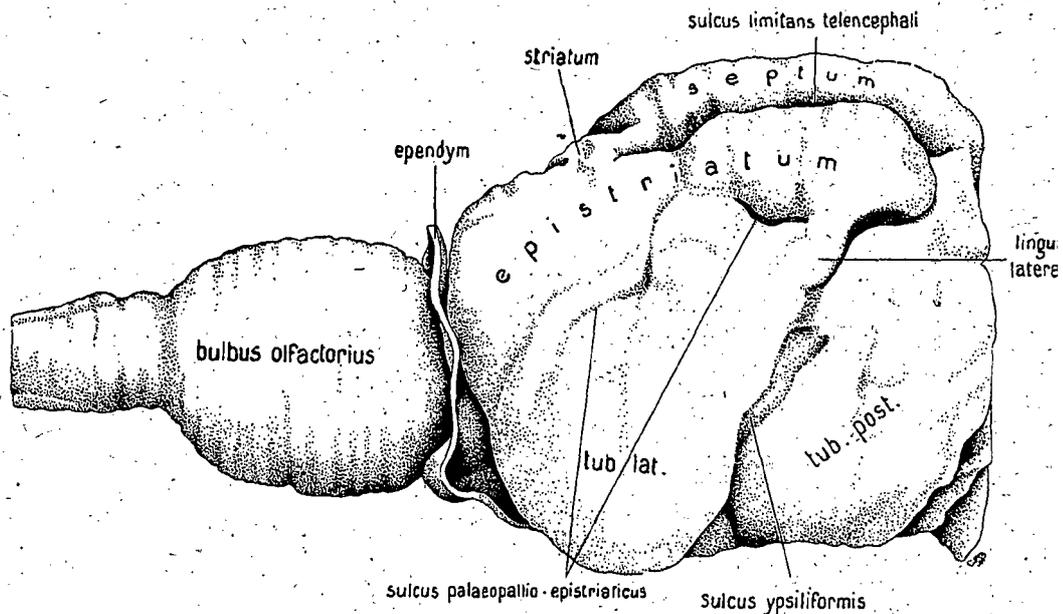
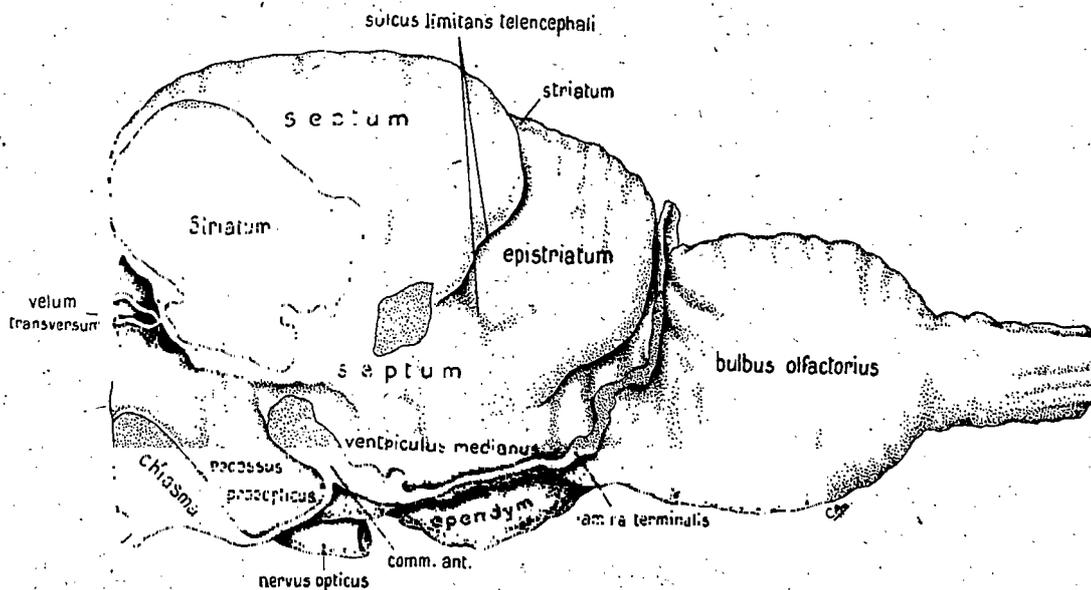


Fig. 1. *Monopterus albus*. Wax model of the fore-brain Lateral side.

The fissura endorhinalis is very deep owing to the great development of the lateral portion of the fore-brain (tuberculum laterale and tuberculum posterius of SHELDON (6)). As SHELDON has described of the carp, so also in *Monopterus* this fissure deviates at the place of the sulcus ypsiliformis rather decidedly in a lateral direction.

Thus seen from the ventral side, the fissura endorhinalis is shaped like two half arcs, which form an obtuse angle with each other. The anterior of these bounds the tuberculum laterale, the posterior the tuberculum posterius.

Not only latero-ventrally, but also caudally the tuberculum posterius is strongly developed like the median portion of the fore-brain. The caudal portion in these fishes thus covers a greater part of the thalamus. One consequence of this is that the posterior fold of the velum transversum points forwards instead of backwards (fig. 2). Whereas the dorsal sack (pulvinar epiphyseos) usually lies on the roof ependyma of the fore-brain, here we see just the reverse; the richly folded dorsal sack is covered by the ependyma of the fore-brain which bends backwards over it.



- Fig. 2. *Monopterus albus*. Wax model of the fore-brain Median side.

A short distance behind the middle of the hemispheres, in a rather frontal position consequently the sulcus ypsilonformis of GOLSTEIN (1) begins at the place where the fissura endorhinalis forms the aforementioned obtuse angle (fig. 1). The sulcus, very deep at this place, proceeds at first perpendicularly upwards, but later on bends in a somewhat caudal direction. As in *Cyprinus*, according to SHELDON'S description, the groove then divides. The two grooves then formed run along the whole dorso-lateral side of the hemispheres. They constitute the boundary between the lateral part of the fore-brain, the palaeopallium (tuberculum laterale and tuberculum posterius),

and the more dorsal epistriatum. These two grooves together may thus very justly be termed the sulcus palaeopallio-epistriaticus, as this has been described by KAPPERS and THEUNISSEN (5) in *Thynnus*.

The most posterior portion of this groove is very deep and narrow; the boundary between the palaeopallium and the epistriatum can therefore be drawn very sharply there. The direction of this portion is almost caudo-frontal. Towards the front, the groove becomes shallower and wider. It then deviates in a ventral direction and reaches the fissura endorhinalis on the front of the hemispheres, getting gradually fainter.

Dorsally from this sulcus palaeopallio-epistriaticus there lies a body which I take to be the epistriatum (the primordium hippocampi of SHELDON). At least the posterior portion, limited by the deep grooves, corresponds exactly in form to the epistriatum of *Gadus*, *Silurus* and other fishes, as has been described by KAPPERS. Thus it shows clearly a lingua lateralis descending in the sulcus ypsilliformis, as well as a lingua posterior projecting backwards. The latter is especially distinct in *Synbranchus* (fig. 6). This part too receives secondary olfactory fibres from the tractus olfactorius medialis pars lateralis, just as the lateral part of the hemispheres lying caudally from the sulcus ypsilliformis. To this very pronounced part of the epistriatum an anterior portion joins, which is connected with it by a narrow strip lying rather deeper, so that one might say that it is separated from it by a broad and shallow groove. Viewed through the microscope, these two parts merge invisibly into each other. I therefore believe that this front portion must also be considered as a part of the epistriatum. Like the caudal portion it is closely connected with the palaeopallium. Both receive secondary olfactory fibres from the tractus olfactorius lateralis. On the other hand, it is fairly sharply divided from the striatum, over which it lies like a hood.

The epistriatum is bounded on the median side by the sulcus limitans telencephali, which has been described by SHELDON, and which forms the boundary between the corpus precommissurale (septum mihi), and the primordium hippocampi of this author (epistriatum mihi) (figs. 1, 2, 3, 4, 5, 6). This sulcus in *Monopterus* is very narrow and deep, as is seen in figs. 3, 4, and 5, specially the posterior portion of the epistriatum (the lingua posterior) is sharply separated by it from the other parts of the hemispheres. In *Synbranchus* the sulcus is not so deep, but this is secondary compared with *Monopterus*, since, here and there in *Synbranchus* a series of ependyma cells is found lying between the epistriatum

and the septum at the same place as where in *Monopterus* the sulcus cuts deep into the hemispheres. From this it is evident that the sulcus limitans telencephali is present at first in *Synbranchus* in the same form as in *Monopterus*, but that later it grows together in a similar way as in the posterior portion of the central canal of the spinal cord, where only a septum ependymale remains. In consequence of this the sulcus is only indicated by a very faint groove in *Synbranchus*.

In *Cyprinus*, where SHELDON has described this groove, the sulcus limitans runs entirely on the median side of the hemispheres and only at its caudal-end does it reach the dorsal surface of the fore-brain then lying on the dorso-median side of the hemispheres. In most of the specimens of Teleosts, which I examined as to this, the groove is found at the same place as in the carp. But in the *Synbranchidae* the course of the sulcus limitans is entirely modified owing to the enormous development of the septum. This body, in most Teleosts, covers the entire median wall of the hemispheres ventrally from the sulcus limitans. Whereas it is comparatively small at the front of the fore-brain there covering only the ventral half of the median wall of the cerebrum, it grows out caudally in a dorsal direction and finally covers the whole median side of the hemispheres.

In *Monopterus* the frontal end of the sulcus limitans lies at the same place as in other Teleosts, about half way up the median wall of the hemispheres. From here this groove runs slightly caudally, but then makes a sharp bend and further proceeds in a dorso-frontal direction to the upper surface of the brain (fig. 2). Here the groove curves gradually in a caudal direction and then runs backwards almost parallel to the median line. (Fig. 1).

This course of the sulcus limitans is, as has been said, caused by the enormous increase of the septum. As in *Cyprinus* the frontal termination of this body occupies only the ventral half of the median side of the hemispheres. But the greater part of it has developed strongly in a dorsal direction. The whole median side of the hemispheres and a part of the dorsal side are covered by it. Moreover it protrudes there somewhat in a frontal direction covering the striatum, in consequence of which the sulcus limitans is bent here in a dorso-frontal direction (fig. 2). This dorsal growth also explains why the sulcus limitans cuts so extremely deep into the fore-brain. This groove also proceeds over the posterior side of the cerebrum and forms there, caudally from the epistriatum, the boundary between the septum and the tuberculum posterius.

In many Teleosts a large part of the surface of the hemispheres is formed by the corpus striatum. KAPPERS (4) has described this in *Gadus* and *Hippoglossus*. On the other hand, in Synbranchidae the corpus striatum is almost completely pushed away from the surface, owing to the septum growing over it from the median side, and the epistriatum from the lateral side. Only a small portion of the striatum remains on the surface, viz. on the dorsal side of the hemispheres, lateral from the frontal point of the septum.

As was already remarked (pag. 217), the cerebra of *Monopterus* and *Synbranchus* are specially remarkable owing to the two hemispheres having partially united (fig. 2).

This junction has an important influence on the relation of the ventricular cavities.

The ventricular cavity dorsal and lateral from the two hemispheres has been called *ventriculus lateralis* by GOLDSTEIN (1), and the slit between the hemispheres has been termed *ventriculus medianus* by the author. This nomenclature may very suitably be employed here, now that the two ventricle portions have been separated by the growth. Ventrally from the coalescence between the hemispheres lies the *ventriculus medianus*, for in spite of the growth the median ventricle remains still clearly visible in these fishes, owing to the fact that the hemispheres of the forebrain always deviate slightly from each other on the ventral side above the lamina terminalis and the commissura anterior. Behind the commissura anterior the median ventricle is connected with the recessus praeopticus, while at the frontal pole of the cerebrum the lateral and median ventricles are continuous. For the rest, the two ventricles are completely separated, also in the front portion of the cerebrum. Here the two halves of the fore-brain lie closely pressed together, each indentation in the one half being filled out by the other half, and we frequently see a blood-vessel passing from the one side to the other (fig. 3). Locally too the two halves have frequently grown together; such a coalescence is rather larger immediately caudad from the bend in the sulcus limitans (fig. 2).

The caudal parts of the hemispheres have completely united. The frontal boundary of this coalescence is not constant. In *Monopterus* it runs differently from that in *Synbranchus*; very probably in individual cases it will not be constant either, and this is not surprising, considering the local coalescence, which can also be found in the frontal portion. On the other hand, the boundary behind the level of the commissura anterior is sharply defined (fig. 2).

Between the two hemispheres, on the dorsal side, is a deep groove,

which penetrates to where the hemispheres lie against each other or are connected with each other. This groove grows shallower and fainter in a caudal direction and finally disappears altogether (Cf. figs. 3-6).

The coalescence of the hemispheres is by no means a superficial one, since it is accompanied by radical changes in the position of the nuclei and in the course of the fibre tracts. Some of the fibres, indeed, which in other fishes decussate in the commissura anterior, here decussate above the ventriculus medianus. The small size of the ventral commissura anterior of these fishes as compared with that of other Teleosts, is hereby explained.

I wish to point out that it is a common feature that a part of a commissure may cross more dorsally if a suitable commissure-bed is present (c.f. the development of the psalterium in reptiles and of the corpus callosum in mammals).

The nuclei and tracts in the fore-brain.

The nuclei and tracts of the fore-brain have been frequently described, and SHELDON in particular has given a most minute and accurate account of it. It is therefore not my intention to describe them all again here, the more so as the position of the nuclei has already been spoken of in discussing the morphology. I will only say a few words concerning some fibre-tracts which differ from the normal type in their course, and concerning the corpus striatum which has been almost quite pushed away from the surface by the other portions of the fore-brain (vide supra).

At the frontal part of the telencephalon, the corpus striatum is seen for a short distance on the medio-dorsal side of the hemispheres between the septum and the epistriatum (fig. 1). Further caudally the growth of the septum pushes it quite away from the surface. Its shape then is oval, in consequence of which in a cross section through this region the septum appears narrowest in the middle (fig. 3). Further caudally the striatum becomes broader; it spreads further in a median direction, dislodging the two septa. This spreading of the striata goes so far that at the level of the posterior boundary of the commissura anterior, they grow together over the median line, whereby the septum becomes divided into a dorsal and a ventral part (fig. 4). We can here distinguish a median and two lateral portions in the striatum.

Further caudally the median connecting portion of the striata is separated from the lateral parts more or less. This separation is

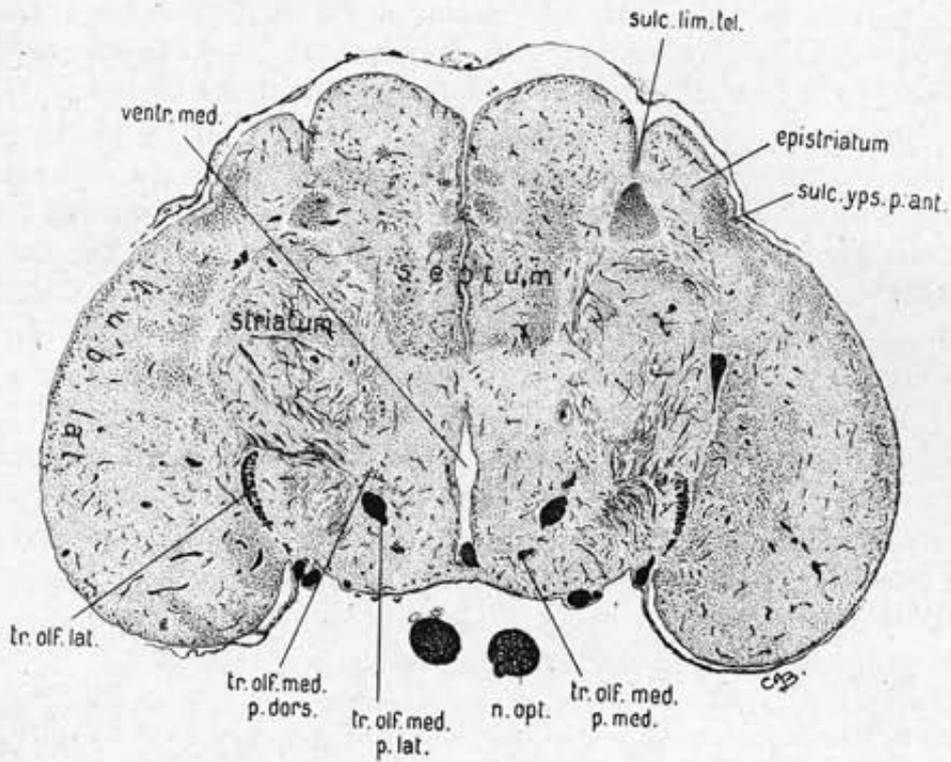


Fig. 3. *Monopterus albus*.

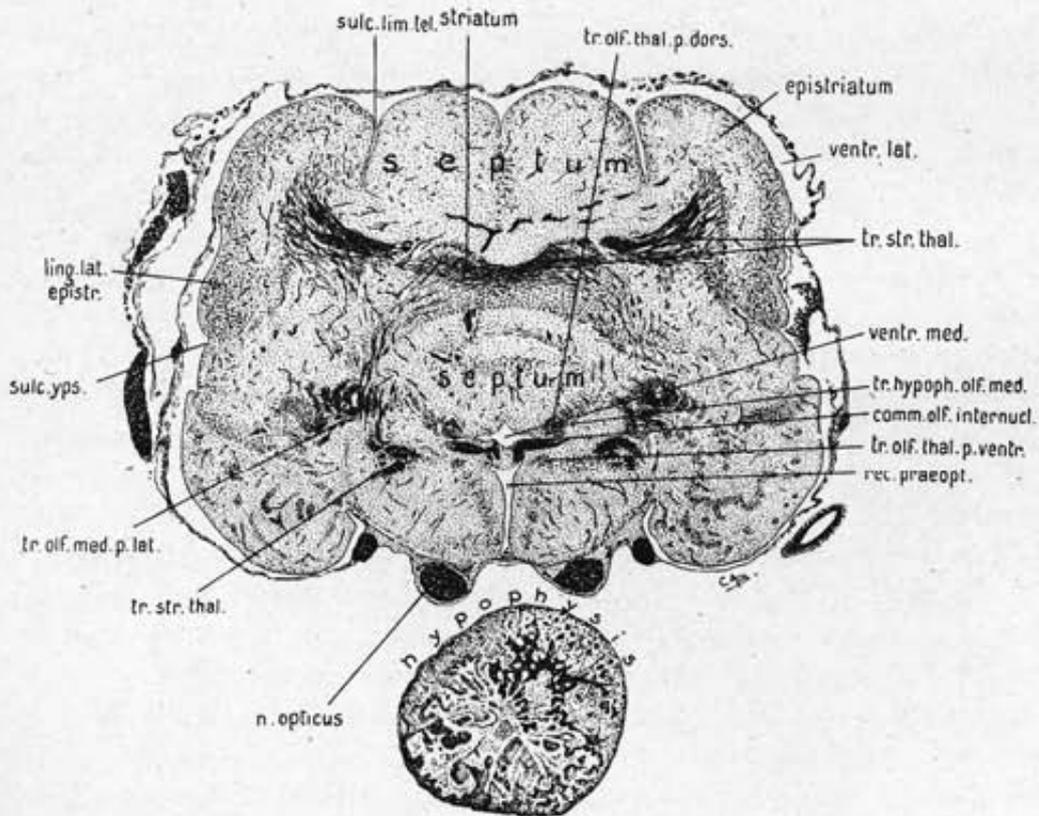


Fig. 4. *Monopterus albus*.

carried further in *Synbranchus* than in *Monopterus*, just as in the former the whole curious development of the fore-brain has reached a further stage than in the latter, as was already pointed out in discussing the sulcus limitans telencephali. The same thing is also clear in considering the caudal end of the striata. In *Monopterus* the striatum is still separated by a part of the septum from the ventriculus medianus and the recessus praeopticus. The lateral portions of the striata extend equally far caudally as the median portion; in the series of sections the striatum is therefore seen to disappear entirely simultaneously, and at the back it is covered by the septum and the lateral portions of the cerebrum, which meet here.

In *Synbranchus*, on the contrary, the striatum in the middle pushes away the ventral portion of the septum, so that the striatum lies directly dorsally from the recessus praeopticus (fig. 6). This median portion of the striata extends further in a caudal direction than the lateral parts. At the back of the fore-brain the striatum is not

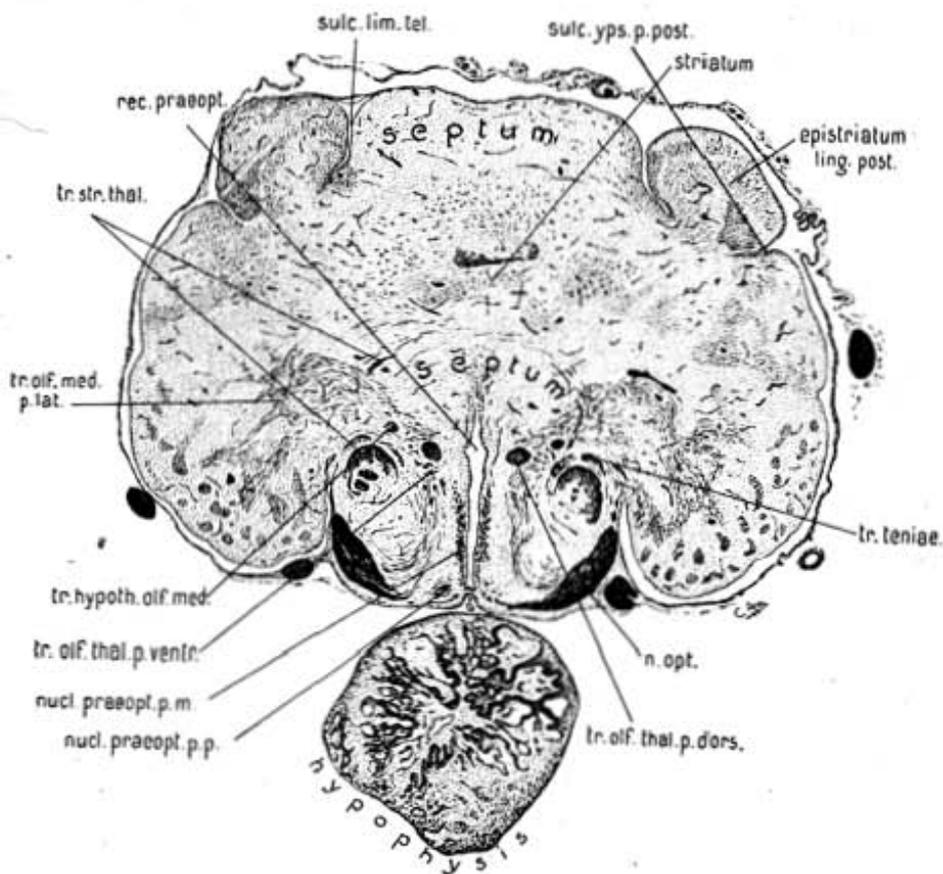


Fig. 5. *Monopterus albus*.

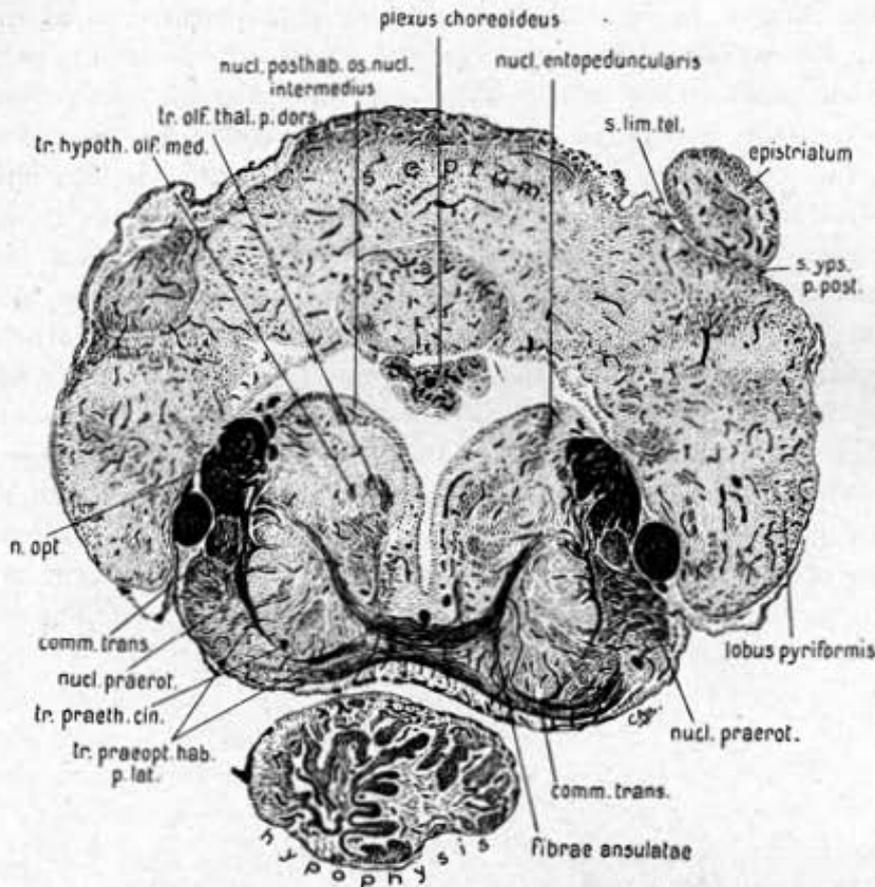


Fig. 6. *Synbranchus marmoratus*.

entirely surrounded by other parts of the cerebrum, though the dorsally situated septum reaches rather further caudally.

Of the fore-brain tracts the tractus olfactorius claims our attention first.

The lateral olfactory tract (tractus olfactorius lateralis) is found in its usual position near the fissura endorhinalis. It sends its fibres into the lateral olfactory regions, the area olfactoria lateralis of KAPPERS and THEUNISSEN (5). In the level of the sulcus ypsiliformis this olfactory tract has entirely disappeared. It is my opinion therefore that in Synbranchidae only that part of the lateral olfactory region which lies in front of the sulcus ypsiliformis is provided with olfactory fibres from the tractus olfactorius lateralis. According to SHELDON in the Cyprinidae the nucleus piriformis and the nucleus taeniae also receive fibres from the lateral olfactory tract.

In the tractus olfactorius medialis I can distinguish three bundles. One, non-medullated, connects the septum with the bulb and is probably the same as SHELDON describes as tractus olfactorius ascendens (running frontally).

The course of the very small tractus olfactorius medialis pars medialis does not differ from that in *Cyprinus*, while on the other hand, the thick medullated tractus olfactorius medialis pars lateralis takes a different course. According to SHELDON (6), KAPPERS (4), GOLDSTEIN (1), and others, this bundle decussates with the commissura anterior in at least the large majority of cases among Teleosts. In *Synbranchus* and *Monopterus*, however, nothing is to be seen of this decussation. The tract here runs somewhat in a lateral and dorsal direction, on to the commissura anterior, and then penetrates between the various bundles of the tractus strio-thalamicus (fig. 4). When slightly lateral from this, i. e. dorsal from the fissura endorhinalis, the bundle dissolves into a dense network of fibres which lie nearly on the boundary of the nucleus piriformis, the striatum and the ventral portion of the septum (fig. 5). The fibres of this network then spread into the nucleus piriformis and the nucleus taeniae, which are not clearly distinguishable from each other here, and further into the caudal part of the epistriatum. This region, behind the sulcus ypsiliformis, is thus provided with olfactory fibres only by the lateral part of the median olfactory tract.

Very slightly caudal from the place where the tractus olfactorius medialis pars lateralis merges into the aforesaid network, medullated fibres from the nucleus piriformis gather (GOLDSTEIN's commissura olfactoria internuclearis, described as a non-medullated bundle by SHELDON under the name of tractus olfactorii mediales partes laterales). These fibres, forming a considerable bundle, decussate with the most posterior part of the commissura anterior (fig. 4). It is possible that in this bundle there are still a few decussating fibres of the tractus olfactorius medialis pars lateralis; but this I could not determine with certainty.

In connection with the coalescence of the two halves of the fore-brain, the course of a part of the so-called tractus strio-thalamicus is very remarkable. The majority of the fibres which form this bundle congregate, as in all Teleosts, from nearly every part of the fore-brain and, after having decussated partly in the commissura anterior, run medially from the fissura endorhinalis to the mid-brain. From the most posterior part of the epistriatum (the lingua posterior), however, a great number of medullated fibres join to a thick bundle, which decussates somewhat further frontally in the median striatal portion connecting the two halves of the telencephalon. (fig. 4). After the decussation this bundle runs a short distance forward in the dorso-lateral portion of the striatum. On the frontal level of the commissura anterior this bundle bends at a right angle

in a ventral direction, and joins the rest of the tractus striothalamicus.

The fore-brain of the Synbranchidae is remarkable, because it forms, as it were, the final stage in the series of development of the telencephalon of Ganoids and Teleosts. For, according to SHELDON, the septum originally forms the ventro-median part of the fore-brain. In *Polypterus*, which forms the first stage in this series of development, this part still lies at its original place. The septum now gradually grows on the median side past the striatum, whereby the striatal portion of the ventricle wall is more and more restricted. This process going on, in some Teleosts the striatum disappears altogether from the ventricular wall, and the sulcus limitans telencephali forms the boundary between the septum and the dorsal part of the cerebrum, the epistriatum. At the caudal end of the fore-brain this process is further advanced than at the frontal end; the sulcus limitans thus lying in front on the median side, at the back on the dorso-median side of the hemispheres.

Only in the Synbranchidae however, this process goes so far that the septum reaches the dorsal surface of the cerebrum, whereby the epistriatum is pushed aside and the sulcus limitans comes to lie on the dorsal, or even dorso-lateral, surface of the hemispheres.

The coalescence of the hemispheres may also be regarded as a final stage in the development. In the Ganoids the two hemispheres are far apart and the ventriculus medianus is broad. This is also the case in primitive Teleosts, such as *Salmo*. In other Teleosts the hemispheres approach each other more and more, and in most Acanthopterygii they lie right against each other; the ventriculus medianus only being open in the ventral part above the lamina terminalis and above the commissura anterior. In the Synbranchidae the hemispheres, at least as regards their caudal half, have almost entirely coalesced, and of the ventriculus medianus only a narrow split remains, ventrally from this junction.

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Astronomy. — “*On the curvature of space*”. By Prof. W. DE SITTER.

(Communicated in the meeting of 1917, June 30).

1. In order to make possible an entirely relative conception of inertia, EINSTEIN¹⁾ has replaced the original field equations of his theory by the equations

$$G_{\mu\nu} - \frac{1}{2} g_{\mu\nu} \lambda = -\kappa T_{\mu\nu} + \frac{1}{2} \kappa g_{\mu\nu} T \quad . \quad . \quad . \quad (1)$$

In my last paper²⁾ I have pointed out two different systems of $g_{\mu\nu}$ which satisfy these equations. The system *A* is EINSTEIN'S, in which the whole of space is filled with matter of the average density ϱ_0 . In a stationary state, and if all matter is at rest without any stresses or pressure, then we have $T'_{\mu\nu} = 0$ with the exception of $T'_{44} = g_{44} \varrho_0$. In the system *B* this “world-matter” does not exist: we have $\varrho_0 = 0$ and consequently all $T'_{\mu\nu} = 0$. The line element in the two systems was there found to be

$$ds^2 = -R^2 \{ d\chi^2 + \sin^2 \chi [d\psi^2 + \sin^2 \psi d\vartheta^2] \} + c^2 dt^2, \quad . \quad . \quad (2A)$$

$$ds^2 = -R^2 \{ d\omega^2 + \sin^2 \omega [d\chi^2 + \sin^2 \chi (d\psi^2 + \sin^2 \psi d\vartheta^2)] \}. \quad (2B)$$

In the system *A* we have

$$\lambda = \frac{1}{R^2}, \quad \kappa \varrho_0 = 2\lambda, \quad . \quad . \quad . \quad (3A)$$

and in *B*:

$$\lambda = \frac{3}{R^2}, \quad \varrho_0 = 0. \quad . \quad . \quad . \quad (3B)$$

In the system *A* χ, ψ, ϑ are real angles; in *B* ψ and ϑ are also real, but ω and χ are imaginary. If, however, we put

$$\begin{aligned} \sin \omega \sin \chi &= \sin \zeta, & r &= R\zeta, \\ \tan \omega \cos \chi &= \tan i\eta, & t &= R\eta. \end{aligned}$$

¹⁾ A. EINSTEIN, *Kosmologische Betrachtungen zur Allgemeinen Relativitätstheorie*, Sitzungsber., Berlin 1917 Febr. 8, p. 142.

²⁾ W. DE SITTER, *On the relativity of inertia*, these Proceedings, 1917 March 31, vol. XIX, p. 1217.

In the footnote to page 1220 of that paper it is stated that the four-dimensional world of the system *B* can be represented as a hyperboloid of two sheets in a space of five dimensions, which is projected on a euclidean space of four dimensions by a “stereographic projection”. This is erroneous. The hyperboloid has only *one* sheet. Its projection fills only part of the euclidean space of four dimensions; the part outside the limiting hyperboloid $1 + \sigma h^2 = 0$ (which is called (*a*) in the quoted footnote) is the projection of the conjugated hyperboloid (which is of two sheets).

where $i = \sqrt{-1}$, then ξ and η are real and (2B) becomes:

$$ds^2 = - dr^2 - R^2 \sin^2 \frac{r}{R} [d\psi^2 + \sin^2 \psi d\vartheta^2] + \cos^2 \frac{r}{R} c^2 dt^2. \quad (4B)$$

If in A we also take $r = R \chi$, then (2A) becomes

$$ds^2 = - dr^2 - R^2 \sin^2 \frac{r}{R} [d\psi^2 + \sin^2 \psi d\vartheta^2] + c^2 dt^2. \quad (4A)$$

The two systems A and B now differ only in g_{44} . For the sake of comparison we add the system C, with

$$\lambda = 0, \quad \rho_0 = 0. \quad (3C)$$

in which the line-element is

$$ds^2 = - dr^2 - r^2 [d\psi^2 + \sin^2 \psi d\vartheta^2] + c^2 dt^2. \quad (4C)$$

Both A and B become identical with C for $R = \infty$.

If in A the origin of coordinates is displaced to a point $\chi_1, \psi_1, \vartheta_1$, and in B to a time-space point $\omega_1, \chi_1, \psi_1, \vartheta_1$, then the line-element conserves the forms (2A) and (2B) respectively. These can then again by the same transformations be altered to (4A) and (4B). In A the variable t , which takes no part in the transformation, remains of course the same. In B on the other hand the new variable t after the transformation is generally not the same as before

I will put, for both systems A and B

$$\chi = \frac{r}{R}$$

In the system B this χ is not the same as in (2B), but it is the angle which was called ξ above. I will continue to use r as an independent variable, and not χ .

2. In the theory of general relativity there is no essential difference between inertia and gravitation. It will, however, be convenient to continue to make this difference. A field in which the line-element can be brought in one of the forms (4A), (4B) or (4C) with the corresponding condition (3A), (3B), or (3C), will be called a field of pure inertia, without gravitation. If the $g_{\mu\nu}$ deviate from these values we will say that there is gravitation. This is produced by matter, which I call "ordinary" or "gravitating" matter. Its density is ρ_1 . In the systems B and C there is no other matter than this ordinary matter. In the system A the whole of space is filled with matter, which, in the simple case that the line-element is represented by (2A) or (4A) produces no "gravitation", but only "inertia". This matter I have called "world-matter". Its density is ρ_0 . When taken over sufficiently large units of volume

this ρ_0 is a constant. Locally however it may be variable the world-matter can be condensed to bodies of greater density, or it can have a smaller density than the average, or be absent altogether. According to EINSTEIN'S view we must assume that *all* ordinary matter (sun, stars, nebulae etc.) consist of condensed world-matter, and perhaps also that all world-matter is thus condensed.

3. To begin with we will neglect gravitation and consider only the inertial field. The three-dimensional line-element is in the two systems *A* and *B*.

$$d\sigma^2 = dr^2 + R^2 \sin^2 \frac{r}{R} [d\psi^2 + \sin^2 \psi d\vartheta^2].$$

If R^2 is positive and finite, this is the line-element of a three-dimensional space with a constant positive curvature. There are two forms of this, viz: the space, of RIEMANN ¹⁾, or *spherical space*, and the *elliptical space*, which has been investigated by NEWCOMB ²⁾. In the spherical space all "straight" (i.e. geodesic) lines which start from one point, intersect again in another point: the "antipodal point", whose distance from the first point, measured along any of these lines, is πR . In the elliptical space any two straight lines have only one point in common. In both spaces the straight line is closed; in the spherical space its total length is $2\pi R$, in the elliptical space it is πR . In the spherical space the largest possible distance between two points is πR , in the elliptical space $\frac{1}{2}\pi R$. Both spaces are finite, though unlimited. The volume of the whole of spherical space is $2\pi^2 R^3$, of elliptical space $\pi^2 R^3$. For values of r which are small compared with R , the two spaces differ only inappreciably from the euclidean space.

The existence of the antipodal point, where all rays of light starting from a point again intersect, and where also, as will be shown below, the gravitational action of a material point (however small its mass may be) becomes infinite, certainly is a drawback of the spherical space, and it will be preferable to assume the true physical space to be elliptical.

The elliptical space can be projected on euclidean space by the transformation

$$r = R \tan \chi \quad (5)$$

The line-element in the systems *A* and *B* then becomes

¹⁾ *Ueber die Hypothesen welche der Geometrie zu Grunde liegen* (1854).
²⁾ *Elementary theorems relating to geometry of three dimensions and of uniform positive curvature*, CRELLE'S Journal Bd. 88, p. 293 (1877).

$$ds^2 = -\frac{dr^2}{\left(1 + \frac{r^2}{R^2}\right)^2} - \frac{r^2 [d\psi^2 + \sin^2 \psi d\vartheta^2]}{1 + \frac{r^2}{R^2}} + c^2 dt^2. \quad (6A)$$

$$ds^2 = -\frac{dr^2}{\left(1 + \frac{r^2}{R^2}\right)^2} - \frac{r^2 [d\psi^2 + \sin^2 \psi d\vartheta^2]}{1 + \frac{r^2}{R^2}} + \frac{c^2 dt^2}{1 + \frac{r^2}{R^2}}. \quad (6B)$$

For $r = \infty$ in the system A all $g_{\mu\nu}$ become zero, with the exception of g_{44} , which remains 1. In the system B g_{44} also becomes zero.

4. The world-lines of light-vibrations are geodetic lines ($ds = 0$) in the four-dimensional time-space. Their projections on the three-dimensional space are the rays of light. In the system A , with the coordinates r, ψ, ϑ , these light-rays are also geodetic lines of the three-dimensional space, and the velocity of light is constant. In the system B this is not so. The velocity of light in that system is, in the radial direction, $v = c \cos \chi$. It is possible, however, in B to introduce space-coordinates, measured in which the velocity of light shall be constant in the radial direction. If the radius-vector in this new measure is called h , we have

$$\cos \chi dh = dr$$

The integral of this equation is

$$\sinh \frac{h}{R} = \tan \frac{r}{R} \quad (7)$$

In the system A we can, of course, also perform the same transformation. The line-element becomes

$$ds^2 = \frac{-dh^2 - \sinh^2 \frac{h}{R} [d\psi^2 + \sin^2 \psi d\vartheta^2]}{\cosh^2 \frac{h}{R}} + c^2 dt^2 \quad (8A)$$

$$ds^2 = \frac{-dh^2 - \sinh^2 \frac{h}{R} [d\psi^2 + \sin^2 \psi d\vartheta^2] + c^2 dt^2}{\cosh^2 \frac{h}{R}} \quad (8B)$$

The three-dimensional line-element

$$d\sigma^2 = dh^2 + \sinh^2 \frac{h}{R} [d\psi^2 + \sin^2 \psi d\vartheta^2]$$

is that of a space of constant negative curvature: the *hyperbolic space* or space of LOBATSCHÉWSKY. When described in the coordinates of this space, the rays of light in the system B are straight (i.e. geodetic) lines, and the velocity of light is constant in all directions,

although the system of reference was determined by the condition that it should be constant in the radial direction.

In this system of reference also all g_{ν} are zero at infinity in the system B , and in A all g_{ν} excepting g_{44} , which remains 1.

To $h = \infty$ corresponds $r = \frac{1}{2} \pi R$. The whole of elliptical space is therefore by the transformation (7) projected on the whole of hyperbolic space. For values of r exceeding $\frac{1}{2} \pi R$, h becomes negative. Now a point $(-h, \psi, \vartheta)$ is the same as $(h, \pi - \psi, \pi + \vartheta)$. The projection of the spherical space therefore fills the hyperbolic space twice. The same thing is true of the projection, by (5), of the elliptical and spherical spaces on the euclidian space.

5. Let the sun be placed in the origin of coordinates, and let the distance from the sun to the earth be a . We still neglect all gravitation.

In the system A the rays of light are straight lines, when described in the coordinates r, ψ, ϑ , i. e. in the elliptical or spherical space.

In the system B the same is true for the coordinates h, ψ, ϑ (hyperbolic space).

In the system A , consequently to triangles formed by rays of light, the ordinary formulas of spherical trigonometry are applicable. The parallax p of a star whose distance from the sun is r , is thus given by the formula

$$\tan p = \sin \frac{a}{R} \cot \frac{r}{R},$$

The square of a/R being negligible, we can write this

$$p = \frac{a}{R} \cot \frac{r}{R} = \frac{a}{r} \dots \dots \dots (9A)$$

In the system B we have similarly, in the coordinates h, ψ, ϑ :

$$\tan p = \sinh \frac{a}{R} \coth \frac{h}{R},$$

or

$$p = \frac{a}{R} \cot h \frac{h}{R} = \frac{a}{R \sin \chi} = \frac{a}{r} \sqrt{1 + \frac{r^2}{R^2}} \dots \dots (9B)$$

In the system A we have consequently $p = 0$ for $r = \frac{1}{2} \pi R$, i. e. for the largest distance which is possible in the elliptical space. If we admitted still larger distances, which are only possible in the spherical space, then p would become negative, and for $r = \pi R$ we should find $p = -90^\circ$.

In the system B p has a minimum value

$$p_0 = \frac{a}{R},$$

which it reaches for $h = \infty$, i.e. $r = \frac{1}{2}\pi R$. For values of r exceeding this distance p increases again, and for $r = \pi R$ we should find $p = +90^\circ$.

Already in 1900 SCHWARZSCHILD¹⁾ gave a discussion of the possible curvature of space, starting from the formulae (9A) and (9B). For the system B we can from the observed parallaxes²⁾ derive a lower limit for R . SCHWARZSCHILD finds $R > 4.10^6$ astronomical units. In the system A the measured parallaxes cannot give a limit for R .

In both systems we can, of course, derive such a limit from distances which have been determined, or estimated, otherwise than from the measured parallaxes. These distances must, in the elliptical space, be smaller than $\frac{1}{2}\pi R$. This undoubtedly leads to a much higher limit, of the order of 10^{10} or more.

6 The straight line being closed, we should, at the point of the heavens 180° from the sun, see an image of the back side of the sun. This not being the case, practically all the light must be absorbed on the long "voyage round the universe". SCHWARZSCHILD estimates that an absorption of 40 magnitudes would be sufficient³⁾. If we adopt the result found by SHAPLEY⁴⁾, viz. that the absorption in intergalactic space is smaller than $0^m.01$ in a distance of 1000 parsecs, then for an absorption of 40 mags we need a distance of 7.10^{11} astronomical units. In the elliptical space we have thus $R > \frac{1}{4} \cdot 10^{12}$.

In the system A we can suppose that this absorption is produced

¹⁾ *Ueber das zulässige Krümmungsmaass des Raumes*, Vierteljahrsschrift der Astron. Gesellschaft, Bd. 35 p. 337.

²⁾ The meaning is of course actually measured parallaxes, not parallaxes derived by the formula $p = a/r$ from a distance which is determined from other sources (comparison of radial and transversal velocity, absolute magnitude, etc.). SCHWARZSCHILD assumes that there are certainly stars having a parallax of $0''05$. All parallaxes measured since then are *relative* parallaxes, and consequently we must at the present time still use the same limit.

³⁾ It might be argued that we should not see the back of the actual sun but of the sun as it was when the light left it. We could thus do without absorption, if the time taken by light to traverse the distance πR exceeded the age of the sun. With any reasonable estimate of this age, we should thus be led to still larger values of R .

⁴⁾ Contributions from the Mount Wilson Solar Observatory Nos. 115–117.

by the world-matter. It is about $\frac{1}{100}$ of the absorption which KING¹⁾ used in his calculation of the density of matter in interstellar space. The density of the world-matter would thus be about $\frac{1}{100}$ of the density found by KING, or $\rho_0 = \frac{2}{3} \cdot 10^{-14}$ in astronomical units. The corresponding value of R (see art. 8) is $R = 2 \cdot 10^{10}$. The total absorption in the distance πR would then be only 3.6 magnitudes. To get the required absorption of 40 magnitudes we must increase ρ_0 , and consequently diminish R . We then find $\rho_0 = 2 \cdot 10^{-12}$, $R = 2 \cdot 10^9$. This value of course has practically no weight, as it is very doubtful whether the considerations by which KING derived the density from the coefficient of absorption are applicable to the world-matter.

The whole argument is inapplicable to the system B , since in this system the light requires an infinite time for the "voyage round the world" One half of this time is

$$T = \int_0^{\frac{1}{2}\pi R} \frac{1}{v} dr,$$

and, since $v = c \cos \chi$, we find $T = \infty$.

7. In the system A g_{44} is constant, in B g_{44} diminishes with increasing r . Consequently in B the lines of the spectra of very distant objects must appear displaced towards the red. This displacement by the inertial field is superposed on the displacement produced by the gravitational field of the stars themselves. It is well known that the Helium-stars show a systematic displacement corresponding to a radial velocity of $+4.3$ Km/sec. If we assume that about $\frac{1}{3}$ of this is due to the gravitational field of the stars themselves²⁾, then there remains for the displacement by the inertial field about 3 Km/sec. We should thus have, at the average distance of the Helium stars

$$f = 1 - 2 \cdot 10^{-5} = \cos^2 \frac{r}{R}.$$

If for this average distance we take $r = 3 \cdot 10^7$ (corresponding to a parallax of $0'' 007$ by the formula $p = a/r$), this gives $R = \frac{2}{3} \cdot 10^{10}$. Also for the M -stars, whose average distance is probably the largest after that of the Helium-stars, CAMPBELL³⁾ finds a systematic displacement of the same order. The other stars, whose average dis-

¹⁾ Nature, Vol. 95, p. 701 (Aug. 26, 1915).

²⁾ Cf. DE SITTER, *On EINSTEIN'S theory of gravitation and its astronomical consequences*, Monthly notices, Vol. 76, p. 719.

³⁾ Lick Bulletin, Vol. 6, p. 127.

tances are smaller, also have a much smaller systematic displacement towards the red, which can very well be explained by the gravitational field of the stars themselves.

Lately some radial velocities of nebulae¹⁾ have been observed, which are very large; of the order of 1000 Km/sec. If we take 600 Km/sec., and explain this as a displacement towards the red produced by the inertial field, we should, with the above value of R , find for the distance of these nebulae $r = 4 \cdot 10^8 = 2000$ parsecs. It is probable that the real distance is much larger.²⁾

About a *systematic* displacement towards the red of the spectral lines of nebulae we can, however, as yet say nothing with certainty. If in the future it should be proved that very distant objects have systematically positive apparent radial velocities, this would be an indication that the system B , and not A , would correspond to the truth. If such a systematic displacement of spectral lines should be shown not to exist, this might be interpreted either as pointing to the system A in preference to B , or as indicating a still larger value of R in the system B .

8. In the paper which has already repeatedly been quoted, SCHWARZSCHILD determined the value of R for elliptical space by the condition that space should be large enough to contain the whole of our galactic system, the star-density being taken constant and equal to the value near the sun. This reasoning cannot be applied to the system A , since the field-equations give a relation between M and ρ , which contradicts SCHWARZSCHILD'S condition.

We have

$${}^* \rho_0 = \frac{2}{R^2}.$$

The volume of the elliptical space is $\pi^2 R^3$. The total mass is therefore $\pi^2 R^3 \rho_0$, or

1) N.G.C. 4594	{	PEASE + 1180 km/sec.
		SLIPHER + 1190 "
N.G.C. 1068	{	SLIPHER + 1100 "
		PEASE + 765 "
		MOORE + 910 "

The nebula in Andromeda however appears to have a considerable negative velocity, viz.:

{	WRIGHT - 304 km/sec.
	PEASE - 329 "
	SLIPHER - 300 "

²⁾ EDDINGTON (Monthly Notices, Vol. 77, p. 375) estimates $r > 100000$ parsecs. This, combined with an apparent velocity of + 600 km/sec., would give $R > 3 \cdot 10^{11}$.

$$M = \frac{2\pi^2}{\kappa} \cdot R.$$

If we take for M the mass of our galactic system, which can be estimated ¹⁾ at $\frac{1}{3} \cdot 10^{10}$ (sun = 1), then the last formula gives $R = 41$, or only about $1\frac{1}{2}$ times the distance of Neptune from the sun. This, of course, is absurd. If we use the other formula we can take for ρ_0 the star-density in the immediate neighbourhood of the sun, which we estimate at 80 stars per unit of volume of KAPTEYN (cube of 10 parsecs side), or $\rho_0 = 10^{-17}$ in astronomical units. We then find $R = 9 \cdot 10^{11}$. The total mass then becomes $M = 7 \cdot 10^{19}$, and consequently the galactic system would only represent an entirely negligible portion of the total world-matter.

It appears probable for many different reasons that outside our galactic system there are many more similar systems, whose mutual distances are large compared with their dimensions. If we take for the average mutual distance 10^{10} astronomical units, then an elliptical space with $R = 9 \cdot 10^{11}$ could contain $7 \cdot 10^6$ galactic systems, of which of course only a small number are known to us by direct observation. If, however, they all actually existed, and their average mass were the same as of our own galaxy, then their combined mass would be about $2 \cdot 10^{16}$, and consequently only one three-thousandth part of the world-matter would be condensed to "ordinary" matter. It is very well possible to construct a world in which the whole of the world-matter would, or at least could, be thus condensed. We must then for ρ_0 take the density not within the galactic system, but the average density over a unit of volume which is large compared with the mutual distances of the galactic systems. With the numerical data adopted above, this leads to $R = 5 \cdot 10^{13}$, and there would then be more than a billion galactic systems.

All this of course is very vague and hypothetical. Observation only gives us certainty about the existence of our own galactic system, and probability about some hundreds more. All beyond this is extrapolation.

9. We now come to the case that there is gravitation, which is produced by "ordinary" matter, with the density ρ_1 . I will consider the field produced by a small sphere at the origin of the system of coordinates, which I will call the "sun". Its radius is r .

In the system A the world-matter has thus everywhere the constant density ρ_0 , except for values of r which are smaller than

¹⁾ Communicated by Prof. KAPTEYN.

R, i. e. within the sun. There the density ¹⁾ is $\rho = \rho_0 + \rho_1$. In the system B , we have $\rho = \rho_1$, and this is zero except for $r < R$.

The line-element then has the form

$$ds^2 = -adr^2 - b [d\psi^2 + \sin^2 \psi d\vartheta^2] + fc^2 dt^2,$$

and in a stationary state a, b, f are functions of r only. The equations become somewhat simpler if we introduce

$$l = lg a, \quad m = lg b, \quad n = lg f.$$

If differential coefficients with respect to r are indicated by accents we find

$$G_{11} = m'' + \frac{1}{2} n'' + \frac{1}{2} m' (m' - l') + \frac{1}{4} n' (n' - l'),$$

$$\frac{a}{b} G_{22} = -\frac{a}{b} + \frac{1}{2} m'' + \frac{1}{4} m' (2m' + n' - l'),$$

$$-\frac{a}{f} G_{44} = \frac{1}{2} n'' + \frac{1}{4} n' (2m' + n' - l'),$$

$$G_{33} = \sin^2 \psi G_{22}.$$

In order to write down the equations (1) we must know the values of $T_{\mu\nu}$. If all matter is at rest, and if there is no pressure or stress in it, these are: $T_{44} = g_{44} \rho$, all other $T_{\mu\nu} = 0$. These values I call $T_{\mu\nu}^0$. If we adopt these, then the equations (1) become, after a simple reduction

$$n'' + n' (m' + \frac{1}{2} n' - \frac{1}{2} l') = a (\kappa \rho - 2 \lambda), \quad \dots \quad (10)$$

$$m'' + \frac{1}{2} m' (m' - n' - l') = -a \kappa \rho, \quad \dots \quad (11)$$

$$-\frac{a}{b} + \frac{1}{2} m' (n' + \frac{1}{2} m') = -a \lambda. \quad \dots \quad (12)$$

It is easily verified that these are satisfied if we take $\rho = \rho_0$, and for $g_{\mu\nu}$ we take the values corresponding to one of the forms (4A), (4B), or (4C) of the line-element, with the conditions (3A), (3B), or (3C) respectively. Similarly for (6A), (6B) and (8A), (8B), if the accents in (10), (11), (12) denote differential coefficients with respect to r , or h respectively. Consequently in the field of pure inertia we have $T_{\mu\nu} = T_{\mu\nu}^0$, i. e. by the action of inertia alone there are produced no pressures or stresses in the world-matter.

¹⁾ This, of course, is not strictly in accordance with EINSTEIN's hypothesis, by which the condensation of the world-matter in the sun should be compensated by a rarefying, or entire absence, of it elsewhere. The mass of the sun however is extremely small compared with the total mass in a unit of volume of such extent as must be taken in order to treat the density of the world-matter as constant. Therefore, if we neglect the compensation, the mass present in the unit of volume containing the sun is only *very* little in excess of that present in the other units. In the real physical world such small deviations from perfect homogeneity must always be considered as possible, and they must produce only small differences in the gravitational field.

If however the mass of the sun is not neglected, then a stationary state of equilibrium, with all matter at rest, cannot exist without internal forces within this matter. The $T_{\rho\rho}$ are then different from $T_{\rho\rho}^0$. If the world-matter is considered as a continuous "fluid", then this fluid can only be at rest if there is in it a pressure or stress. If it is considered as consisting of separated material points then these cannot be at rest. The difference $T_{\rho\rho} - T_{\rho\rho}^0$ vanishes with ρ , for if $\rho=0$, both $T_{\rho\rho}$ and $T_{\rho\rho}^0$ are zero. This difference, therefore, is of the form $\epsilon \cdot \rho$, ϵ being of the order of the gravitation produced by the sun. The right-hand-members of the equations (1), and therefore also of (10), (11), (12) require corrections of the order $\kappa \cdot \epsilon \cdot \rho$. If these are neglected, the equations are no longer exact.

10. The mass of the sun being small, the values of α, b, f will not differ much from those of the inertial field. We can then, in the system A , and for the coordinates r, ψ, ϑ , put

$$a = 1 + \alpha \quad , \quad b = R^2 \sin^2 \chi (1 + \beta) \quad , \quad f = 1 + \gamma,$$

and in a first approximation we can neglect the squares and products of α, β, γ . The equations then became:

$$\gamma'' + \frac{2}{R} \gamma' \cot \chi = a \kappa \rho_1, \quad \dots \dots \dots (13)$$

$$\beta'' + \frac{\cot \chi}{R} (2\beta' - \alpha' - \gamma') + \frac{2\alpha}{R^2} = -a \kappa \rho_1 \quad \dots \dots (14)$$

$$\beta \operatorname{cosec}^2 \chi - a \cot^2 \chi + (\beta' + \gamma') \frac{\cot \chi}{R} = 0. \quad \dots \dots (15)$$

From (13) we find, remembering that the accents denote differentiations with respect to $r = R \cdot \chi$.

$$\gamma' \sin^2 \chi = \int_0^r a \kappa \rho_1 \sin^2 \chi dr$$

Outside the sun we have $\rho_1 = 0$. Thus if we put

$$a = R^2 \int_0^R a \kappa \rho_1 \sin^2 \chi dr$$

then outside the sun

$$\gamma' = \frac{a}{R^2 \sin^2 \chi},$$

from which

$$\gamma = -\frac{a}{R} \cot \chi = -\frac{a}{r} \quad \dots \dots \dots (16)$$

For $r = \frac{1}{2} \pi R$, i.e. for the largest distance which is possible in the elliptical space, we have thus $\gamma = 0$. For still larger distances, which are only possible in the spherical space, γ becomes positive, and finally for $r = \pi R$ we should have $g_{44} = \infty$, however small the mass of the sun may be, as has already been remarked above (art. 3).

If now from (14) and (15) we endeavour to determine α and β , we are met by difficulties. It appears that the equations (13), (14), (15) are contradictory to each other. If we make the combination

$$(13) + (14) - 2 \cdot (15) = R \tan \chi \frac{d(15)}{dr}$$

we find

$$\gamma' \tan \chi = 0, \dots \dots \dots (17)$$

which is absurd. If the equations were exact, they should, in consequence of the invariance, be dependent on each other. They are however not exact, since on the right-hand-sides terms of the order of $\epsilon \cdot \kappa \rho$ have been neglected, ϵ being of the order of α, β, γ . In the world-matter we have¹⁾ $\kappa \rho = \kappa \rho_0 = 2\lambda$, and these corrections can only be neglected if λ is also of the order ϵ . This has not been assumed in the equations (13), (14), (15). If we wish to assume it, then we must also develop in powers of λ . We can then use the coordinates r, ψ, ϑ . We put thus

$$a = 1 + \alpha, \quad b = r^2(1 + \beta), \quad f = 1 + \gamma.$$

The equations, in which now the accents denote differentiations with respect to r , then become, to the first order

$$\begin{aligned} \gamma'' + \frac{2}{r} \gamma' &= \kappa \rho_1, \\ \beta'' + \frac{2}{r} \beta' - \frac{1}{r} (\alpha' + \gamma') &= -\kappa \rho_1 - 2\lambda, \\ \beta - \alpha + r (\beta' + \gamma') &= -\lambda r^2, \end{aligned}$$

which are easily verified to be dependent on each other.

We can thus add an arbitrary condition. If we take e.g.

$$a = 2\beta,$$

then we find, to the first order, outside the sun

$$\alpha = -2\lambda r^2 + \frac{a}{r}, \quad \beta = -\lambda r^2 + \frac{1}{2} \frac{a}{r}, \quad \gamma = -\frac{a}{r},$$

¹⁾ Of course, if beside the world matter there is also "ordinary matter", i. e. if the density of the world matter is not constant, this relation is also only approximatively true, and requires a correction of the order λ, ϵ . (See also art. 11).

where $a = \int_0^R \kappa \varrho_1 r^2 dr$. If a is neglected these are the terms of the first order in the development of (6 A) in powers of $\lambda = 1/R^2$.

11. Consider again the equations (10), (11), (12). If these were exact, they would be dependent on each other. They are, however, not exact, and consequently they are contradictory. If we make the combination:

$$2 \cdot \frac{d(12)}{dr} + 2 [m' - l'] (12) - [m' + n'] \cdot (11) - m' \cdot (10),$$

we find¹⁾

$$0 = n' a \kappa \varrho. \quad (18)$$

Consequently the equations are dependent on each other, i.e. a stationary equilibrium, all matter being at rest without internal forces, is only possible, when either $\varrho = 0$ or $n' = 0$, i.e. $g_{44} = \text{constant}$. In the system A ϱ is never zero, since outside the sun $\varrho = \varrho_0$. A stationary equilibrium is then only possible if g_{44} is constant, i.e. if no "ordinary" matter exists, for all ordinary matter will, by the mechanism of the equation (10) or (13) produce a term γ in g_{44} which is not constant. If ordinary or gravitating matter does exist then not only in those portions of space which are occupied by it, but throughout the whole of the world-matter $T_{\mu\nu}$ will differ from $T_{\mu\nu}^0$. We can e.g. consider the world-matter as an adiabatic incompressible fluid. If this is supposed to be at rest, we have

$$T_u = -g_u p, \quad T_{44} = g_{44} \varrho_0,$$

where p is the pressure in the world-matter. I then find

$$p = \varrho_0 \left(\frac{1}{\sqrt{f}} - 1 \right)$$

and, to the first order, and for the coordinates r, ψ, ϑ :

$$\alpha = \beta = -\gamma = a \cdot \left(\frac{\cos 2\chi}{R \sin \chi} + \frac{1}{R} \right),$$

$$\kappa \varrho_0 = 2\lambda - 3 \frac{a}{R^3} = 2\lambda \left(1 - \frac{3}{2} \frac{a}{R} \right).$$

For our sun a/R is of the order of 10^{-20} .

For $\chi = \frac{1}{2} \pi$ we have $\gamma = 0$, and for $\chi = \pi$ we should find

¹⁾ It is easily verified that (18) becomes identical with (17) if all terms of higher orders than the first are neglected.

$\gamma = \infty$, as in the approximate solution (16), in which p was neglected.

For the planetary motion we must go to the second order. I find a motion of the perihelion amounting to

$$\delta\tilde{\omega} = -\frac{3}{2} \lambda a^2 nt. \quad \dots \quad (19)$$

which is of course entirely negligible on account of the smallness of λa^2 . In my last paper¹⁾ it was stated that there is no motion of the perihelion. In that paper the values $T_{\mu,0}$ were used, i.e. the pressure p was neglected. The motion (19) can thus be said to be produced by the pressure of the world-matter on the planet. It will disappear if we suppose that in the immediate neighbourhood of the sun the world-matter is absent!

12. In the system B outside the sun we have $\rho = 0$, and the equations are dependent on each other and can be integrated.

Within the sun $n'axv_1$ must be of the second order, and consequently n' must be of the first order. If we put

$$f = \cos^2 \chi (1 + \gamma),$$

then $n' = -\frac{2}{R} \tan \chi + \frac{\gamma'}{1+\gamma}$, thus $\frac{\tan \chi}{R}$ must be of the first order.

Since $\chi = r/R$ we find that $1/R^2$ must be of the first order, as in system A .

Developing f in powers of $1/R$ we find, to the first order

$$f = 1 - \frac{r^2}{R^2} + \gamma,$$

In the first approximation we find for γ the same value as in the systems A and C , viz: $\gamma = -a/r$. Here however we have also the term $-r^2/R^2$. Thus classical mechanics according to NEWTON'S law can only be used as a first approximation if this term, and consequently also $\lambda = r^3/R^2$ is of the *second* order. Investigating the effect of this term on planetary motion, we find a motion of the perihelion²⁾ amounting to

$$\delta\tilde{\omega} = \frac{3a^3}{2a R^2} nt.$$

¹⁾ These Proceedings, Vol. XIX, page 1224.

²⁾ In my last paper (these Proceedings Vol. XIX, p. 1224) I found

$$\delta\tilde{\omega} = \frac{3a^3}{4a R^2} nt - \frac{cnt^2}{2R^2}.$$

The difference is due to the use of a different system of reference, with a different time and different radius-vector, in the two cases, the formulas for the transformation of the space-variables (especially the radius-vector) from one system to the other depending on the time.

From the condition that this shall for the earth not exceeds ay 2" per century we find

$$R > 10^8.$$

Then $1/R^2 < 10^{-16}$ is actually of the second order compared with $\alpha = 25 \cdot 10^{-8}$. This limit of R is still considerably lower than the value which was found above from the displacement of the spectral lines. For the planetary motion — and generally for all mechanical problems which do not involve very large values of r — we can therefore in both systems A and B neglect the effect of λ entirely.

Chemistry. — “Investigations into PASTEUR’S Principle of the Connection between Molecular and Crystallonomical Dissymmetry: III. Racemic and Optically Active Complex Salts of Trivalent Rhodium. By Prof. Dr. F. M. JAEGER.

(Communicated in the meeting of June 30, 1917.)

§ 1. In immediate continuation of previous investigations concerning the complex *tri-ethylenediamine*-salts of trivalent *cobaltum*¹⁾, the results of the study of the corresponding complex salts of trivalent *rhodium* are communicated in the present paper, namely in so far as the data already obtained possibly allow a more general discussion of some problems connected with this subject.

For the preparation of the salts investigated, we started from pure *rhodium-trichloride*. Originally WERNER’S method²⁾ was followed, who transformed the *chloride* into *sodium-rhodium-chloride*: $Na_3\{Rho Cl_3\} + 12 H_2O$, which afterwards was dissolved in gently heated *ethylenediamine-hydrate*. It appeared, however, that the troublesome purification of the complex salt from the adhering *sodiumchloride* may be prevented, when the *rhodium-trichloride* itself is dissolved immediately into the base mentioned, on gently heating it with the last. If some few precautions be taken, the required substance is obtained from an aqueous solution immediately in very beautiful, colourless crystals. It must, moreover, be remarked in this connection, that a miscibility between the complex *rhodium-salt* and *sodium-chloride* in the solid state, as supposed by the author mentioned because of an eventually existing isomorphism of two crystal-species of cubic symmetry, does in reality *not* occur. No such isomorphism is present here, as the complex *rhodium-salt* has *ditrigonal*, the *sodium-chloride* on the contrary *cubic* symmetry. Probably only occlusion or mechanical removal of the one salt by the other may be the cause of the phenomenon observed. Moreover, it must appear remarkable, that almost all data concerning the amount of water of crystallisation present in these *rhodium-salts*, differ exactly by the number of *half* a molecule H_2O in comparison with those of the corresponding *cobalti-salts*. As the last mentioned salts are, however,

¹⁾ F. M. JAEGER, *Proceed. Kon. Akad. Amsterdam*, **17**. 1217; **18**. 49. (1915); *Zeits. f. Kryst. u. Miner.* **55**. 209. (1915).

²⁾ A. WERNER *Ber. d. d. Chem. Ges.* **45**. 1228. (1912).

in by far the most cases, *directly isomorphous* with the *rhodium-salts* of corresponding constitution, suspicion arises that the content of crystallisation-water is really the same in the two series of complex salts. The divergence mentioned would then be explained by a systematical error in the rather difficult determinations of the element *rhodium* in these cases.

§ 2. In the following pages the result of the direct measurements of the *racemic* salts and of the *optically active* components are in the first place dealt with, and the data concerning the rotation-dispersion of these perfectly colourless salts are subsequently communicated. Some considerations of a more general character, regarding the stereometrical configuration of these complex substances will then be inserted.

The results of the study of some other compounds of this series will be published later-on.

SODIUM-RHODIUM-CHLORIDE.



This salt may be prepared by dissolving the calculated quantity of *rhodium-trichloride* in a concentrated solution of *sodium-chloride*, evaporating the solution on the water-bath, and by crystallisation at room-temperature. The solution of the black-red, often voluminous

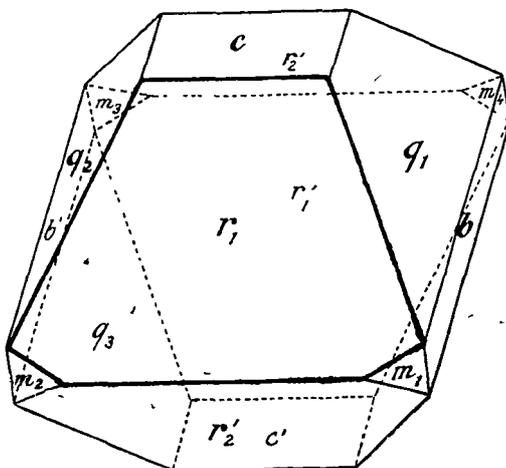


Fig. .1

Sodium-Rhodium-Chloride.

and apparently octahedral crystals, has a beautiful crimson colour. The crystals are hygroscopical, and they soon become dull, when softly heated.

Monoclinic-prismatic.

$$a : b : c = 1,2034 : 1 : 1,4576 ;$$

$$\beta = 57^\circ 9\frac{1}{2}'$$

Forms observed: $c = \{001\}$, small but lustrous; ordinarily the facet $(00\bar{1})$ appears much broader than (001) ; $r_1 = \{101\}$, $r_2 = \{\bar{1}01\}$, and $q = \{011\}$, commonly equally well developed,

Angles.	Observed	Calculated:
$c : r = (001) : (101) =^*$	71°32'	—
$r_1 : r_2 = (101) : (10\bar{1}) =^*$	63 8	—
$c : q = (001) : (011) =^*$	50 46	—
$c : r = (001) : (101) =$	45 30	45°20'
$q : q = (011) : (01\bar{1}) =$	78 28	78 28
$b : q = (010) : (011) =$	39 20	39 14
$r : q = (101) : (011) =$	63 47	63 41
$r : q = (\bar{1}01) : (011) =$	77 0	77 4
$c : s = (001) : (021) =$	67 56	67 47½
$b : m = (010) : (430) =$	52 40	52 49
$m : m = (430) : (4\bar{3}0) =$	74 40	74 22

The crystals are cleavable parallel to {001}.

§ 3. RACEMIC TRI-ETHYLENEDIAMINE-RHODIUM-CHLORIDE.
 $\{Rho (Eine)_3\} Cl_3 + 3H_2O.$

The salt was prepared from the corresponding *iodide* in solution, by treating it with freshly precipitated *silver-chloride*. The substance crystallises in big, rectangular-shaped, prismatic individuals, or in smaller, strongly refracting crystals, which often possess uneven faces yielding multiple reflexes.

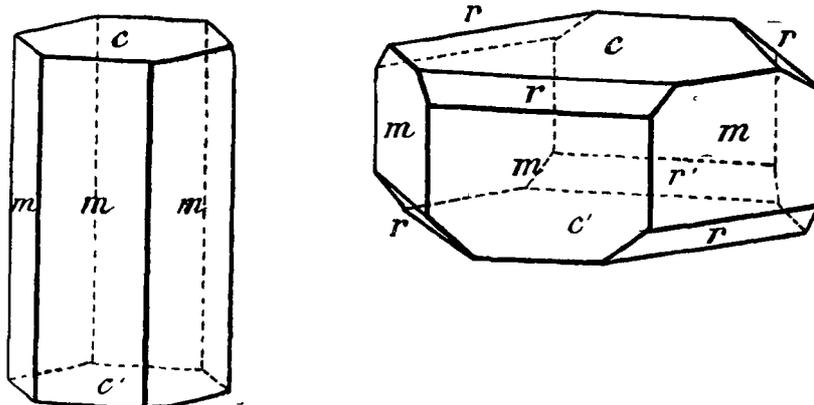


Fig. 2.

Racemic Tri-ethylenediamine-Rhodium-Chloride.

Ditrigonal-scalenohedral.

$$a : c = 1 : 0,6730.$$

Forms Observed: $c = \{0001\}$, predominant, often rough, but lustrous; $m = \{10\bar{1}0\}$, well developed, always present, and lustrous; $r = \{10\bar{1}1\}$, narrow, often absent; $x = \{1\bar{1}01\}$, smaller than r , and only rarely present. The crystals are plates parallel to {0001}, or prisms parallel to the c -axis.

The substance is perfectly isomorphous with the corresponding

Co-salt¹⁾); WERNER's supposition of their being cubic and isomorphous with *NaCl*, is erroneous, as has been already said.

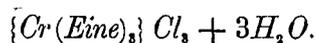
Angles:	Observed:	Calculated:
$c : r = (0001) : (10\bar{1}1) =^*$	37° 51'	—
$m : r = (10\bar{1}0) : (1011) =$	52 9	52° 9'
$m : m = (10\bar{1}0) : (01\bar{1}0) =$	60 0	60 0
$c : x = (0001) : (1\bar{1}01) =$	38 1	37 51

No distinct cleavability was found.

The crystals are uniaxial, their birefringence is negative. The interference-image is sometimes slightly disturbed, as was observed also in the case of the *Co*-salt.

The corresponding *bromide* was completely isomorphous with the *chloride* here described.

§ 4. RACEMIC TRI-ETHYLENEDIAMINE-CHROMI-CHLORIDE.



Beautiful, orange, very transparent and lustrous prismatic crystals, which commonly only exhibit the forms *c* and *m*. Occasionally also hexagonal plates occur parallel to $\{0001\}$; once a form $r = \{10\bar{1}1\}$ was observed as a very narrow truncation of the edge $c : m$.

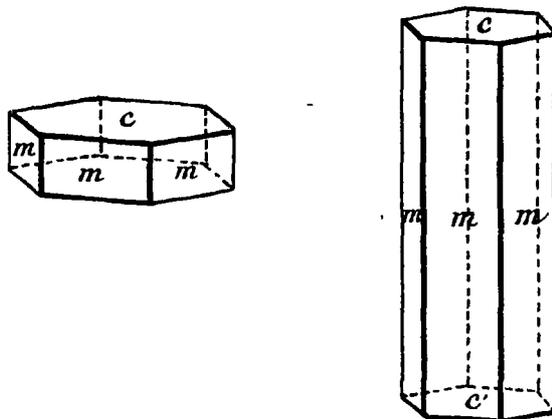


Fig. 3

Racemic Tri-ethylenediamine-chromi-chloride.

Ditrigonal-scalenohedral.

$$a : c = 1 : 0,6930.$$

Forms observed: $c = \{0001\}$, and $m = \{10\bar{1}0\}$, both very lustrous, while sometimes *c*, sometimes however *m* is developed predominantly; $r = \{10\bar{1}1\}$, mostly absent, and in all cases very narrow.

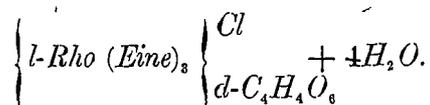
¹⁾ F. M. JAEGER, *Proceed. Kon. Acad. Amsterdam*, 18. 50. (1915).

Angles:	Observed:	Calculated:
$c:r = (0001) : (10\bar{1}1) = *$	$38^\circ 40'$	—
$r:m = (1011) : (10\bar{1}0) =$	$51 \quad 20$	$51^\circ 20'$
$m:m = (10\bar{1}0) : (0110) =$	$60 \quad 0$	$60 \quad 0$

No distinct cleavability was observed.

The crystals show a feeble dichroism: on m they are orange-yellow for vibrations parallel to the c -axis, and lemon-yellow for such as are perpendicular to that direction. Optically uniaxial, occasionally with disturbed interference-image. The character of birefringence is negative as it was in the cases of the *Co*-, and *Rho*-salts.

§ 5. LAEVOGYRATE TRI-ETHYLENEDIAMINE-RHODIUM-
-CHLORO-D-TARTRATE.



Beautiful, rather big colourless and parallelogram-shaped plates or short prisms. They are well developed and possess constant angular values.

Monoclinic, and having apparently *prismatic* symmetry. Of the facets of o and ω commonly only three, e.g. ω_2 , o_2 and o_4 , are present.

$$a:b:c = 0,9158:1:0,6965;$$

$$\beta = 72^\circ 35\frac{2}{3}'.$$

Forms observed: $m = \{110\}$, well developed, commonly predominant with two parallel faces and having high lustre; $c = \{001\}$, large and also perfectly reflecting; $\omega = \{\bar{1}11\}$, larger than $o = \{111\}$, both rather dull and giving weak reflections. The crystals are plates parallel to $\{110\}$, with a slight elongation in the direction of the c -axis.

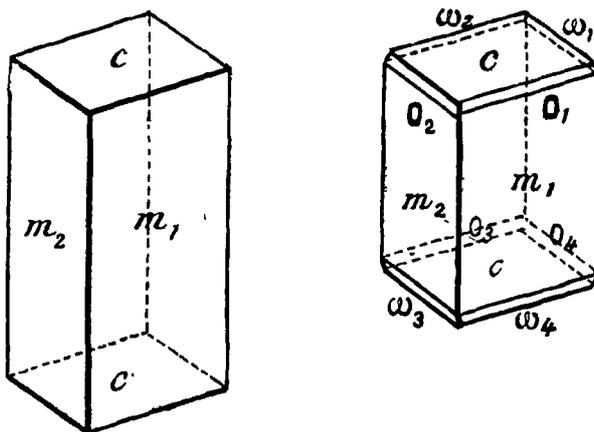


Fig. 4.

l-Tri-ethylenediamine-rhodium-chloro-d-tartrates.

Angles:	Observed:	Calculated:
$c : m = (001) : (110) = *$	76° 59'	—
$m : m = (110) : (\bar{1}\bar{1}0) = *$	82 18	—
$c : o = (001) : (\bar{1}\bar{1}1) = *$	51 53	—
$m : o = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}0) =$	51 8	51° 8'
$c : o = (001) : (111) =$	38 40	38 43
$m : o = (110) : (111) =$	38 19	38 16
$m : \bar{o} = (\bar{1}\bar{1}1) : (110) =$	86° circa	85 40

Cleavage parallel to c and m .

On $\{110\}$ the extinction-angle is small, only 5°—10° with respect to the edge $m : m$. The plane of the optical axes is $\{010\}$.

§ 6. LAEVOGYRATE TRI-ETHYLENEDIAMINE-RHODIUM-BROMIDE.



The substance was prepared from pure laevogyrate *iodide* by heating its solution with freshly precipitated *silver-bromide*. After filtration the solution was concentrated on the water-bath, and crystallised at room-temperature. Very big, hexagonal thick plates are deposited from the colourless solution, which are strongly refracting and give extremely sharp reflexes.

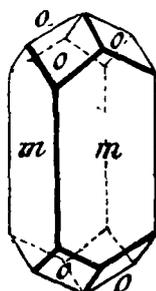


Fig. 5.

Laevogyrate Triethylene-diamine-
Rhodium-Bromide.

Ditetragonal, apparently *bipyramidal*, and completely isomorphous with the corresponding *cobalti-salt*.

$$a : c = 1 : 0,8330.$$

Forms observed $m = \{110\}$, ordinarily with two predominant parallel faces, very lustrous, but often uneven; $o = \{101\}$, splendidly reflecting and with well-developed faces. The shape of

the crystals is that of thick plates parallel to faces of the prism; elongation parallel to the c -axis. No *indication of hemihedrism* was observed in any case, just as was stated in the case of the corresponding *cobalti-salts*.

Angles:	Observed:	Calculated:
$o : o = (101) : (011) = *$	53°49'	—
$o : m = (101) : (110) =$	63 5½'	63°5½'
$m : m = (110) : (\bar{1}\bar{1}0) =$	90 0	90 0

No distinct cleavability was observed.

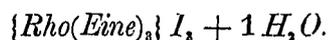
The crystals are optically uniaxial; a plate perpendicular to the

c-axis shows in convergent polarised light the axial image characteristic of uniaxial crystals *without circular polarisation*. The character of the birefringence is negative.

§ 7.

Rotation-Dispersion of Laevogyrate Tri-ethylenediamine-Rhodium-Bromide.		
The solution contained 7,310 grams of the anhydrous salt in 100 grams of the solution. The length of the tube applied was 20 c.m.		
Wave-length in ÅNGSTRÖM-Units	Specific Rotation $[\alpha]$ in Degrees	Molecular rotation $[M]$ in Degrees.
6780	- 46,66	- 2440°
6640	- 48,0	- 2510
6520	- 49,66	- 2597
6380	- 53,08	- 2776
6260	- 56,57	- 2960
6140	- 59,0	- 3086
6030	- 62,66	- 3277
5890	- 66,1	- 3457
7500	- 71,07	- 3717
5510	- 76,40	- 3996
5340	- 81,33	- 4253
5180	- 85,30	- 4461
5100	- 87,62	- 4583
4860	- 91,93	- 4808
4710	- 94,60	- 4947
4310	- 97,20	- 5083
4150	- 97,34	- 5091

§ 8. RACEMIC TRI-ETHYLENEDIAMINE-RHODIUM-IODIDE.



Very small, colourless, strongly refracting and well-developed crystals, which are completely isomorphous with the corresponding *cobalti-salt*¹⁾. In the last case, however, the symbol {111} was

¹⁾ F. M. JAEGER, *Proceed.* 18. 62. (1915).

attributed to the form $w = \{112\}$, so that the value of $b : c$ in the former case is analogous to $b : 2c'$ in the present.

Rhombic-bipyramidal.

$$a \cdot b \cdot c = 0,8541 : 1 : 0,8632.$$

Forms observed: $o = \{111\}$, predominant and very lustrous; $c = \{001\}$, also well-developed and giving splendid reflexes; $w = \{221\}$, very narrow, but exactly measurable; $q = \{041\}$, small, very lustrous, and often absent.

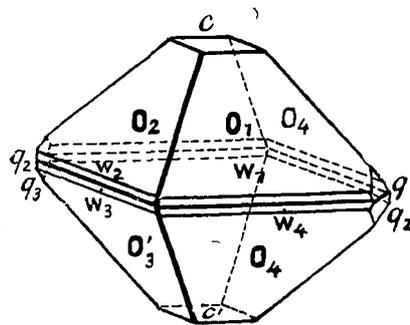


Fig. 6.

Racemic

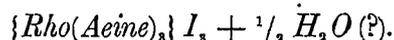
Tri-ethylenediamine Rhodium Iodide

Angles:	Observed:	Calculated:
$c : o = (001) \cdot (111) =^*$	$53^\circ 3'$	—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =^*$	$74 51$	—
$o : w = (111) : (221) =$	$16 11$	$16^\circ 20'$
$w : w = (221) : (2\bar{2}\bar{1}) =$	$41 33$	$41 14$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$73 55$	$73 54$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$62 43$	$62 43$
$o : q = (111) : (041) =$	$47 59$	$48 16$
$q : w = (041) : (\bar{2}\bar{2}\bar{1}) =$	$60 52$	$60 56$
$w : o = (\bar{2}\bar{2}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	$70 52$	$70 48$

No distinct cleavage was found.

When considered as a rhombic, but pseudo-tetragonal crystal, c becomes $\{100\}$, and $a : b : c = 1,0106 : 1 : 1,1708$.

§ 9. LAEVOGYRATE TRI-ETHYLENEDIAMINE-RHODIUM-IODIDE.



Small, colourless and only feebly reflecting crystals, which are however well measurable and possess constant angular values. Occasionally very lustrous, nicely shaped and regularly developed little crystals were met with.

Rhombic; perhaps *bisphenoidical*, although the geometrical appearance is completely holohedral.

$$a : b : c = 0,8064 : 1 : 0,7380.$$

Forms observed: $c = \{001\}$, well-developed and lustrous; $o = \{121\}$, and $\omega = \{1\bar{2}1\}$, almost equally large, and only very rarely ω somewhat broader than o . This different size of o and ω is the only indication of the substance eventually being bisphenoidical. Further:

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$r = \{101\}$, smaller than $s = \{201\}$ and $a = \{100\}$; $t = \{021\}$ and $w = \{041\}$, both equally large and greater than $b = \{010\}$; $q = \{011\}$, commonly absent, but if present, rather large, $m = \{110\}$, absent in almost every case, always small and receding into the background

Undoubtedly the crystals are isomorphous with those of the optically active *cobalti*-salts, whose expected bisphenoidal symmetry did not reveal itself in any distinct way either. The rather appreciable divergence of the values a b of the salts, as well as the differences in shape and combined forms in the two cases, may probably be connected with the eventually existing slight difference in the content of water of crystallisation, mentioned previously.

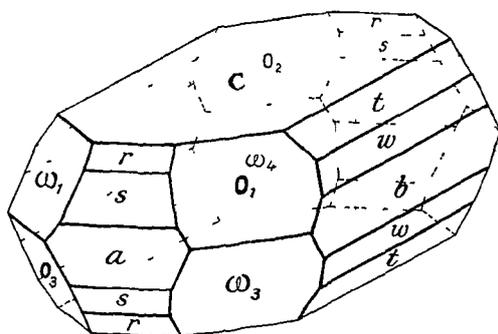


Fig. 7 (1).
Laevogyrate

Tri ethylenediamine Rhodium-Iodide.

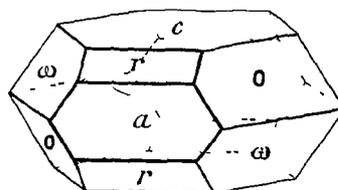


Fig. 7 (2).
Laevogyrate

Tri-ethylenediamine Rhodium Iodide.

Angles:	Observed	Calculated:
$c:t = (001):(021) =^*$	$55^{\circ}53'$	—
$c:o = (001):(121) =^*$	$60^{\circ}4'$	—
$t:w = (021):(041) =$	$15\ 26$	$15^{\circ}24\frac{1}{4}'$
$w:b = (041):(010) =$	$18\ 46$	$18\ 42\frac{3}{4}$
$c:r = (001):(101) =$	$42\ 21$	$42\ 28$
$r:s = (101):(201) =$	$18\ 54$	$18\ 53$
$s:a = (201):(100) =$	$28\ 45$	$28\ 39$
$o:o = (121):(12\bar{1}) =$	$59\ 52$	$59\ 52$
$o\ o = (\bar{1}2\bar{1}):(121) =$	$85\ 10$	$85\ 8$
$a:o = (100):(121) =$	$62\ 45$	$62\ 50$
$b:o = (010):(121) =$	$42\ 40$	$42\ 34$
$t:o = (021):(121) =$	—	$27\ 10\frac{1}{3}$
$w.o = (041):(121) =$	$57\ 40$	$57\ 29\frac{1}{3}$
$b:q = (010):(011) =$	$53\ 26$	$53\ 34$
$o.\omega = (121):(\bar{1}21) =$	$54\ 26$	$54\ 20$

No distinct cleavability could be observed.

The external aspect of the crystals is almost isometrical, with a slight flattening parallel to $\{001\}$, and a distinct elongation parallel to the direction of the direction of the a -axis.

The optical axes are situated in $\{001\}$; the a -axis is first bisectrix.

§ 10.

Rotation-dispersion of laevogyrotory Tri-ethylenediamine-rhodium-iodide.		
The solution investigated contained 4,535 grams anhydrous salt in 100 grams of solution; the length of the tube applied was 20 c.m.		
\circ Wave-length in ÅNGSTRÖM-Units :	Specific rotation [α] in Degrees.	Molecular rotation [M] in Degrees :
6840	— 30,91	— 2051 ^o
6660	— 32,89	— 2183
6520	— 34,98	— 2322
6380	— 37,18	— 2468
6260	— 38,50	— 2555
6140	— 41,14	— 2730
6030	— 44,11	— 2928
5890	— 45,54	— 3023
5800	— 47,08	— 3125
5700	— 49,06	— 3256
5605	— 50,49	— 3351
5510	— 52,36	— 3475
5420	— 54,12	— 3592
5340	— 55,22	— 3665
5260	— 57,20	— 3796
5180	— 58,30	— 3869
5100	— 59,73	— 3964
5020	— 61,05	— 4052
4945	— 61,93	— 4110
4860	— 63,36	— 4205
4780	— 64,46	— 4278
4710	— 65,34	— 4337
4650	— 66,66	— 4424
4560	— 67,32	— 4468
4480	— 67,87	— 4505
4420	— 68,42	— 4541
4310	— 68,53	— 4548
4260	— 68,64	— 4556
4150	— 68,82	— 4567
4060	— 69,10	— 4585
4010	— 69,19	— 4592
3940	— 69,24	— 4596
3880	— (60,5)	— (4016)
3820	— (55,2)	— (3664)
3780	— (51,2)	— (3398)
3740	— (48,7)	— (3232)
3700	— (48,5)	— (3219)

§ 11. RACEMIC TRI-ETHYLENEDIAMINE-RHODIUM-NITRATE.
 $\{Rho(Eine)_3\}(NO_3)_3$.

This compound is always obtained, when a solution of the racemic chloride is mixed with a solution of $AgNO_3$. It crystallises from an aqueous solution in splendid, colourless, and distinctly *hemimorphic* crystals, showing a strongly variable aspect, and often distorted in a most particular way. Some of the forms most often met with are reproduced in fig. 8 *a*, *b*, and *c*. For the purpose of immediate comparison with the corresponding *cobalti*-salt, which is completely isomorphous with it, the heteropolar binary axis of the crystals is also in this case adopted as *a*-axis.

To the well-developed pyramid *o*, which never fails and always gives good reflexes, the symbol $\{111\}$ has been attributed, so that the ratio *c* : *b* is now exactly *half* the corresponding ratio of the *cobalti*-salt studied previously: there the symbol $\{112\}$ was given to the form *o*.

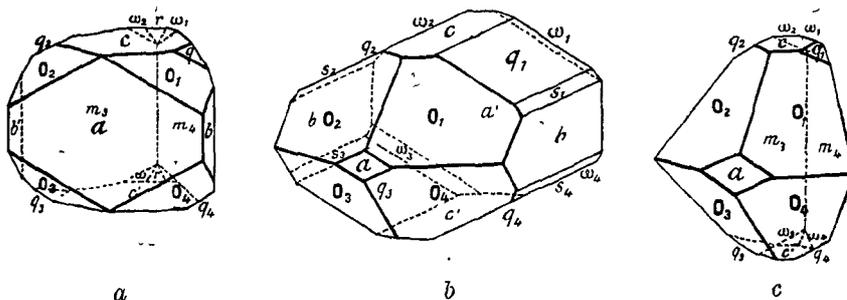


Fig. 8.

Racemic Tri-ethylenediamine-Rhodium-Nitrate.

Rhombic-pyramidal.

$$a : b : c = 0,7874 : 1 : 0,5606.$$

Forms observed: $a = \{100\}$, well-developed, occasionally predominant and always very lustrous; $a' = \{100\}$, mostly absent or extremely narrow, sometimes, however, very large and reflecting perfectly; $o = \{111\}$, large and lustrous; $m = \{120\}$, if present large and lustrous, but occasionally absent; $c = \{001\}$, well-developed and giving very sharp reflexes; $\omega = \{111\}$, never failing, but always much smaller than *o*; $q = \{011\}$, occasionally absent, in most cases, however, large and lustrous; $s = \{021\}$, much narrower than *q*, but giving good images; $r = \{20.01\}$, small and dull, ordinarily absent; $b = \{010\}$, always sharply reflecting, and sometimes equally large as *q* and *c*, but occasionally much smaller or totally absent; $p = \{120\}$, extremely small, only rarely present.

The colourless crystals always exhibit a distinctly hemimorphic shape; the polar axis is the a -axis. The substance possesses a strong tendency to crystallisation, but the various individuals are in general smaller than those of the corresponding *cobalti*-salt.

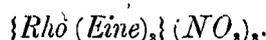
The external aspect is in most cases rather isometrical, but occasionally a slight elongation parallel to the direction of the a -axis could be stated.

Angles:	Observed:	Calculated:
$o:o = (111) : (\bar{1}\bar{1}) = *$	$49^\circ 5\frac{1}{3}'$	—
$a:o = (100) : (111) = *$	$58 9\frac{1}{2}$	—
$o:o = (111) : (1\bar{1}\bar{1}) =$	$95 36$	$95^\circ 38'$
$b:o = (010) : (111) =$	$65 24$	$65 27\frac{1}{2}$
$o:q = (111) : (011) =$	$31 47$	$31 50\frac{1}{2}$
$c:o = (001) : (111) =$	$42 10$	$42 11$
$c:q = (001) : (011) =$	$29 10$	$29 16\frac{1}{2}$
$q:s = (011) : (021) =$	$19 10$	$19 0$
$s:b = (021) : (010) =$	$41 44$	$41 43\frac{1}{2}$
$\omega:q = (\bar{1}\bar{1}1) : (011) =$	$31 50$	$31 50\frac{1}{2}$
$c:\omega = (001) : (\bar{1}\bar{1}1) =$	$42 7$	$42 11$
$m:m = (\bar{1}20) : (\bar{1}20) =$	$115 16$	$115 10$
$a:m = (100) : (\bar{1}20) =$	$122 22\frac{1}{2}$	$122 25$
$c:r = (001) : (\bar{2}0.01) =$	$85 0$	$84 54$
$r:r = (\bar{2}0.01) : (\bar{2}0.01) =$	$9 56$	$10 12$
$o:m = (111) : (\bar{1}20) =$	$85 50$	$85 55$

No distinct cleavage was observed.

On $\{100\}$ the optical extinction is parallel and perpendicular to the c -axis. The plane of the optical axes is $\{010\}$.

§ 12. LAEVOGYRATORY TRI-ETHYLENEDIAMINE-RHODIUM-NITRATE.



This compound was prepared from the laevogyrate *iodide* by means of *silver-nitrate*. It crystallises in beautiful, triangularly-shaped plates, or, in most cases, in crystals of the form reproduced in fig. 9.

The various individuals are distorted in most capricious ways, a fact which to no slight degree opposes their investigation.

Rhombic-bisphenoidical.

$$a : b : c = 0,8642 : 1 : 0,6049.$$

Forms observed: $a = \{100\}$ and $o = \{\bar{1}\bar{1}1\}$, almost equally large; $r = \{101\}$, commonly present with only two faces; $m = \{110\}$,

small but well reflecting; $p = \{120\}$, much smaller than m , and often totally absent. The shape of the crystals is that of plates parallel to $\{100\}$, or to two parallel faces of m . They are completely *isomorphous* with those of the *cobalti*-salt.

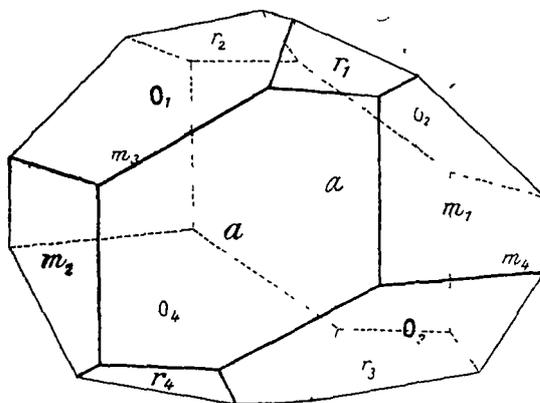


Fig. 9.
Laevogyrate Tri ethylenediamine-Rhodium-Nitrate.

Angles:	Observed:	Calculated:
$a : m = (100) : (110) = *$	$40^{\circ}50'$	—
$a : o = (100) : (\bar{1}\bar{1}\bar{1}) = *$	$59 \ 5$	—
$a : r = (100) : (101) =$	$55 \ 1$	$55^{\circ} \ 1/2'$
$o : r = (\bar{1}\bar{1}\bar{1}) : (101) =$	$26 \ 13$	$26 \ 21\frac{1}{3}$
$m : p = (110) : (120) =$	$19 \ 11$	$19 \ 7$
$o : m = (\bar{1}\bar{1}\bar{1}) : (110) =$	$84 \ 15$	$84 \ 21$
$o : m = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{0}) =$	$47 \ 15$	$47 \ 12\frac{1}{2}$
$o : o = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	$52 \ 46$	$52 \ 42\frac{1}{3}$
$o : p = (\bar{1}\bar{1}\bar{1}) : (120) =$	$82 \ 47$	$82 \ 42\frac{1}{2}$
$a : p = (100) : (120) =$	$59 \ 37$	$59 \ 57$

No distinct cleavability could be found.

The plane of the optical axes is $\{010\}$; in the corner of the image, one optical axis is visible under the microscope, when a plate parallel to m is used.

§ 13.

In the accompanying figure 10 the dispersion-curves of both the last mentioned salts have been reproduced. Their shape is absolutely different from that of the corresponding curves of the optically-active *cobalti*-salts.

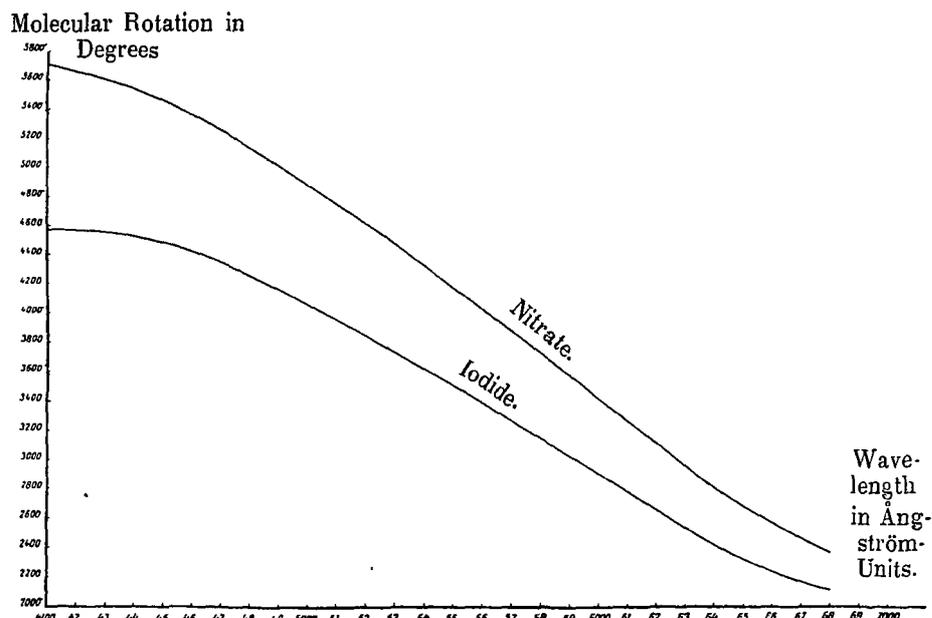


Fig 10. Molecular Rotation-Dispersion of Laevogyrate Triethylenediamine-Rhodium-Nitrate and -Iodide.

Rotation-Dispersion of Laevogyrate Tri-ethylenediamine-rhodium-nitrate.		
The liquid contained 3,372 grams of salt in 100 grams of the solution.		
Wave-length in ÅNGSTRÖM-Units :	Specific rotation $[\alpha]$ in Degrees :	Molecular rotation $[M]$ in Degrees :
6840	— 51,11	— 2397 ^o
6660	— 55,44	— 2600
6520	— 56,50	— 2650
6380	— 60,55	— 2840
6260	— 63,55	— 2981
6140	— 67,99	— 3189
6030	— 71,21	— 3340
5890	— 76,75	— 3600
5800	— 78,81	— 3696
5700	— 82,37	— 3863
5605	— 85,77	— 4023
5510	— 89,48	— 4196
5420	— 91,70	— 4301
5340	— 93,92	— 4405
5260	— 97,18	— 4558
5180	— 98,66	— 4627
5100	— 100,59	— 4718
4945	— 105,63	— 4955
4780	— 110,45	— 5180
4650	— 114,22	— 5357
4480	— 117,27	— 5500
4310	— 119,85	— 5621

§ 14. In first instance it may be remarked in this connection, that the expected hemihedrism of the crystal-forms of the optically active *bromide* and *iodide* investigated, does *not* manifest itself in any distinct and convincing way, notwithstanding the enormous value of the optical rotation of these salts.

This fact is completely analogous to our previous experience in the case of the corresponding *cobalti*-salts. It proves once more that even if PASTEUR's principle be considered as principally correct, the chemical identity of the dissymmetrically arranged substitutes must be looked upon as a very unfavourable factor for the eventual manifestation of the hemihedrism predicted. These facts seem to sustain our view previously explained, according to which the dissymmetrical arrangement as such determines chiefly the size of the optical rotation of the molecule, while the chemical contrast between the different substitutes is the predominant factor for the manifestation of the crystallonomical enantiomorphism.

Moreover, WERNER¹⁾, on the supposition, that analogously built dissymmetrical molecules always should combine with the same optically active radical into compounds showing *analogous solubility-relations*, concluded that the *laevogyrate Rho*-salts of the kind here described, and the *dextrogyrate Co*-salts would possess the same *stereometrical configuration*.

For from the *less soluble chloro-d-tartrates* of both series, the oppositely rotating *Rho*-, resp. *Co*-salts are set free, after the *d-tartaric acid* has been removed from them.

The Swiss scientist does not give sufficient and rational proof of the correctness of his starting hypothesis²⁾. On the contrary: the solubility of chemical compounds is a constitutive property of so highly a complicated nature, that there is every reason to doubt à priori the *general* correctness of the supposition mentioned above. Then, however, at the same time the value of WERNER's considerations, suggestive as they may be, has become appreciably diminished, in so far as they concern the specific influence of the central metal-atom on the direction of the optical rotation of the molecule.

As a counterpart of the views exposed by him, we therefore wish here to bring forward the following arguments which, in our opinion, appear to be founded on a firmer basis.

¹⁾ A. WERNER, loco cit Berl. Ber. 45. 1229 (1912). Bull. de la Soc. Chim. (1912), p. 21; G. URBAIN et L. SÉNÉCHAL, Introduction à l'Etude des Complexes, (1913), p. 174.

²⁾ Some cases are mentioned in his paper: however, there is no certainty that really no inversion has occurred here during the experiment.

In the preceding paragraphs we were able to demonstrate :

1. that in analogously built, optically-*inactive* complex salts of trivalent *cobalt* and trivalent *rhodium*, the two metals will replace each other strictly *isomorphously*. This fact is in full agreement with what can be expected because of the place these elements occupy in the eighth group of the periodical system.

2. that in analogously built, optically-*active* complex salts of trivalent *rhodium* and *cobalt*, this *isomorphous* mutual substitution of the central atoms *remains*. This specific property of the metal-atoms obviously appears therefore *not* influenced by the special dissymmetry of the molecules, in which they are present.

Now we will suppose that the *dextro*-gyrate, and just in the same way the *laevo*-gyrate *tri-ethylenediamine-cobalti-chloride* is transformed into the corresponding *chloro-tartrates* by means of *silver-d-tartrate*. Of course the crystal-forms of both these compounds *d'd* and *l'd*, being no longer each other's mirror-images, will be *different* from each other. For among all properties of chemical molecules none is certainly so closely connected with their molecular configuration, as the crystal-form is. With respect to the identical *d-tartrate*-radical in the two compounds, it is therefore the two special configuration of the *d'*-, resp. *l'*-*tri-ethylenediamine-cobalti*-radicals, which determines the differences of crystal-form in the case of the two *chloro-d-tartrates* just mentioned.

If now, while completely preserving the existent stereometrical arrangement of the radicals round the central *Co*-atom, we think this last simply replaced by the *Rho*-atom which, according to what is mentioned sub 2^o) in the above, will replace it in the way of a perfect *isomorphous* element, — then it will be evident that the two complex *Rho*-compounds thus obtained will be perfectly isomorphous with the two corresponding *Co*-salts just mentioned, and more particularly each of them with that *Co*-salt which possesses an analogous configuration of its radicals in space. This conclusion is compelling, quite independent of the other question concerning the special influence which this substitution eventually may have on the size and even on the sense of the optical rotation of the original molecule, or on its solubility. The *chloro-d-tartrates* of *Co*-an *Rho*-complexes with corresponding configuration therefore will exhibit perfectly *isomorphous* crystal-forms, independently of their specific optical properties or of the differences in their solubilities.

Also the number of molecules of water of crystallisation in the two isomorphous crystal-species will be exactly the same.

Experience now teaches us that the less soluble *tri-ethylene-*

diamine-cobalti-chloro-tartrate has *triclinic-pedial* symmetry¹⁾, the less soluble *tri-ethylenediamine-rhodium-chloro-tartrate*, however, *monoclinic* and perhaps *sphenoidical* symmetry, *without the least analogy of the parameters existing between them*. No analogy of form whatever can be stated between the two kinds of *chloro-tartrates*; and in agreement with this lack of isomorphism, direct analysis showed that, while the *cobalti-salt* crystallises with 5 molecules H_2O , the less soluble *rhodium-salt* contains only 4 molecules of water of crystallisation, — the respective data in WERNER'S paper being obviously erroneous. There can be therefore not the least doubt about the truth of the fact that we have *not* to deal here with isomorphous salts of corresponding constitution, but with quite different substances. In connection with what was said above, we are therefore compelled to conclude from these facts, that the complex *tri-ethylenediamine-rhodium-ion* present as a radical in the corresponding *chloro-d-tartrate*, has *not the same* configuration in space as the radical occurring in the less soluble *cobalti-chloro-d-tartrate*, but that it possesses on the contrary, precisely the antilogous stereometrical configuration in comparison with it. And because the *tri-ethylene-diamine-rhodium-iodide* set free from this *chloro-d-tartrate*, and all salts derived from it, appear to be *laevogyrotory*, it follows from this that the stereometrical configuration of optically-active *triethylenediamine-cobalti-*, and *rhodium-*ions of the same direction of rotation, must be the same also, — a fact which *à priori* might have appeared most probable.

The *d-cobalti-salts* must therefore possess *the same* arrangement of the radicals round their central metal-atom as the *d-rhodium-salts*, and the *l-cobalti-salts* the same as the *l-rhodium-salts*.

§ 15. With this conclusion at the same time WERNER'S supposition of the strange, rather arbitrarily conjectured specific influence of the central *Rho*-atom, concerning *the total inversion of the direction of rotation* of the original dissymmetrical complex, needs to be given up. The analogously arranged dissymmetrical complexes containing *Cr*, *Co*, or *Rho*, must all exhibit *the same* direction of rotation, and only the absolute size of it may be different and varying in the way indicated by WERNER. This specific rotation is therefore evidently determined chiefly by the special configuration in space of the radicals placed round the central atom, and by the specific dissymmetry of

¹⁾ F. M. JAEGER, Proceed. Kon. Acad. Amsterdam, 18, 54, 55. (1915).

that arrangement. Only in second instance the *mass* and the *chemical nature* of the central-atom seem to be of influence, and more especially in so far as concerns the changes of the size of the rotation, when the one kind of central atom is replaced by another isomorphous element.

It is worth remarking here, that the crystals of the optically-active *tri-ethylenediamine-cobalti-*, and *-rhodium-nitrate* here investigated, exhibit sphenoids of opposite algebraic signs in the case of active salts rotating in the same direction: the *laevo-gyrate cobalti-salt* manifest the *right-handed* sphenoid, while the *laevo-gyrate rhodium-nitrate* exhibits precisely the *left-handed* form.

On the surface of it, it may seem to be correct to consider this fact as an argument in favour of WERNER'S view about the antilogous configurations of *cobalti-* and *rhodium-*salts of the same rotation-direction. But this conclusion must appear completely unjustified, as soon as the facts hitherto stated are taken into account, — scanty as these facts for the rest may be at this moment. The question: in how far is there any rational connection between the external appearance of form of a crystal and the stereometrical configuration of its molecules? — seems to be quite unanswerable at the present moment, because this external appearance of the crystal, depending on a great number of accidental circumstances during the process of crystallisation, is a very capricious and variable phenomenon. It is, for instance, well known, that the *K-*, (ΔNH_4)-, *Rb-*, and *Co-dextro-bitartrates*, all undoubtedly having the same stereometrical configuration (namely: of *d-tartaric acid*), may exhibit preferentially the forms $\{111\}$ or $\{\bar{1}\bar{1}\bar{1}\}$ in a predominant way, if certain salts (e. g. *sodium-citrate*) be purposely added to their solutions, or if circumstances during the crystallisation be arbitrarily varied. In the case of the complex salts under consideration, which, moreover, appear to vary their outward appearance to a most intense degree under circumstances only slightly altered, such arguments, based only on this external form, can hardly have any value at all for judging the internal structure of their molecules, unless full certainty is obtained that the salts compared are deposited under exactly the same circumstances, as e. g. this may be assumed in cases, where racemoids are separated by so-called spontaneous crystallisation, the two kinds of crystals here being deposited simultaneously from the same mother-liquid.

At this moment the only conclusion can be, that the same configuration must be attributed to the *dextro-*, respectively *laevo-gyrate* complex-salts of *cobalt* and *rhodium*, when they exhibit a rotation of the same direction.

On comparing the molecular rotation of the *bromides*, *iodides* and *nitrates* of the two series:

<i>Tri-ethylenediamine-</i> <i>Cobalti-Bromide:</i> $[M]_D = \pm 6000^\circ$	<i>Tri-ethylenediamine-</i> <i>Cobalti-Iodide:</i> $[M]_D = \pm 6120^\circ$	<i>Tri-ethylenediamine-</i> <i>Cobalti-Nitrate:</i> $[M]_D = \pm 4600^\circ$
<i>Tri-ethylenediamine-</i> <i>Rhodium-Bromide:</i> $[M]_D = \pm 3500^\circ$	<i>Tri-ethylenediamine-</i> <i>Rhodium-Iodide:</i> $[M]_D = \pm 3020^\circ$	<i>Tri-ethylenediamine-</i> <i>Rhodium-Nitrate:</i> $[M]_D = \pm 3600^\circ$

we see that the *Co*-salts, besides exhibiting a much greater rotation-dispersion, also possess a much greater absolute rotation.

This fact will appear conceivable, if we bear in mind the very different chemical nature of the two isomorphous central atoms, and the rather appreciable difference in their atomic weights (59 and 103).

Some experiments on the properties of the analogous *Ir*-salts in this respect, are planned in this laboratory.

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Chemistry. — *Investigations into PASTEUR'S Principle of the Connection between Molecular and Crystallonomical Dissymmetry: IV. Racemic and Optically-active Complex Salts of Rhodium-tri-oxalic Acid.* By Prof. Dr. F. M. JAEGER.

(Communicated in the meeting of June 30, 1917).

§ 1. In our previous papers we had occasion to draw attention to the fact that the crystals of the optically active components which, according to WERNER'S theory, may be obtained under definite circumstances from the racemic complex salts of the general type: $\{Me X''_3\} Y_n$, exhibit occasionally the non-superposable hemihedrism to be expected according to PASTEUR'S principle, but that in other cases of this kind no evidence whatever of this hemihedrism is detectable by any experimental method at hand.

At the same time attention was drawn to the other fact that the molecular dissymmetry in cases as these, is by no means caused by a total absence of symmetry-properties in the molecule, but that the complex ions of the type mentioned, if once WERNER'S theory be adopted, must possess a configuration of their radicals in space, possessing the symmetry of the *trigonal-trapezohedral* class (D_3). From the established fact that the non-superposable hemihedrism of the crystal-forms could not be stated in several cases where derivatives of the complex *tri-ethylenediamine-cobalti-ion* $\{Co(Eine)_3\}$... were studied, we were compelled to conclude that the cause of this abnormal behaviour must be ascribed to the particular circumstance that the radicals placed round the central metal-atom are chemically identical here. It was remarked, however, that the expected hemihedrism could be stated without exception in all cases, where in the salts investigated radicals containing oxygen¹⁾ were present.

It was of interest to study other instances of this kind. Thus such analogously composed salts were chosen in the first place, as contained the oxygen-bearing radicals immediately linked to the central-atom in the form of the radicals of bivalent carboxylic acids. Our choice was finally fixed upon salts derived from the complex

¹⁾ F. M. JAEGER, *Proceed. Kon. Acad. Amsterdam*, **17**, 1217. (1915); **18**, 49. (1915); *Zeits. f. Kryst. u. Min.* **55**, 209. (1915).

rhodium-tri-oxalic acid, for which the possibility of a fission into the optically-active components had been proved experimentally¹⁾. Moreover, a detailed investigation of these salts appeared also desirable from another point of view, because in WERNER's original paper some facts are mentioned concerning the crystallisation-phenomena of the optically-active components, which à priori must be considered very improbable, and therefore worth controlling again by means of new experiments.

For instance, the fact was there brought to the fore, that from solutions of the racemic compound under favourable conditions crystals of both the enantiomorphous modifications would be deposited spontaneously, which hemihedral crystals of the optically active components, if brought at room-temperature into a concentrated solution of the racemoid, would increase slowly and grow to big individuals within a few weeks. But, as we found during our investigations, that the optically active forms are much more soluble under the same circumstances than the racemic substance is, it seemed highly probable that an error was made here, because, moreover, the facts mentioned cannot be right from a theoretical standpoint. The drawings in WERNER's paper, intended to give an impression of the crystal-forms obtained, rather point to distorted, and accidentally non-superposable *triclinic* crystals of the racemoid being present here, than to enantiomorphous crystals of true hemihedral symmetry. Moreover, WERNER himself mentions the *triclinic* symmetry of these crystals, and therefore the validity of PASTEUR's principle in his case cannot yet be considered as proved by the data given in this paper. Repeatedly we have made attempts in the way indicated by WERNER, to perform a spontaneous fission of the racemic salt; but the solution of it saturated just above 100° C., first being rapidly cooled down to 90° C., and subsequently cooled down to room-temperature, never deposited other crystals than the capriciously distorted individuals of the triclinic racemoid. The microscopically small crystals often obtained by very rapid cooling of the hot solution, appeared to be no crystals of the active forms either; they were rhombic individuals exhibiting prismatic, domatic and basal facets, of a new hydrate of the racemic compound, probably at higher temperatures stable, and containing less water of crystallisation. These experiments, if varied in several ways, gave unexceptionally bigger or smaller crystals of the racemic compound. The appreciably greater solubility of the active forms in comparison with that of

¹⁾ A. WERNER, Ber. d. d. Chem. Ges. 47. 1954. (1914).

the racemic salt at all temperatures between 15° and 100° C. characterizes the racemoid undoubtedly as the more stable solid phase within this range of temperature, with respect to the mixture of these antipodes. The experiment described by WERNER can therefore *never* lead to a spontaneous fission, and surely it must be quite impossible, that under these conditions an optically active crystal should increase, when brought at room-temperature into the saturated solution of the racemic salt. This may readily be deduced from BAKHUIS ROOZEBOOM'S well-known graphical representations¹⁾ of the solubility-relations here prevailing. Indeed, it could be proved on the contrary by often repeated experiments, that a crystal of one of the optically-active forms, if brought into a feebly supersaturated or saturated solution of the racemic salt, *immediately disintegrates and subsequently disappears completely*, and that after some lapse of time, *triclinic* crystals of the racemic compound are deposited from the solution. These last crystals are often rudimentarily developed, so that occasionally they make the impression of *pedial*, unsymmetrical crystals, which of course must therefore appear non-superposable with their mirror-images. If dissolved in water, the solutions of these crystals were in every case optically *inactive*. There can be no doubt whatever therefore about the fact, that the crystals obtained and reproduced by WERNER must have been distorted triclinic crystals of the racemic salt; it remains, however, doubtful whether the solutions obtained by him in dissolving these crystals, can really have been "optically-active", unless some optically-active crystals for inoculation-purposes were previously introduced into the solutions.

We were able, moreover, to demonstrate the remarkable fact that the crystals of the pure optically active components exhibit exactly the same symmetry as that previously deduced for the complex ions of this type themselves. Indeed, they are *trigonal-trapezohedral*, and they show forms which externally are quite comparable with the typical forms of some dextro- or laevogyrotory *quartz*-crystals.

The racemic salt was prepared from freshly precipitated and washed *rhodium-hydroxide* obtained from *sodium-rhodium-chloride* by means of a dilute *sodium hydroxide*-solution at 40° C.; the pure *rhodium-hydroxide* was then dissolved in a hot solution of *potassium-bi-oxalate*. The fission into its components, which is a rather tedious process, was executed by means of the *strychnine*-salt, from which afterwards the *strychnine* was readily eliminated in the form of its *indide*.

¹⁾ H. W. BAKHUIS ROOZEBOOM, Zeits. f. phys. Chemie, 28. 494. (1899).

§ 2. A solution of the active components containing 3,79% of the anhydrous salt, exhibits in a layer of 10 cm. an absorption-spectrum, in which all violet, blue, and green rays are lacking, while of the yellow light only a small portion is transmitted. With increasing dilution a small extension of the spectrum is stated; more particularly the yellow and green rays are gradually better transmitted and become more and more visible. In the case of a solution of 0,5% even some greenish-blue rays were visible. In a layer of 20 cm., the limits between which the light was not appreciably absorbed, appeared to be about as follows:

Concentration of the solution in percentages of anhydrous salt:	Limits of the transmitted light (in A.U.) for a layer of 20 c.m.:
10.96	7000--5800
3.79	7000--5700
2.75	7000--5500
1.97	7000--5500
1.09	7000--5100
0.55	7000--4900
0.50	7000--4800

These data may give an approximate impression of the extension of the light-transmission for several wave-lengths. In the red part of the spectrum, the limit is situated at about 7700 A U.; however it could not be fixed any more, because of the micrometer-screw of the monochromator not going so far.

By the study of the seven solutions just mentioned, the rotation for any of these wave-lengths was measured in a way analogous to that previously described¹⁾. The total behaviour of these orange-red to orange-yellow coloured solutions is most remarkable. For instance, if only sufficiently concentrated solutions of the *right*-handed salt be investigated (e.g. of 10%), and thus only a limited spectral region be taken into account, the observer would readily come to the conclusion, that his salt is *laevogyratory*. The following data, obtained within several spectral regions, by means of the seven solutions mentioned, and which appeared, after controlling, to be sufficiently exact, may elucidate this strange behaviour²⁾ with the simultaneous

¹⁾ F. M. JAEGER, *Proceed. Kon. Acad. Amsterdam* 17. 1227 (1915).

²⁾ A. WERNER, *loc. cit.* 1955.

of fig. 1. The numbers given for the specific rotation $[\alpha]$, are mean values of commonly three or four different values obtained various series of measurements; they always relate to a content anhydrous salt in 100 weight-parts of the solution:

Rotation-Dispersion of dextrogyrate Potassium-Rhodium-oxalate.		
<i>Wave-length in ANGSTRÖM-Units:</i>	<i>Specific rotation in Degrees:</i>	<i>Molecular rotation in Degrees:</i>
4860	+ 356°	+ 17240
4950	+ 293	+ 14190
5020	+ 253	+ 12250
5100	+ 206	+ 9975
5180	+ 172,1	+ 8335
5260	+ 141,7	+ 6860
5340	+ 114,3	+ 5535
5420	+ 85	+ 4115
5510	+ 67,1	+ 3250
5605	+ 46,4	+ 2250
5700	+ 30,1	+ 1460
5800	+ 16,3	+ 790
5890	+ 6,2	+ 300
5900	+ 5,1	+ 247
5970	0	0
6030	- 4,5	- 218
6140	- 11,5	- 557
6260	- 17	- 823
6380	- 21	- 1017
6520	- 23,5	- 1140
6660	- 25,1	- 1215
6800	- 26	- 1260
6945	- 27,4	- 1330

From this it becomes evident that the solutions of the right-handed are only dextrogyratory in reality, if green and yellow light-

rays be taken into account, for the red and orange rays however, these solutions appear to be laevogyrate.

Such solutions are optically *inactive* for a wave-length of 5970 A. U. At this wave-length, invariable moreover for solutions of widely different concentrations, there is no longer any detectable difference between solutions of the two antipodes.

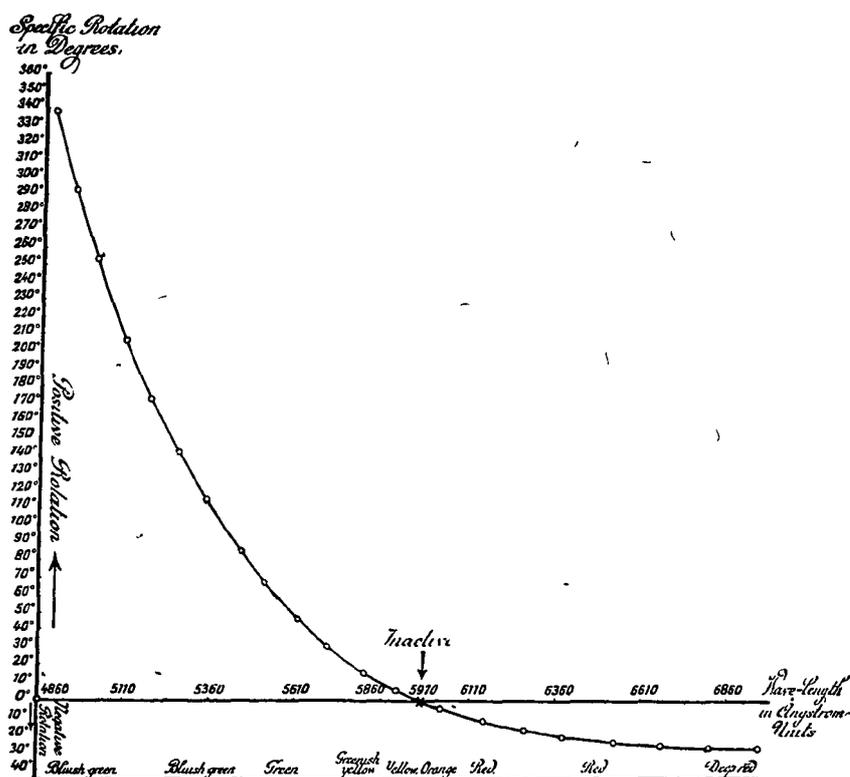


Fig 1.
Specific Rotation-dispersion of right-handed Potassium-Rhodium-Oxalate.
(All molecular rotations are 50 times as great).

It is worth attention, that the solutions do *not* exhibit for this wave-length any trace of an absorption-line. Our former supposition connecting the abnormal rotation-dispersion with the eventual occurrence of selective absorption, thus appears *no* longer justified. As WERNER points out, the phenomenon is met with in the study of all complex metal-oxalates hitherto investigated: those of *rhodium*, *chromium*, and *cobaltum*, exhibit this property in a very pronounced way¹⁾.

¹⁾ To an investigator studying the heterogeneous equilibria between the racemic salt and both its antipodes in solution, there could no longer be any difference between the solutions of the *d*- and *l*-component or their mixtures, if he worked under conditions which enabled him only to use light of a wave-length of $\lambda = 5970$ A. U. Indeed, all such solutions would then be found optically *inactive*. In such circum-

Finally it may be remarked, that the optically-active salts have no appreciable tendency to auto-racemisation. After heating on the water-bath during some time, no appreciable diminution of the original rotatory power appears to have occurred. A slight hydrolysis, however, could be stated in these cases. The salts are slowly decomposed by the continued action of violet light or by strong heating, while a black powder (*Rho* ?), and some *rhodium-hydroxide* are set free.

§ 3. I. RACEMIC POTASSIUM-RHODIUM-OXALATE (+ 4½ H₂O).

This compound crystallizes in big, ordinarily flattened, garnet-red,

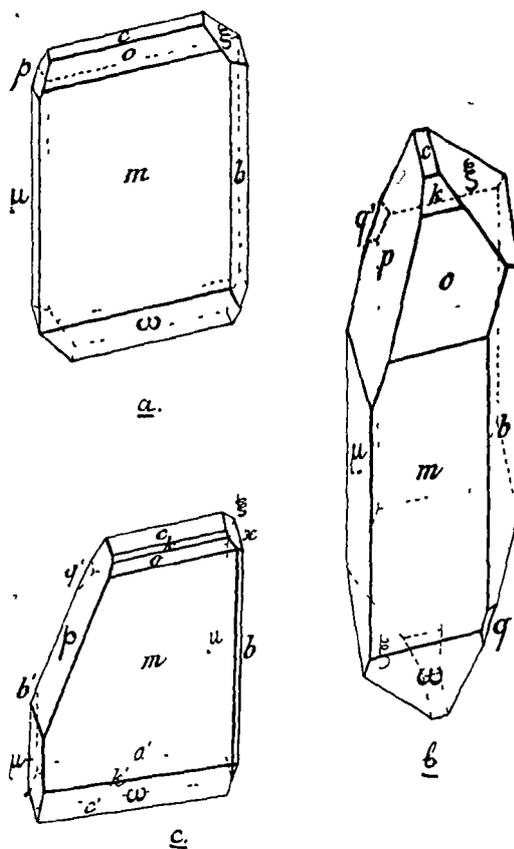


Fig. 2.

Racemic Potassium-Rhodium-Oxalate (+ 4½ H₂O).

stances no difference would apparently be any longer present here and in the well-known case of *sodium-chlorate*; in other words: in this singular point the descriptive number of components would be diminished with one. However, it must be insisted, that this is only valid for one definite temperature and one definite pressure, as $[\alpha]$ is a function of both. For wave lengths only slightly smaller or greater than 5970 A.U., the system is again a *ternary* one, in which the functions of *d*- and *l*-components are reversed.

very lustrous, and perfectly transparent crystals. Their shape is very variable, and some of the most frequent forms are reproduced in fig. 2 *a-c*. The external aspect is often highly unsymmetrical (fig. 2*c*); in such cases individuals are occasionally met with, which may be looked upon as apparently enantiomorphous. However, their symmetry is most probably holohedral, the present forms therefore only being special and accidental forms of growth.

The crystals are identical with those studied by DUFET¹⁾; they differ from those only in aspect, as DUFET's crystals exhibited the form $\mu = \{1\bar{1}0\}$ predominant.

Triclinic-pinacoidal.

$$a : b : c = 1,0732 : 1 : 1,0316.$$

$$\begin{array}{ll} A = 92^{\circ}45\frac{1}{2}' & \alpha = 98^{\circ}10\frac{2}{3}' \\ B = 102\ 4\frac{1}{3} & \beta = 104\ 17\frac{1}{3} \\ C = 67\ 24\frac{1}{2} & \gamma = 66\ 11\frac{2}{3} \end{array}$$

Forms observed: $m = \{110\}$, very lustrous and predominant; $\mu = \{1\bar{1}0\}$, smaller, but also well reflecting; $b = \{010\}$, commonly a little broader than μ ; $\omega = \{11\bar{1}\}$, broad and yielding good reflexes; $\xi = \{1\bar{1}\bar{2}\}$, well developed and very lustrous; $p = \{1\bar{1}1\}$, commonly smaller, but rarely also much greater than ξ , and giving eminent reflexes; $c = \{001\}$, commonly very narrow, occasionally somewhat broader; $o = \{111\}$, broad and beautifully reflecting; $x = \{\bar{1}\bar{1}1\}$, small and lustrous, often absent; $k = \{112\}$, commonly absent, occasionally very narrow, rarely broad; $q = \{02\bar{1}\}$, very small, but well measurable.

Angles:	Observed:	Calculated:
$m : b = (110) : (010) = *$	$54^{\circ} 10'$	—
$m : \bar{\mu} = (110) : (1\bar{1}0) = *$	$93\ 3$	—
$m : \omega = (110) : (11\bar{1}) = *$	$45\ 24\frac{1}{2}$	—
$b : \omega = (010) : (11\bar{1}) = *$	$61\ 48$	—
$\mu : \omega = (1\bar{1}0) : (11\bar{1}) = *$	$96\ 34\frac{1}{2}$	—
$c : b = (001) : (010) =$	$87\ 15$	$87^{\circ} 14\frac{1}{2}'$
$b' : \mu = (0\bar{1}0) : (1\bar{1}0) =$	$32\ 45$	$32\ 45\frac{1}{2}$
$m : p = (110) : (1\bar{1}1) =$	$86\ 18$	$86\ 23$
$\omega : c' = (11\bar{1}) : (00\bar{1}) =$	$57\ 50\frac{1}{2}$	$57\ 40$
$m : \xi = (110) : (1\bar{1}2) =$	$77\ 33$	$77\ 35$
$c : p = (00\bar{1}) : (1\bar{1}0) =$	$95\ 11$	$95\ 19$
$\mu : \xi = (1\bar{1}0) : (1\bar{1}5) =$	$51\ 20$	$51\ 24$
$o : c = (111) : (001) =$	$42\ 14$	$42\ 14$
$m : o = (110) : (111) =$	$34\ 31$	$34\ 35$

¹⁾ H. DUFET, Bull. de la Soc. Min. 12. 466. (1889); Cf.: E. LEIDÉ, Ann. de Chim. et Phys (6). 17. 307. (1889).

	Observed:	Calculated
$b':\xi = (0\bar{1}0) : (1\bar{1}\bar{2}) =$	51 25	51 25
$^{\omega}\xi = (1\bar{1}\bar{1}) : (1\bar{1}\bar{2}) =$	70 8	70 7
$\xi:x = (\bar{1}\bar{1}\bar{2}) : (\bar{1}\bar{1}1) =$	20 47	20 45
$x:\mu' = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}0) =$	30 40	30 40
$\nu:o' = (1\bar{1}0) : (\bar{1}\bar{1}1) =$	88 59	89 1
$b:o = (010) : (111) =$	64 19	64 24
$o:p = (111) : (168) =$	11 35	68 38
$\nu:p = (1\bar{1}0) : (\bar{1}\bar{1}1) =$	27 58	28 4
$c':\xi = (00\bar{1}) : (1\bar{1}\bar{2}) =$	43 59	43 55
$c:p = (001) : (\bar{1}\bar{1}1) =$	57 4	57 10
$c:k = (001) : (112) =$	27 4	26 56
$k:o = (112) : (111) =$	15 10	15 18
$b:k = (010) : (112) =$	714 3	71 56
$b:q = (010) : (02\bar{1}) =$	25 4	25 3 $\frac{1}{2}$
$c':q = (00\bar{1}) : (02\bar{1}) =$	67 41 $\frac{1}{2}$	67 42

No distinct cleavability was found.

The crystals are dichroitic: on $\{110\}$ for vibrations including an angle of 60° with the edge $m:\mu$ they are orange-yellow; for such perpendicular to those, reddish-orange. On $\{110\}$ one of the directions of extinction includes an angle of 31° with the intersection $m:\mu$; the plane of the optical axes is almost parallel to the edge $\omega:m$.

§ 4. After transformation of the racemic salt into the corresponding strychnine-salt und fractional crystallisation, the oxalate was resolved into its antipodes. The *d-rhodium*-salt, namely, combines into a less soluble *strychnine*-salt than the *l*-salt does. By treatment with *potassium-iodide*, all *strychnine* may be eliminated as the little soluble *strychnine-iodide*, and in this way the optically active potassium-salts may be obtained. It is a tedious task to get a sufficient quantity of the laevogyrate antipode, because always some *strychnine-d-oxalate* is withdrawn with the *l-oxalate*; therefore the last mother-liquids always deposit the racemic salt besides the laevogyrate. Moreover, the result is also diminished by the hydrolysis of the *strychnine*-salt during the concentration of the mother-liquid on the water-bath.

Finally, however, sufficient quantities of both antipodes were obtained. The crystallographical description of these salts is given in the following paragraphs.

§ 5. II. DEXTROGYRATORY POTASSIUM RHODIUM-OXALATE (+ 1H₂O).

Splendid, sometimes colossal, very lustrous, blood-red and perfectly transparent crystals. Their external aspect is very variable with the

particular circumstances of crystallisation, and as a consequence of their numerous and most capricious distortions, the right interpretation of the measurements is often very troublesome. Some of the most frequently occurring forms are reproduced in fig. 3 *a* and *b*.

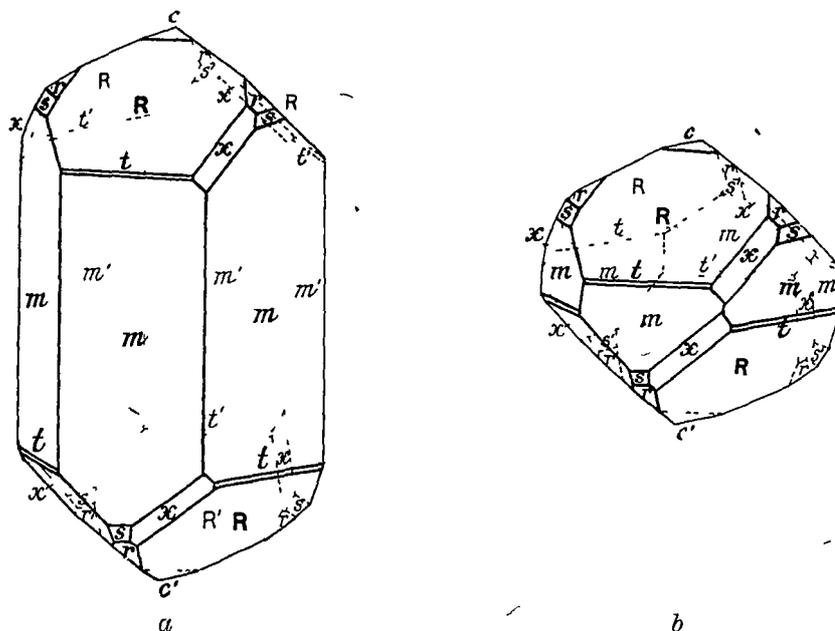


Fig. 3.

Dextrogyrate Potassium-Rhodium Oxalate (+1 H₂O).

Trigonal-trapezohedral.

$$a : c = 1 : 0,8938 \text{ (BRAVAIS)}; \alpha = 100^{\circ}38' \text{ (MILLER)}.$$

Forms observed. ¹⁾ $R = \{10\bar{1}1\} [100]$, always present, and exhibiting large faces; $c = \{0001\} [111]$, always present too, sometimes very small, but in most cases rather large, $r = \{0\bar{1}\bar{1}1\} [221]$, and $s = \{02\bar{2}1\} [11\bar{1}]$, rarely failing, well reflecting, but much smaller than R ; $t = [20\bar{2}1] [5\bar{1}\bar{1}]$, often absent, always narrow and dull, $m = \{10\bar{1}0\} [2\bar{1}1]$, always present, occasionally with small, mostly with well-developed faces, and rarely predominant, $x = \{22\bar{4}1\} [7\bar{1}5]$, as a right-handed, positive, trigonal bipyramid, occasionally absent, but in several cases with faces almost $\frac{1}{2}$ or $\frac{1}{3}$ of those of R . The different faces of x are in all cases of very different sizes. The aspect of the crystals is occasionally like that of *quartz* (fig. 3*a*), and appreciably distorted; sometimes ν is a little broader, so that the external shape gets a more *hexagonal* form. No distinct cleavage

¹⁾ The symbols between [] are MILLERIAN symbols, relating to the polar edges of R as axes of reference.

was found. On $\{10\bar{1}0\}$ occasionally unsymmetrical corrosion-figures, like trapezia, are observed.

Angles:	Observed:	Calculated:
$R:R = (\bar{1}101):(10\bar{1}1) =^*$	$76^{\circ}55'$	—
$c:R = (0001):(10\bar{1}1) =$	$45\ 59$	$45^{\circ}54\frac{1}{4}'$
$c:r = (0001):(01\bar{1}1) =$	$45\ 58$	$45\ 54\frac{1}{4}$
$r:s = (01\bar{1}1):(02\bar{2}1) =$	$18\ 25$	$18\ 15$
$s:m = (02\bar{2}1):(01\bar{1}0) =$	$25\ 31$	$25\ 51$
$m \cdot R = (01\bar{1}0):(10\bar{1}1) =$	$68\ 54\frac{1}{2}$	$68\ 57\frac{1}{3}$
$m \cdot t = (01\bar{1}0):(02\bar{2}1) =$	$25\ 43$	$25\ 51$
$s \cdot R = (02\bar{2}1):(10\bar{1}1) =$	$51\ 14$	$51\ 12$
$r:R = (10\bar{1}1):(01\bar{1}1) =$	$42\ 8$	$42\ 5\frac{1}{3}$
$R:m = (10\bar{1}1):(10\bar{1}0) =$	$44\ 5$	$44\ 5\frac{3}{4}$
$x:m = (2\bar{2}41):(10\bar{1}0) =$	$40\ 55$	$40\ 54\frac{1}{4}$
$x:R = (2\bar{2}41):(01\bar{1}1) =$	$77\ 58$	$78\ 17$
$m:x = (01\bar{1}0):(2\bar{2}41) =$	$40\ 55\frac{1}{2}$	$40\ 54\frac{1}{3}$
$x:R = (2\bar{2}41):(10\bar{1}1) =$	$28\ 2$	$28\ 3$
$x:r = (2\bar{2}41):(01\bar{1}1) =$	$28\ 2$	$28\ 3$
$c:x = (0001):(2\bar{2}41) =$	$60\ 48$	$60\ 46\frac{1}{2}$
$x:x = (2\bar{2}41):(2\bar{2}41) =$	$58\ 24$	$58\ 23$

Intergrowths of two crystals occur, with their trigonal axes intersecting under right angles, and one individual rotated about it through 180° .

The crystals are distinctly dichroitic: on $\{10\bar{1}0\}$ for vibrations parallel to the direction of the c -axis, they are orange, for vibrations perpendicular to the first, blood-red.

Plates parallel to $\{0001\}$ show in convergent polarised light the interference-image of an uniaxial crystal without circular polarisation: the bars of the black cross are regularly extended to the centre of the image. The character of the birefringence is negative for all colours, and it is strong. For Na -light is $n_o = 1,6052$. $n_e = 1,5804$; the birefringence is therefore $0,025$.

When the axial image is very much enlarged, it appears, on closer examination, to be properly *biaxial*, with an extremely small apparent angle of the axes, and with the axial-plane perpendicular to one of the edges $c:r$. Although the rotatory power of the crystals is obviously very weak, it is, however, rather probable that they represent pseudo-symmetrical intergrowths of lamellae of lower symmetry.

§ 6. III. LAEOGYRATE POTASSIUM-RHODIUM-OXALATE (+ $1H_2O$).

From the last mother-liquids, in which the more soluble strychnine-salt is accumulated, the laevogyrate salt, together with some

racemic oxalate, is obtained by means of *potassium-iodide*. First the less soluble racemic salt crystallizes in the form of fig. 2, subsequently the laevogyrate antipode in splendid, garnet-red, flattened crystals.

Commonly the external aspect is that of fig. 4*a*, with a flattening parallel two opposite faces of the rhombohedron, of which one is often excavated and uneven. Occasionally also crystals of the aspect

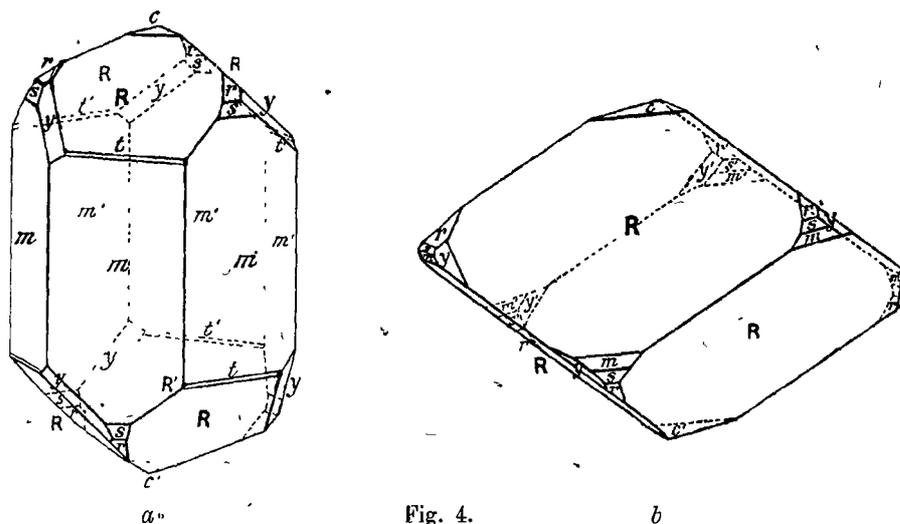


Fig. 4.
Laevogyrate Potassium-Rhodium-Oxalate (+ 1 H₂O).

of fig. 4*b* were obtained. Both combinations are also met with in the case of the dextrogyrate salt, but the antipodes differ in the occurring of a *left-handed* trigonal bipyramid $y = \{4\bar{2}21\} [7\bar{5}\bar{1}]$ in the *laevogyrate* forms, where the dextrogyrate manifested the *right-handed* trigonal bipyramid $x = \{22\bar{1}\bar{1}\} [71\bar{5}]$. For the rest the angular values are the same as found in the case of the dextrogyrate salt. A review of some values may convince the reader of this:

Angles:	Observed:	Calculated:
$R:R = (\bar{1}101):(10\bar{1}\bar{1}) = *$	77° 0'	—
$c:R = (0001):(10\bar{1}\bar{1}) =$	46 1	45°54'
$c:r = (0001):(0\bar{1}\bar{1}\bar{1}) =$	45 52	45 54
$r:s = (0\bar{1}\bar{1}\bar{1}):(02\bar{2}\bar{1}) =$	18 3	18 15
$s:m = (02\bar{2}\bar{1}):(01\bar{1}\bar{0}) =$	26 0	25 51
$m:t = (0\bar{1}\bar{1}\bar{0}):(02\bar{2}\bar{1}) =$	26 1	25 51
$y:m = (4\bar{2}2\bar{1}):(10\bar{1}\bar{0}) =$	40 58	40 54
$y:r = (4\bar{2}2\bar{1}):(1\bar{1}\bar{0}\bar{1}) =$	28 0	28 2
$y:R = (4\bar{2}2\bar{1}):(1\bar{1}\bar{0}\bar{1}) =$	78 8	78 17

The geometrical as well as the optical properties, with the exception of the peculiarity just mentioned, are in both cases perfectly agreeing. There can be no doubt whatever as to the fact that the two optically active salts crystallise in non-superposable mirror-images, although the crystals themselves do not show a distinct rotatory power. Stereographical projections of the dextro- and laevogyrate crystal-forms are given here in fig. 5a and 5b, for the purpose of surveying the general zonal relations.

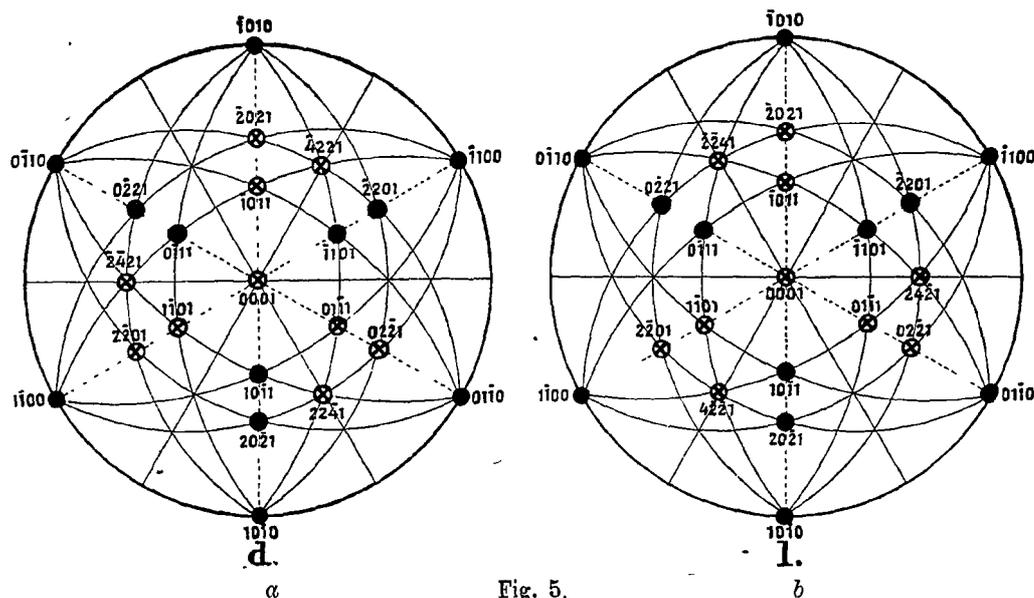


Fig. 5.
Stereographical Projection of the Crystal-forms of dextro- and laevo- Potassium-Rhodium-Oxalate. (+ 1 H₂O).

From these facts it becomes clearly evident that in the case investigated PASTEUR'S principle appears fully confirmed. Indeed, a non-superposable hemihedrism of the crystal-forms can be stated as inseparably accompanying the enormously strong optical activity of the solutions of these salts. However, it is worth attention that even here this hemihedrism only manifests itself by the occurrence of a single trigonal bipyramid, and never by the presence of any "trapezohedral" face, as e.g. in the case of *quartz*; this fact again may in some way or other be connected also with the lack of chemical contrast between the dissymmetrically arranged substitutes.

Finally it may be remarked that a solution of these salts after three days, exposure to the light and even to the sun-light, did not exhibit any appreciable photochemical decomposition. In aqueous solution, however, the substance exposed in *quartz*-vessels to the

action of a strong quartz-lamp during some few hours, appeared decomposed to a detectable degree: metallic *rhodium* covered the walls of the quartz-apparatus in the form of a black mirror, while carbon-dioxide was set free. As the violet and blue rays are almost completely absorbed by the solutions (see above), the relatively rapid photochemical destruction of the molecule by rays of short wavelength may be considered as to be in full accordance with DRAPER'S law.

§ 7. If a solution of *potassium-rhodium-oxalate* be treated with *silver-nitrate*, the *silver-salt*: $\{Rho(C_2O_4)_3\}Ag_3$ is precipitated as a vividly red compound, which is only little soluble in cold, somewhat more in hot water, and which crystallises in long needles much alike the *bichromate*.

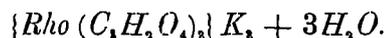
From this *silver-salt*, as well as directly from the *potassium-salts*, by interchange with *tri-ethylenediamine-rhodium-halogenides*, complex salts of the type $\{Rho(Eine)_3\}\{Rho(C_2O_4)_3\}$, may be obtained as pale yellow to orange-yellow crystalline precipitates, which are almost insoluble in all kinds of solvents. as was to be expected beforehand.

By combination of the *racemic* and optically-*active* ions, we have finally obtained the following nine isomeric salts:

$\{r-Rho(Eine)_3\}\{r-Rho(C_2O_4)_3\}$; $\{r-Rho(Eine)_3\}\{d-Rho(C_2O_4)_3\}$;
 $\{r-Rho(Eine)_3\}\{l-Rho(C_2O_4)_3\}$; $\{d-Rho(Eine)_3\}\{r-Rho(C_2O_4)_3\}$;
 $\{l-Rho(Eine)_3\}\{r-Rho(C_2O_4)_3\}$; $\{d-Rho(Eine)_3\}\{d-Rho(C_2O_4)_3\}$;
 $\{l-Rho(Eine)_3\}\{l-Rho(C_2O_4)_3\}$; $\{d-Rho(Eine)_3\}\{l-Rho(C_2O_4)_3\}$;
and $\{l-Rho(Ein\bar{e})_3\}\{d-Rho(C_2O_4)_3\}$.

§ 8. Furthermore some measurements may be recorded here concerning *potassium-rhodium-malonate*: $K_3\{Rho(C_2H_2O_4)_3\} + 3H_2O$, a new compound obtained in a way analogous to that described for the corresponding *oxalate*, and which is now also used in fission-experiments. Finally the description has been given here also of *potassium-iridium-oxalate*: $K_3\{Ir(C_2O_4)_3\} + 4\frac{1}{2}H_2O$, of which the fission into its antipodes is now being investigated also in the author's laboratory. The available data prove once more plainly the full *isomorphism* between *Rho*- and *Ir*-derivates of analogous structure.

§ 9. RACEMIC POTASSIUM-RHODIUM-MALONATE.



This compound was prepared from freshly precipitated and washed *rhodium-hydroxyde*, by boiling it during a long time with a solution of *potassium-bimalonate*, to which some *free malonic acid* was added. Complete solution occurs only after heating during a very

long time; moreover the salt is more easily hydrolysed than the corresponding *oxalate*. It contains 9.32% of water, corresponding to the presence of three molecules of crystallisation-water.

The salt crystallises from an aqueous solution in the form of thin, hexagonally bordered, orange-red plates, or occasionally in somewhat thicker crystals, exhibiting however the same combination-forms. They show appreciable oscillations of their angular values.

Monoclinic-prismatic.

$$a : b : c = 1,2309 : 1 : 1,0783 ; \beta = 86^{\circ}36'$$

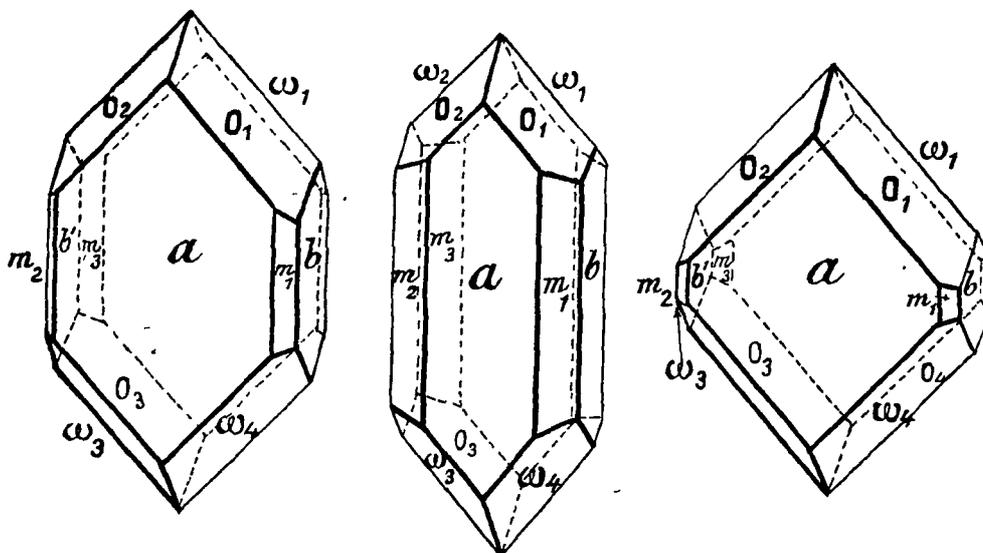


Fig. 6.

Racemic Potassium-Rhodium Malonate (+3 H₂O).

Forms observed: $a = \{100\}$, always predominant and very lustrous; $o = \{111\}$ and $\omega = \{\bar{1}\bar{1}\bar{1}\}$, commonly equally large, occasionally o much broader than ω , and yielding sharp reflexes; $m = \{210\}$, larger or smaller, but always well reflecting; $b = \{010\}$, ordinarily narrow, often absent, sometimes even broader than m . The external habit is that of plates parallel to $\{100\}$, with a slight elongation in the direction of the c -axis.

Angles:	Observed:	Calculated:
$b : o = (010) : (111) = *$	51°48'	—
$a : o = (100) : (111) = *$	57 30	—
$w : a = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{0}\bar{0}) = *$	60 55	—
$a : m = (100) : (210) =$	31 32	31°34'
$m : b = (210) : (010) =$	58 28	58 26
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	76 15	76 24
$o : \omega = (111) : (\bar{1}\bar{1}\bar{1}) =$	61 40	61 35
$\omega : \omega = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	79 20	79 44
$b : \omega = (010) : (\bar{1}\bar{1}\bar{1}) =$	50 25	50 8

No distinct cleavability has been found. At {100} corrosion-figures having the shape of isosceles triangles were observed; their symmetry is in accordance with that of the monoclinic-prismatic class. The crystals are only feebly dichroitic. The plane of the optical axes is {010}; one optical axis is observable at the border of the optical field, under appreciable inclination to the plane {100}. The dispersion is inclined and weak, with $\rho > v$. The birefringence has negative character.

§ 10. RACEMIC POTASSIUM-IRIDIUM-OXALATE ($+ 4\frac{1}{2}H_2O$).

The substance was obtained by dissolving freshly precipitated *iridium-hydroxide* in *oxalic acid*. The process goes on extremely slowly and is accomplished only by heating during about 30 hours at a reflux-cooler, until the liquid has got a pure yellow colour. It is then neutralized with *potassium-carbonate* and slowly evaporated at room-temperature¹⁾. Besides much *potassium-oxalate*, orange coloured crystals of the *iridium-salt* are deposited. They are selected, purified, and recrystallised several times from aqueous solutions.

The salt is deposited from aqueous solutions in beautiful orange crystals, which are very lustrous and suited for precise measurements.

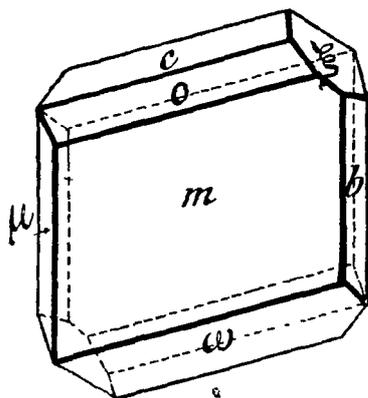


Fig. 7.

Racemic Potassium-Iridium-Oxalate
($+ 4\frac{1}{2}H_2O$).

Trichlinic-pinacoidal.

$$a : b : c = 1,0771 : 1 : 1,0405;$$

$$A = 93^\circ 22\frac{1}{2}'. \quad \alpha = 98^\circ 38\frac{1}{2}'.$$

$$B = 101^\circ 36\frac{3}{4}'. \quad \beta = 104^\circ 3'.$$

$$C = 67^\circ 27'. \quad \gamma = 66^\circ 9\frac{1}{2}'.$$

Forms observed: $m = \{110\}$, predominant, much larger than $\mu = \{1\bar{1}0\}$, and $b = \{010\}$; the vertical zône exhibits occasionally appreciable fluctuations of the angular values, and multiple reflexes; $c = \{001\}$, smaller than μ , but very lustrous; $o = \{111\}$, a little larger than c , and $\omega = \{1\bar{1}1\}$, much broader than o ; all three forms yield very good reflexes; $\xi = \{112\}$, large and very lustrous. The external form appears flattened parallel to m ; the plates are commonly very thick.

¹⁾ Cf. C. GIALDINI, Rend. Acad. Linc. Roma (5^a). 16. II. 551. (1907); the crystals were measured by F. ZAMBONINI, (Zeits. f. Kryst. u. Min. 47. 621, (1910), who also demonstrated their isomorphism with the analogous rhodium-compound. However, his interpretation of the occurring forms is different from the one given by us.

Angles:	Observed: Calculated		
	(JAEGER):	(ZAMBONINI):	
$m : b = (110) : (010) =^*$	53°54'	53° 59'	--
$m : \omega = (110) : (1\bar{1}\bar{1}) =^*$	45 33	45 30	--
$b : \mu = (0\bar{1}\bar{0}) : (1\bar{1}\bar{0}) =^*$	32 40	32 37	--
$c : \mu = (00\bar{1}) : (1\bar{1}\bar{0}) =^*$	94 40	94 38	--
$c : m = (001) : (110) =^*$	76 40	--	--
$\bar{m} : \mu = (110) : (1\bar{1}\bar{0}) =$	93 20	93 24	93°26'
$\mu : \omega = (1\bar{1}\bar{0}) : (11\bar{1}) =$	96 25	96 18	96 30 $\frac{1}{3}$
$c : \xi = (00\bar{1}) : (1\bar{1}\bar{2}) =$	43 42	--	43 59
$m : o = (110) : (111) =$	34 38	--	34 20
$c : o = (001) : (111) =$	42 20	--	42 20
$c : \omega = (00\bar{1}) : (11\bar{1}) =$	57 46	56(?)46	57 46
$m : \xi = (110) : (1\bar{1}\bar{2}) =$	78 13	--	77 59
$\omega : \xi = (11\bar{1}) : (1\bar{1}\bar{2}) =$	70 17	70 16	70 13
$\mu : \xi = (1\bar{1}\bar{0}) : (1\bar{1}\bar{2}) =$	50 58	50 51	51 45
$a : \mu = (100) : (1\bar{1}\bar{0}) =$	--	--	34 47
$a : m = (100) : (110) =$	--	--	58 39

No distinct cleavability was found.

On all faces oblique extinction. The crystals are strongly dichroitic: on m yellow and orange, quite analogous to the corresponding *rhodium*-compound. --

There can be no doubt about the complete *isomorphism* of the crystals in this case with those of the *Rho*-salt. The corresponding *Co*-salt was investigated by COPAUX; it is also triclinic-pinacoidal, but not isomorphous with the two other salts, probably because of a difference in its content of water of crystallisation. Attempts will be made to obtain the analogous *cobalti*-salt.

Afterwards we will communicate in detail about our fission-experiments of *potassium-rhodium-malonate* and of *potassium-iridium-oxalate*, as soon as their optical antipodes will have been obtained.

*Laboratory for Inorganic and Physical Chemistry
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Chemistry. — “Two Crystallised, Isomeric *d*-Fructose-Penta-acetates”. By Prof. Dr. F. M. JAEGER.

(Communicated in the meeting of June 30, 1917.)

§ 1. Nine years ago¹⁾ the crystallonomical character was described of a *d*-Fructose-tetra-acetate (rupt: 132° C.), prepared by Dr. D. H. BRAUNS. The compound is *monoclinic-sphenoidical*, with the parameters: $a:b:c = 1,3463:1:1,5733$, and $\beta = 52^\circ 12'$. A short time ago HUDSON and BRAUNS²⁾ succeeded in obtaining two isomeric crystallised *d*-Fructose-penta-acetates, whose form-analogy is strikingly evident, as will be clear from what follows.

Both *penta-acetates* possess the same cycle of atoms in their molecules, as is proved by the fact that they both are obtainable from *d*-Fructose-tetra-acetate, namely the α -modification by means of $ZnCl_2$ and *acetic acid-anhydride*, the β -modification by means of strong *sulphuric acid* and *acetic-acid-anhydride*.

§ 2. I. *a*-*d*-FRUCTOSE-PENTA-ACETATE.

The substance melts at 70° C.; its specific rotation at 20° C. is: $[\alpha]_D = +34,75$ in chloroform-solution. Its taste is a little bitter, and it crystallises from a mixture of alcohol and chloroform in prismatic crystals which are reproduced in fig. 1.

Rhombic-bisphenoidical.

$$a : b : c = 0,4946 : 1 : 0,3349$$

Forms observed: $m = \{110\}$, predominant, and $b = \{010\}$, appreciably smaller. The prism-zône shows often disturbances, and its angular values may oscillate within rather wide limits. Furthermore: $q = \{011\}$, large and lustrous; $\omega = \{111\}$, small and lustrous; $s = \{021\}$, smaller and somewhat duller. The external form is elongated parallel the *c*-axis.

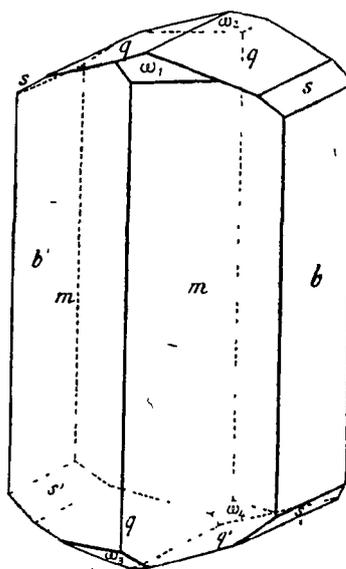


Fig. 1.

¹⁾ F. M. JAEGER, *Proceed. Kon. Acad. Amsterdam*, **10**. 563. (1908): *Zeits. f. Kryst. u. Miner.* **45**. 539. (1908).

²⁾ C. S. HUDSON and D. H. BRAUNS, *Journ. Amer. Chem. Soc.* **37**. 1283, 2736. (1915).

Angles:	Observed:	Calculated:
$m:m = (110) : (\bar{1}\bar{1}0) =$	$52^{\circ}38'$	—
$q:q = (011) : (0\bar{1}\bar{1}) =$	$37^{\circ}2'$	—
$m:b = (110) : (010) =$	$63^{\circ}41'$	$63^{\circ}41'$
$q:b = (011) : (010) =$	$71^{\circ}29'$	$71^{\circ}27'$
$\omega:b = (111) : (010) =$	$74^{\circ}23'$	$74^{\circ}30'$
$\omega:m = (111) : (110) =$	$52^{\circ}59'$	$52^{\circ}56'$
$\omega:q = (111) : (011) =$	$32^{\circ}28'$	$32^{\circ}42'$
$\omega:m = (111) : (\bar{1}\bar{1}0) =$	$68^{\circ}42'$	$68^{\circ}33'$
$s:q = (021) : (011) =$	$15^{\circ}7'$	$15^{\circ}18'$
$s:m = (021) : (110) =$	$75^{\circ}44'$	$75^{\circ}43'$
$m:q = (110) : (211) =$	$81^{\circ}57'$	$81^{\circ}54\frac{1}{2}'$

Cleavable imperfectly parallel to $\{110\}$.

On m rectangular extinction.

§ 3. II. β -*D*-FRUCTOSE-PENTA-ACETATE.

This isomeric compound melts at 109° C.; its specific rotation in chloroform-solution is at 20° C. : $[\alpha]_D = -120^{\circ},9$; in benzene $[\alpha]$ is : $-105^{\circ},5$.

The crystals here described were obtained from a solution in ether;

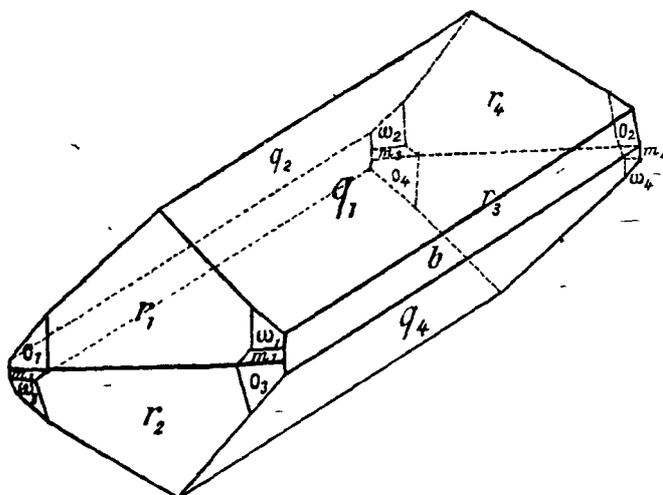


Fig. 2.

β -*D*-Fructose-penta-acetate.

from benzene the substance crystallises in individuals containing 1 molecule of benzene.

Colourless, well-developed, prismatic crystals, which have a feebly bitter taste.

Rhombic-bisphenoidal.

$$a : b : c = 0,4941 : 1 : 0,9094,$$

Forms observed: $q = \{011\}$, very predominant, but yielding bad reflexes; $b = \{010\}$, smaller, much better reflecting than q ; $r = \{101\}$,

large and lustrous; $\omega = \{111\}$, small, but giving good reflexes; $o = \{1\bar{1}\bar{1}\}$, larger than ω , but duller; $m = \{110\}$, very small, yielding sharp images. The habit of the crystals is elongated parallel to the a -axis.

Angles:	Observed:	Calculated:
$b:q = (010) : (011) =^*$	47°43'	—
$r:r = (101) : (10\bar{1}) =^*$	57 2	—
$q:q = (011) : (0\bar{1}\bar{1}) =$	84 34	84°34'
$q:r = (0\bar{1}\bar{1}) : (10\bar{1}) =$	69 16	69 19
$r:m = (101) : (1\bar{1}0) =$	37 58	38 1
$m:q = (1\bar{1}0) : (0\bar{1}\bar{1}) =$	72 36	72 39 $\frac{1}{2}$
$q:o = (011) : (111) =$	53 49	53 41 $\frac{1}{2}$
$o:o = (1\bar{1}\bar{1}) : (1\bar{1}\bar{1}) =$	72 22	72 37
$o:m = (111) : (110) =$	25 54	25 57
$m:o = (110) : (111) =$	25 59	25 57
$b:o = (010) : (111) =$	66 39	66 32
$b:\omega = (0\bar{1}0) : (1\bar{1}\bar{1}) =$	66 31	66 32
$o:\omega = (111) : (1\bar{1}\bar{1}) =$	23 24	23 28
$b:m = (010) : (110) =$	63 55	63 42 $\frac{1}{3}$

Perfectly cleavable parallel to $\{011\}$.

The plane of the optical axes is $\{100\}$, probably the c -axis is first bisectrix.

§ 4. From these measurements it is obvious that both isomerides possess *the same symmetry*, and, — within the limits of experimental errors, — *the same parameter $a:b$* ($= 0,4944$). Such relations are met with often in the case of polymorphic modifications of the same substance¹⁾. The identity of the cyclic structure in both molecules compels us to believe that it is this cyclic of atoms common to both, which determines the value of $a:b$. In no cases of polymorphism where up till now such analogy in the values of one of the parameter-ratios was observed, there could be indicated the existence of a reversible transition between the two modifications. In the case of α - and β -*d-Fructose-penta-acetates* too, as HUDSON and BRAUN demonstrate, no such reversibility seems to exist either (*monotropy*). It may seem probable that in cases like this, no ordinary polymorphism is present, but that in last instance the differences observed between such modifications are always caused by true *chemical isomerism*, in which a great part of the molecule is common to the two modifications.

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¹⁾ F. M. JAEGER, Zeits. f. Kryst. u. Miner. **40**. 131. (1905): thus in the case of α and β -1-3-4 *Dinitro diethyl-aniline*; of α - and β -*Benzyl-phtalimide* (ibid. **40**. 371. (1905); of α - and β -*Mannite*, (GROTH's Chem. Kryst. **III**. 431. (1910); etc.

Chemistry. — “*On Complex Salts of Ferri-Malonic-Acid*”. By
Prof. Dr. F. M. JAEGER and Dr. R. T. A. MEES.

(Communicated in the meeting of June 30, 1917.)

§ 1. For certain purposes connected with the investigations into PASTEUR'S principle as made in this laboratory, it appeared desirable to prepare optically-active complex salts of trivalent *iron* with the radicals of *bivalent* carboxylic acids.

Such salts are already known derived from *oxalic acid*; some of them derived from *malonic acid* were prepared by SCHOLZ¹⁾, but in a not very recommendable way. The data given by this author concerning the content of crystallisation-water in these salts, do *not* agree with our numbers, moreover.

There exist in reality several series of hydrates here, as may become clear in the following paragraphs.

Moreover, analogous complex salts may be obtained, as we found, from *tartronic acid*, and from some *substituted tartronic acids*, as we shall demonstrate later-on.

§ 2. All attempts made by us with the purpose of resolving these racemic salts into their optically-active components, never gave really positive results, neither with derivatives of *oxalic*, nor with those of *malonic acid*.

In the case of the complex *malonates* the fission was attempted by means of the *strychnine*-, *brucine*-, and *cinchonine*-salts. These last gave sirupy, very viscous liquids, which did not crystallise. The *strychnine*- and *brucine-ferri-malonates* crystallise in small, greenish-yellow crystals, but after fractional crystallisation and elimination of the alcaloids from the salts obtained, no optically active solutions were obtained. The *tri-strychnine*-salt whose constitution, from analysis, could be established to be: $\{Fe(C_2H_2O_4)_3\} Str_3 + 6 H_2O$, showed a rotation corresponding about to the amount of *strychnine* present in it.

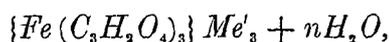
After the base had been removed by means of *KI*, the potassium-salt obtained appeared to be optically *inactive*, probably by very rapid racemisation. No attempts made with the purpose of prevent-

¹⁾ A. SCHOLZ, Monatshefte f. Chemie 29. 439. (1908).

ing this autoracemisation by experimenting in liquids containing much acetone and by working very fast, gave any better results. Analogous experience was gathered in the case of the *brucine*-salts.

In the same way we prepared the *tri-strychnine-ferri-oxalate*, which, from analysis, was seen to have the composition: $\{Fe(C_2O_4)_3\} Str_3 + 2 H_2O$, and here also several attempts were made to resolve it into its antipodes. The result was always negative, and the same occurred with: *Diammonium-strychnine-ferri-oxalate*, *diammonium-quinine*-, *diammonium-cinchonine*- and *diammonium-morphine-ferri-oxalates*. Only from the solution of the *strychnine*-salt a green substance was obtained, which, however, did not show an activity other than that corresponding to the amount of *strychnine* present. The corresponding salts of *hydroxylamine* did not give a positive result either.

§ 3. In this paper only racemic salts of the type:



are described in which Me' is replaced successively by K , (NH_4) , Na , Rb , Cs , and Tl . The Ba -salt could also be prepared, from which other salts could be obtained by interchange with soluble sulphates. The *sodium*-salt crystallises badly, and its description is therefore omitted here.

From warm solutions often *pale* green salts are obtained, possessing *rhombic* symmetry, and containing $1 H_2O$, not $2 H_2O$ as SCHOLZ¹⁾ believed. The corresponding K -salt crystallises badly, and the results obtained, although pointing in any case to a distinct isomorphism with the other salts, have therefore not been separately given here.

The most common K -salt, however, is a *triclinic* salt, crystallising with $4 H_2O$. Of the Rb -salt we obtained, besides the rarely occurring *rhombic* crystals ($+ 1 H_2O$), also darkly coloured *triclinic* crystals, containing only $1 H_2O$ too, but not well measurable. At least there must, therefore, be *three* series of hydrates possible here: *rhombic* and *triclinic* with $1 H_2O$, and *triclinic* ones with $4 H_2O$. But in no case we met with the crystals indicated by SCHOLZ, containing $2 H_2O$. A systematical investigation of the eventually possible hydrates, is very desirable.

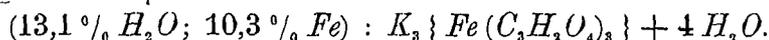
The different salts can be prepared from concentrated solutions of the *alkali-malonates* by adding the calculated amount of free *malonic acid*, heating on the water-bath, and by finally adding freshly precipitated and well-washed *ferri-hydroxide* prepared from

¹⁾ A. SCHOLZ, loco cit. p. 443. 445.

the calculated quantity of *ferrisulfate*. The beautifully green solutions, after evaporation on the water-bath, deposited crystals of the salts here described.

§ 4. POTASSIUM-FERRI-MALONATE.

Splendid, pale emerald-green, ordinarily flattened, very big and perfectly transparent crystals. They are well developed, but in the zone of the prism and that of the clinodoma they often show oscillations of the angular values to an amount of $\frac{1}{2}^\circ$. Analysis proved the composition to be



The salt possesses therefore $2 H_2O$ more than mentioned by SCHOLZ¹⁾.

Triclinic-pinacoidal.

$$a : b : c = 0,4924 : 1 : 0,4897.$$

$$A = 96^\circ 33' \quad \alpha = 98^\circ 5'$$

$$B = 103^\circ 43' \quad \beta = 104^\circ 30'$$

$$C = 84^\circ 41' \quad \gamma = 82^\circ 52\frac{1}{2}'$$

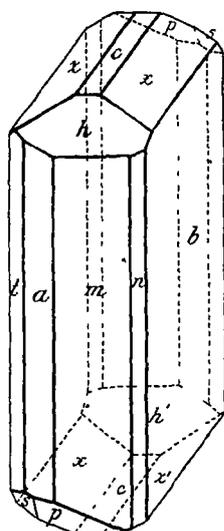


Fig. 1.
Potassium-Ferri-
Malonate
(+ 4 H₂O).

Forms observed: $b = \{010\}$, large and lustrous; $m = \{110\}$, and $a = \{100\}$, almost equally large; $p = \{120\}$, somewhat smaller than m ; $t = \{110\}$, narrow, but well reflecting; $o = \{111\}$, and $q = \{011\}$, well developed, and like $r = \{101\}$, giving perfect images; $c = \{001\}$, small; $s = \{021\}$, well-developed; $\omega = \{111\}$, as a narrow truncation of the edge $r:b$. The external habit is elongated parallel to the c -axis, and in most cases somewhat flattened parallel to $\{010\}$.

Angles: Observed: Calculated:

$a : b = (100) : (010) =^*$	95° 19'	—
$b : c = (010) : (001) =^*$	83 27	—
$c : a = (001) : (100) =^*$	76 17	—
$a : m = (100) : (110) =^*$	26 39	—
$b : q = (010) : (011) =^*$	59 13	—
$b : m = (010) : (110) =$	68 40	68° 40'
$c : q = (001) : (011) =$	24 14	24 14
$b : p = (010) : (120) =$	48 16	48 6 $\frac{1}{3}$
$p : m = (120) : (110) =$	20 34	20 33 $\frac{2}{3}$
$a : t = (100) : (110) =$	25 0	25 7
$t : b' = (110) : (010) =$	59 43	59 34

¹⁾ A. SCHOLZ, Monatshefte f. Chemie, 29. 445. (1908).

Observed: Calculated:

$c:s = (001) \cdot (0\bar{2}1) =$	47 30	47 $36\frac{1}{3}$
$s:b' = (0\bar{2}1) \cdot (0\bar{1}0) =$	48 59	48 $56\frac{2}{3}$
$b:o = (010) \cdot (\bar{1}11) =$	60 36	60 36
$o:r = (\bar{1}11) \cdot (\bar{1}01) =$	20 5	20 10
$r \cdot b' = (\bar{1}01) \cdot (0\bar{1}0) =$	99 20	99 14
$m:r = (110) \cdot (10\bar{1}) =$	59 59	60 0
$r:q = (\bar{1}01) \cdot (011) =$	52 38	52 45
$q \cdot m = (011) \cdot (\bar{1}\bar{1}0) =$	67 14	67 $15\frac{1}{2}$
$b \cdot o = (010) \cdot (111) =$	72 26	72 17
$a \cdot q = (100) \cdot (011) =$	80 26	80 24
$q \cdot o = (011) \cdot (111) =$	36 32	36 31
$o \cdot a = (111) \cdot (100) =$	43 44	43 53
$a' \cdot o = (\bar{1}00) \cdot (\bar{1}11) =$	54 42	54 $58\frac{1}{2}$
$o:q = (\bar{1}11) \cdot (011) =$	44 42	44 $37\frac{1}{2}$
$c \cdot o = (001) \cdot (111) =$	38 32	38 $20\frac{1}{2}$
$o:m = (111) \cdot (110) =$	35 34	35 $48\frac{1}{2}$
$m:c = (110) \cdot (001) =$	74 16	74 9
$p:q = (120) \cdot (011) =$	60 18	60 22
$a:r = (100) \cdot (10\bar{1}) =$	51 59	52 $3\frac{1}{2}$
$r \cdot c = (\bar{1}01) \cdot (001) =$	51 48	51 $39\frac{1}{2}$

No distinct cleavability could be found.

Distinctly dichroitic: on $\{010\}$ for vibrations parallel to the c -axis green, for those perpendicular to the former: yellow. On p and m the dichroism is only unappreciable.

On b and m is the angle of extinction about 27° , on p 44° with respect to the direction of the vertical axis. The plane of the optical axes intersects the edge $b:q$ on $\{010\}$ under an angle of about 21° .

AMMONIUM-FERRI-MALONATE.

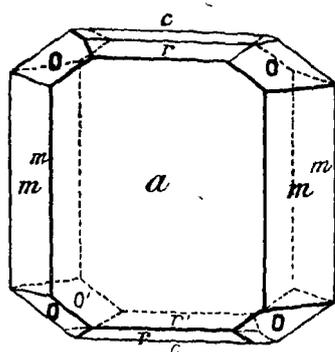
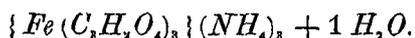


Fig. 2.
Ammonium-Ferri-Malonnate.



Pale green, flattened, very lustrous, small crystals.

Rhombic-bipyramidal.

$$a : b : c = 0,9407 : 1 : 0,6860.$$

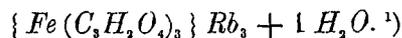
Forms observed: $a = \{100\}$, predominant, giving sharp reflexes; $m = \{110\}$, well-developed and highly lustrous; $o = \{111\}$, well-developed, and like $r = \{102\}$ yielding good reflexes; $s = \{101\}$, and $c = \{001\}$, very narrow and badly reflecting.

Angles:	Observed:	Calculated:
$a:m = (100):(110) =^*$	$43^{\circ}15'$	—
$a:o = (100):(111) =^*$	$58\ 59$	—
$o:o = (111):(\bar{1}\bar{1}1) =$	$62\ 5$	$62^{\circ}\ 3'$
$m:m = (110):(\bar{1}\bar{1}0) =$	$93\ 31$	$93\ 30$
$a:s = (100):(101) =$	$54\ 0$	$53\ 54$
$s:r = (101):(102) =$	$15\ 53$	$16\ 4$
$a:r = (100):(102) =$	$69\ 52$	$69\ 58$
$r:c = (102):(001) =$	$20\ 8$	$20\ 2$
$r:o = (102):(111) =$	$32\ 33$	$32\ 48$
$m:o = (110):(111) =$	$44\ 59$	$44\ 58$
$c:o = (001):(111) =$	$45\ 2$	$45\ 2$
$o:o = (111):(\bar{1}\bar{1}1) =$	$57\ 52$	$58\ 0$
$o:s = (111):(101) =$	$28\ 56$	$29\ 0$
$m:o = (\bar{1}\bar{1}0):(\bar{1}\bar{1}1) =$	$92\ 30$	$92\ 28\frac{1}{2}$

No distinct cleavability was observed.

The pale green crystals are distinctly dichroitic: on {100} pale yellowish-green for vibrations parallel to the *c*-axis, for those perpendicular to them, pale green. The plane of the optical axes is {001}, with the *a*-axis as first bisectrix, probably of positive character. The birefringence is weak; the apparent axial angle is very small.

RUBIDIUM-FERRI-MALONATE.



Pale green, rhombical limited crystals.

Rhombic-bipyramidal.

$$a : b : c = 0,9442 : 1 : 0,6985.$$

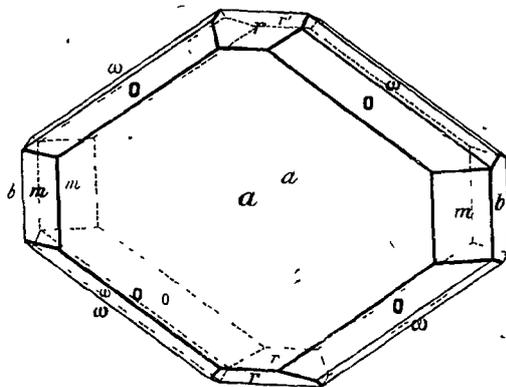


Fig. 3. Rubidium-Ferri Malonate (+ 1 H₂O).

¹⁾ This content of water of crystallisation is adopted because of the isomorphism with the other salts. The numbers of the analysis were unsatisfactory, the quantity of material at hand being too small.

Forms observed: $a = \{100\}$, strongly predominant and highly lustrous; $o = \{111\}$, and $r = \{102\}$, well-developed and yielding good reflexes, $m = \{110\}$, well reflecting; $b = \{010\}$, and $\omega = \{122\}$, narrow, built exactly measurable; $x = \{11\bar{2}\}$, small, often absent.

Angles:	Observed:	Calculated:
$a : o = (100) : (111) =^* 58^{\circ}46'$	—	—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =^* 58\ 38$	—	—
$o : \omega = (111) : (122) = 14\ 14$	—	$14^{\circ}22'$
$\omega : r = (122) : (102) = 33\ 22$	—	$33\ 14\frac{1}{2}$
$a : m = (100) : (110) = 43\ 20$	—	$43\ 21\frac{1}{2}$
$m : b = (110) : (010) = 46\ 40$	—	$46\ 40\frac{1}{2}$
$a : r = (100) : (102) = 69\ 48$	—	$69\ 42$
$r : r = (100) : (\bar{1}02) = 40\ 24$	—	$40\ 36$
$o : x = (111) : (11\bar{2}) = 18\ 46$	—	$18\ 32$
$\omega : \omega = (122) : (\bar{1}\bar{2}\bar{2}) = 34\ 0$	—	$33\ 44$

No distinct cleavage.

Noticeably dichroitic: on $\{100\}$ yellowish-white for vibrations parallel to the c -axis, for those perpendicular to them: pale green. The plane of the optical axes is $\{001\}$; the a -axis is first bisectrix. The apparent axial angle is very small.

No exact measurements could hitherto be made of the triclinic Rb -salt with $1 H_2O$, because of the bad crystals only at hand.

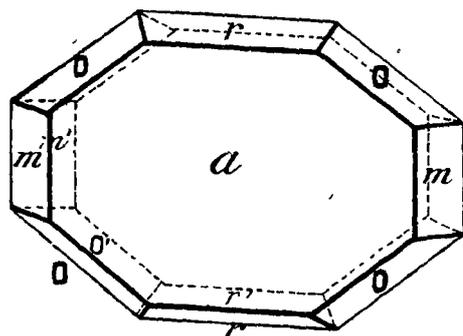
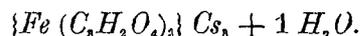


Fig. 4.
Caesium-Ferri-Malonate.

CAESIUM-FERRI-MALONATE.



Pale green, kite-shaped crystals.

Rhombic-bipyramidal.

$$a : b : c = 0,9548 : 1 : 0,7089.$$

Forms observed:

$a = \{100\}$, predominant and giving good reflexes; $o = \{122\}$, well reflecting, and, like $r = \{102\}$, rather largely

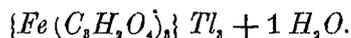
developed; $m = \{110\}$, narrow and smaller than r ; $b = \{010\}$, small but well measurable.

Angles:	Observed:	Calculated:
$a : o = (100) : (122) =^* 73^{\circ} 9$	—	—
$a : r = (100) : (102) =^* 69\ 38$	—	—
$o : o = (122) : (\bar{1}\bar{2}\bar{2}) = 33\ 42$	—	$33^{\circ}42'$
$r : r = (102) : (\bar{1}02) = 40\ 46$	—	$40\ 44$
$a : m = (100) : (110) = 43\ 48$	—	$43\ 40\frac{1}{2}$
$m : b = (110) : (010) = 46\ 12$	—	$46\ 19\frac{1}{2}$
$o : r = (122) : (102) = 33\ 28$	—	$33\ 36$
$o : o = (122) : (\bar{1}\bar{2}\bar{2}) = 66\ 56$	—	$67\ 0$
$o : b = (122) : (010) = 56\ 30$	—	$56\ 24$

No distinct cleavability could be found.

The crystals are dichroitic: on {100} greenish-yellow for vibrations parallel to the c -axis, for those perpendicular to them: pale green. The plane of the optical axis is {001}; the apparent axial angle is small, with the a -axis as first bisectrix. The birefringence is weak.

THALLO-FERRI-MALONATE.



Beautiful, pale green, flattened crystals with rectangular borders.

Rhombic-bipyramidal.

$$a : b : c = 0,9615 : 1 : 0,7050.$$

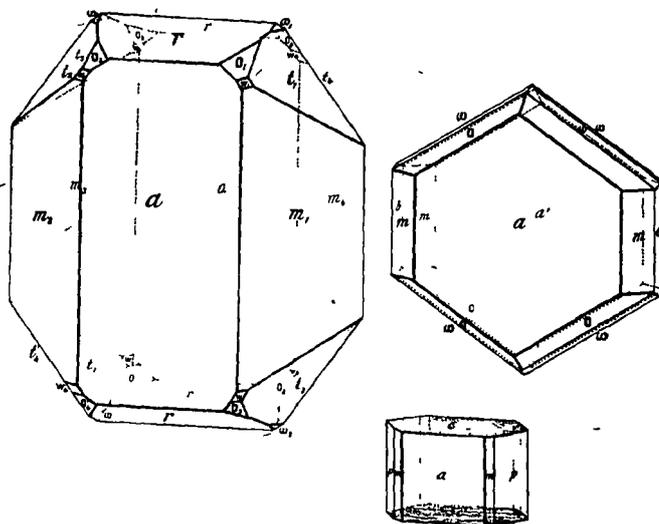


Fig. 5.

Thallo-Ferri-Malonate.

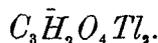
Forms observed: $a = \{100\}$, predominant and very lustrous; $r = \{102\}$, large and lustrous; $c = \{001\}$, commonly hardly visible, sometimes however well developed and striated parallel to $c \cdot a$; $m = \{110\}$, commonly well developed, very lustrous, occasionally narrow, while $p = \{120\}$, which form is ordinarily absent, is much broader in that case than m , but much duller; $o_1 = \{111\}$, well developed; $t = \{121\}$, also well-developed and lustrous; $w = \{221\}$, much smaller than o , but giving good reflexes; $\omega = \{122\}$, very narrow, but exactly measurable; $b = \{010\}$, very narrow.

<i>Angles :</i>	<i>Observed :</i>	<i>Calculated :</i>
$a:r = (100):(102) =^* 69\ 52'$		—
$a:o = (100):(111) =^* 59\ 4$		—
$r:r = (102):(\bar{1}02) = 40\ 16$		40°16'
$o\omega = (111):(122) = 14\ 6$		14 15
$\omega\omega = (122):(\bar{1}22) = 33\ 37$		33 22
$a:w = (100):(221) = 49\ 40$		49 41½'
$w.t = (221):(121) = 17\ 5$		17 19½'
$a:t = (100):(121) = 66\ 58$		67 1
$a.p = (100):(120) = 62\ 40$		62 31½'
$a:m = (100):(110) = 43\ 50$		43 52½'
$m:m = (100):(\bar{1}10) = 92\ 20$		92 15
$m.p = (110):(120) = 18\ 50$		18 39
$m:b = (110):(010) = 46\ 10$		46 7½'
$o:r = (111):(102) = 33\ 4$		33 6

No distinct cleavability.

The crystals are noticeably dichroitic: on {100} yellow-green for vibrations parallel to the *c*-axis, and pale green for those perpendicular to the former. The plane of the optical axes is {001}, with the *a*-axis as first bisectrix of positive character. The apparent axial angle is very small.

THALLO-MALONATE.



Crystallised from water, the salt is deposited in very big, transparent crystals; they are *anhydrous* (79.93% *Tl*; calc: 80%). The compound is very soluble, and crystallisation starts only in highly supersaturated solutions.

Monoclinic-prismatic.

$$a:b:c = 0,5707:1:1,0833:$$

$$\beta = 81^\circ 30\frac{1}{3}'$$

Forms observed: $c = \{001\}$, very lustrous; $b = \{010\}$, gives good reflexes; in the same way: $m = \{110\}$, and $o = \{111\}$; $s = \{\bar{1}01\}$, narrow and often badly measurable, $r = \{102\}$, not measurable, because the faces are either concave, or strongly curved. Besides the forms

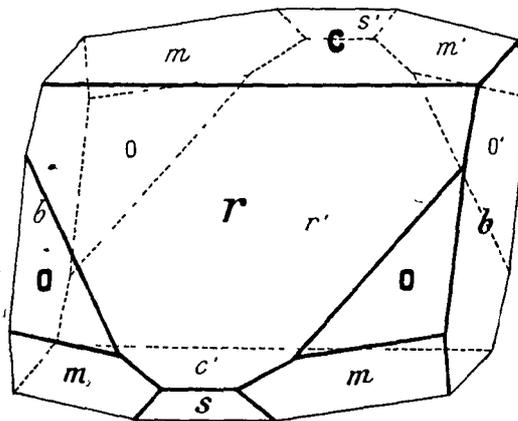


fig. 6

Anhydrous Thallo-Malonate.

reproduced in fig. 6, also plates parallel to {010} as a predominant form, are occasionally observed.

<i>Angles :</i>	<i>Observed :</i>	<i>Calculated :</i>
$c : m = (001) : (110) = *$	$82^{\circ}36\frac{1}{4}'$	—
$b : m = (010) : (110) = *$	$60\ 33\frac{1}{2}$	—
$c : o = (001) : (111) = *$	$59\ 21\frac{3}{4}$	—
$m : m = (110) : (\bar{1}\bar{1}0) =$	$58\ 53$	$58^{\circ}53'$
$o : o = (111) : (\bar{1}\bar{1}1) =$	$50\ 28$	$50\ 29$
$b : o = (010) : (111) =$	$64\ 46$	$54\ 45\frac{1}{2}$
$o : m = (111) : (110) =$	$23\ 14\frac{1}{2}$	$23\ 14\frac{1}{2}$
$m : s = (110) : (10\bar{1}) =$	$40\ 49$	$40\ 42$
$c : s = (001) : (\bar{1}01) =$	$69\ 1$	$69\ 1\frac{1}{2}$

Very perfectly cleavable parallel to {001}.

According to HAUSHOFER ¹⁾ the corresponding *potassium*-salt crystallises with 1 H₂O, and is also *monoclinic*, but without distinct form-analogy with the *thallo*-salt here described. ($a : b : c = 1,4945 : 1 : 0,9174$; $\beta = 61^{\circ}15'$).

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of the University Groningen, Holland.*

¹⁾ K HAUSHOFER, Zeits. f. Kryst. u. Miner **6**. 120 (1881).

Chemistry — “On some isomeric, complex *cis-* and *trans-*Diethylenediamine-Salts of Cobaltum, and on Tri-ethylenediamine-Zinc-Chloride.” By Prof. Dr. F. M. JAEGER and Dr. JUL. KAHN.

(Communicated in the meeting of June 30, 1917)

§ 1. According to WERNER's theory concerning the stereometrical configuration of inorganic salts derived from the complex radical: $\{MeX'_6\}$, there must exist two isomerides of derivatives containing ions of the special type: $\left(Me \begin{matrix} Y'_2 \\ X'_4 \end{matrix} \right)$, which are distinguished as *cis-* and *trans-*isomerides.

If the six co-ordination-loci round the central atom be considered as situated in space like the six corners of a regular octahedron, the substitutes Y' are located in the *cis-*derivatives as near as possible to each other, while, on the contrary, in the *trans-*derivatives they are elongated as far as possible from each other, being placed at the two ends of an axis of the octahedron.

If in the complex salts of this kind, the four co-ordination-loci X'_4 be occupied by *two* bivalent radicals X''_2 , it is obvious that the configuration of the molecule in the *cis-*derivatives possesses the *axial* symmetry of C_2 ; the heteropolar binary symmetry-axis of these complex ions joins of course the middle of the octahedron-edge $Y'Y'$ with that of the opposite and parallel edge. The symmetry of these ions is therefore exactly that of the monoclinic-sphenoidal class of crystallonomy and to every configuration of this kind corresponds therefore a *non-superposable* mirror-image, because the complex of atoms possesses *only axial* symmetry. The *cis-*compounds of the type $\left(Me \begin{matrix} Y'_2 \\ X''_2 \end{matrix} \right)$ must, for that reason, be considered as *racemic* compounds eventually resolvable into two optically active and oppositely rotating antipodes. The possibility of such a fission is demonstrated by WERNER in an experimental way for several salts of this kind.

The *trans-*derivatives of the same type $\left(Me \begin{matrix} Y'_2 \\ X''_2 \end{matrix} \right)$, however, possess the symmetry of the group D_2^H . Their configuration is therefore identical with its mirror-image, so that they are *not* resolvable into such antipodes. ¹⁾

¹⁾ See: F. M. JAEGER, Lectures on The Principle of Symmetry and Its Applications in all Natural Sciences, Elsevier-Company, Amsterdam, (1917), p. 228—256.

In the following paragraphs some of these resolvable and unresolvable salts will be described more in detail.

§ 2. RACEMIC CIS-DIAMINO-DIETHYLENEDIAMINE-COBALT-CHLORIDE.

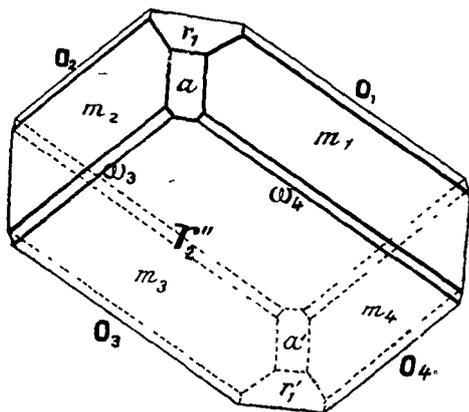
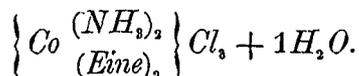


Fig. 1.

Furthermore: $m = [110]$, well-developed and very lustrous; $r_1 = [101]$, small, but giving sharp reflexes; $o = [121]$ and $\omega = [\bar{1}21]$, both very narrow, and almost equally developed; $\alpha = [100]$, small, but very lustrous; $q = [011]$, mostly narrow, but yielding splendid reflexes.

Red-brown, well-developed, and very lustrous small crystals, which obviously are isomorphous with the corresponding *bromide* and *iodide*.

Monoclinic-prismatic.

$$a : b : c = 1,1172 : 1 : 0,8325;$$

$$\beta = 87^\circ 56' \frac{1}{3}.$$

Forms observed: $r'_2 = [\bar{1}01]$, predominant; the external shape of the crystals appears ordinarily flattened parallel to this form.

Angles:	Observed:	Calculated.
$a : m = (100) : (110) =^*$	$48^\circ 9'$	—
$a : r'_2 = (\bar{1}00) : (\bar{1}01) =^*$	$54 38$	—
$a : r_1 = (100) : (101) =^*$	$51 59$	—
$m : r'_2 = (\bar{1}10) : (\bar{1}01) =$	$67 14$	$67^\circ 17' \frac{1}{4}$
$m : \omega = (\bar{1}10) : (\bar{1}21) =$	$32 24$	$32 23$
$m : m = (110) : (\bar{1}10) =$	$83 42$	$83 42$
$r'_2 : q = (\bar{1}01) : (011) =$	$52 17$	$52 23$
$r_1 : r'_2 = (101) : (\bar{1}01) =$	$73 21$	$73 23$
$m : r_1 = (110) : (101) =$	$65 24$	$65 45$
$o : q = (121) : (011) =$	$29 13$	$29 12$
$r_1 : q = (101) : (011) =$	$51 22$	$51 31$
$m : o = (110) : (121) =$	$34 59$	$35 15$

Perhaps cleavable parallel to m .

The crystals are only slightly dichroitic, in a way analogous to that of the *iodide*. They are evidently identical with crystals described

previously ¹⁾, if only the following symbols be adopted there:
 $a = [\bar{1}01]$, $o = [\bar{1}10]$, $r = [\bar{1}00]$, $s = [101]$, and $\omega = [\bar{1}21]$.

In contradiction to the data given in literature, all three *halogenides* must have the same content of crystallisation-water, and, according to the analytical investigation, $1 H_2O$.

§ 3. RACEMIC CIS-DIAMINO-DIETHYLENEDIAMINIC-COBALTI-BROMIDE.

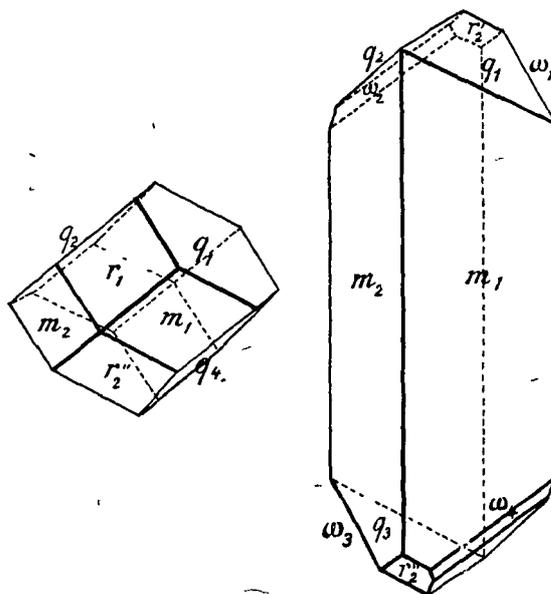
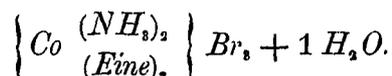


fig 2.

cis-Diamino-diethylenediamine cobalti-bromide.

The substance crystallises in flat and long brownish-red needles prismatic in the direction of the c -axis, or in short, thick and small crystals, having a slight elongation in the direction of the a -axis.

Monoclinic-prismatic.

$$a : b : c = 1,1177 : 1 : 0,8322.$$

$$\beta = 88^\circ 5'.$$

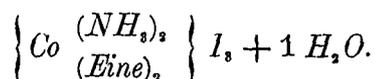
Forms observed. $m = [110]$, and $q = [011]$, large and lustrous. Occasionally m is predominant, and eventually q . Furthermore: $r_1 = [101]$ and $r'_2 = [\bar{1}01]$, almost equally large and giving good reflexes; $\omega = [\bar{1}21]$, commonly small, but also, if $q = [011]$ be only slightly developed, occasionally almost equally large as r'_2 , $a = [100]$, very narrow, and mostly absent. The substance is completely isomorphous with the corresponding *iodide*.

¹⁾ F. M. JAEGER, Zeits. f. Kryst. 39. 545. (1904).

Angles:	Observed	Calculated.
$a : m = (100) : (110) =^*$	48°10'	—
$r'_2 : m = (\bar{1}01) : (\bar{1}10) =^*$	67 15	—
$r'_2 : q = (\bar{1}01) : (011) =^*$	52 14	—
$m : m = (110) : (\bar{1}10) =$	83 40	83°40'
$q : q = (011) : (0\bar{1}1) =$	79 13	79 13
$r'_2 : q = (\bar{1}01) : (0\bar{1}1) =$	52 14	52 14
$r_1 : q_1 = (101) : (011) =$	51 23½	51 23½
$r_1 : m = (101) : (\bar{1}10) =$	65 48	65 51
$m : \omega = (\bar{1}10) : (\bar{1}21) =$	32 19	32 23
$\omega : q = (121) : (011) =$	27 52	28 1

The crystals are distinctly cleavable parallel to $[110]$. They are slightly dichroitic, analogously to the *iodide*. The angle of extinction also, about 20° with respect to the c -axis on m , has a size also comparable with that found in the case of the *iodide*.

§ 4. RACEMIC CIS-DIAMINO-
DIETHYLENEDIAMINE-COBALTI-IODIDE.



Big, splendidly developed, brown-red and highly lustrous crystals with very constant angular values.

Monoclinic-prismatic.

$$a : b : c = 1,0975 : 1 : 0,8178 ;$$

$$\beta = 87^\circ 28 \frac{2}{3}'$$

Forms observed: $m = [110]$, predominant and very lustrous; $a = [100]$, smaller than m ; $q = [011]$, large and sharply reflecting, $r_1 = [101]$ and $r'_2 = [\bar{1}01]$, almost equally well-developed and yielding excellent reflexes; $o = [121]$, and $\omega = [\bar{1}21]$, almost equally large and well reflecting. The habit is prismatic parallel to the c -axis.

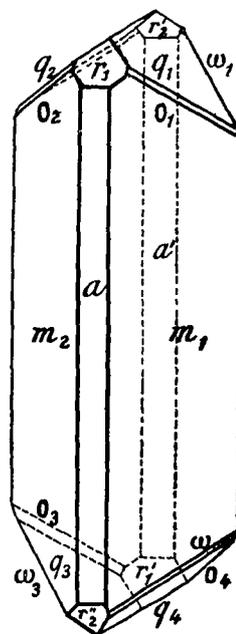


fig 3

Racemic cis-Diamino-diethylenediamine cobalti-iodide.

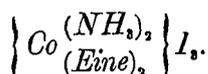
Angles:	Observed:	Calculated.
$a : m = (100) : (110) =^*$	47°38'	—
$q : q = (011) : (0\bar{1}1) =^*$	78 30½	—
$r_1 : r'_2 = (101) : (\bar{1}01) =^*$	73 22	—
$m : m = (110) : (\bar{1}10) =$	84 44	84°44'
$a' : r'_2 = (\bar{1}00) : (\bar{1}01) =$	54 59	54 56½
$r_1 : a = (101) : (100) =$	51 44	51 40
$m : o = (110) : (121) =$	35 20	35 31

	<i>Observed:</i>	<i>Calculated:</i>
$o : q = (\overline{121}) : (011) =$	29 13	29 12
$m : \omega = (\overline{110}) : (\overline{121}) =$	32 14	32 20
$m : r_1 = (\overline{110}) : (101) =$	65 20	65 17
$m : r_2' = (\overline{110}) : (\overline{101}) =$	67 12	67 13 $\frac{1}{2}$
$r_1 : q = (101) : (011) =$	51 16	51 6
$r_2 : q = (101) : (011) =$	52 3	52 9
$m : q = (\overline{110}) : (011) =$	64 38	64 43
$m' : q = (\overline{110}) : (011) =$	60 31	60 38
$\omega : q = (\overline{121}) : (011) =$	27 57	28 18

Perfectly cleavable parallel to m .

The crystals are feebly dichroitic: on a yellow-orange for vibrations in the direction of the c -axis, and for those perpendicular to them: red-orange. On m is the angle of extinction about 28° with respect to the vertical axis.

§ 5. TRANS-DIAMINO-DIETHYLENEDIAMINE-COBALTI-IODIDE.



Small, often badly developed crystals with a dark red-brown colour; their aspect is that of hexagonal plates (fig. 4).

Rhombic-bipyramidal.

$$a : b : c = 1,2449 : 1 : 1,2842.$$

Forms observed: $a = [100]$, distinctly predominant and very lustrous; $o = [111]$, and $m = [120]$, well-developed and giving sharp mirror-images.

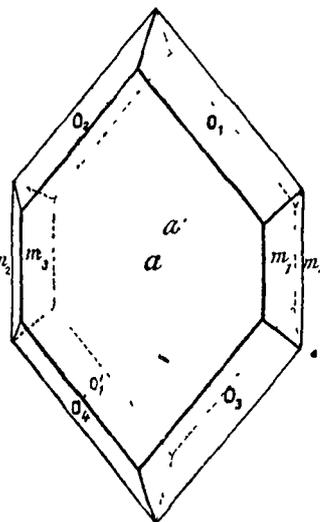
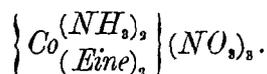


Fig. 4.
trans-Diamino diethylene-diamino-cobalti iodide.

<i>Angles:</i>	<i>Observed:</i>	<i>Calculated:</i>
$a : o = (100) : (111) =$	* 57°58'	—
$a : m = (100) : (120) =$	* 68 7	—
$o : o = (111) : (\overline{111}) =$	64 12	64°14'
$m : m = (120) : (\overline{120}) =$	43 46	43 46'
$m : o = (120) : (111) =$	35 46	35 51
$o : o = (111) : (\overline{111}) =$	83 58	83 57 $\frac{1}{2}$

The crystals are slightly dichroitic: on a orange-red for vibrations parallel to the c -axis, dark orange-red for such as are perpendicular to them. The plane of the optical axes is $[100]$; the a -axis is first bisectrix. The apparent axial angle is large, the dispersion is rather strong, with $\rho < v$ round the a -axis.

§ 6. RACEMIC CIS-DIAMINO-DIETHYLENEDIAMINE-COBALTI-NITRATE.



Beautiful, well-developed, yellow-brown or red-brown pyramids, with lustrous faces. They are nicely built, and have very constant angular values.

Rhombic-bipyramidal.

$$a : b : c = 0,9473 : 1 : 0,6758.$$

Forms observed: $o = [111]$, with highly lustrous faces. The external form of the crystals is that of flattened octahedra.

Angles.

	<i>Observed.</i>	<i>Calculated:</i>
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =^*$	$91^\circ 0'$	—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =^*$	$61 11$	—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$57 48$	$57^\circ 38'$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$89 2$	$89 0$

No distinct cleavage was observed.

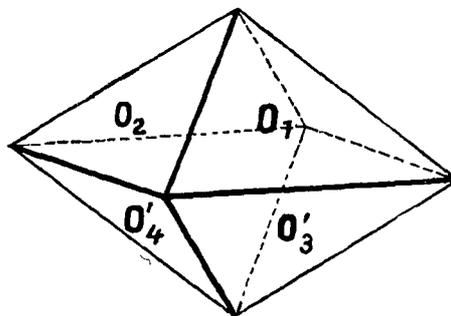
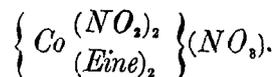


Fig. 5.

cis-Diamino-diethylenediamine-Cobalti-Nitrate.

§ 7. RACEMIC CIS-DINITRO-DIETHYLENEDIAMINE-COBALTI-NITRATE.

(*Flavo-salts*).



Small, flattened, yellow-red prismatic crystals. They are identical with those previously measured¹⁾ by us, which we had received from WERNER, but they have other combination-forms, and somewhat deviating angular values. The aspect of the crystals is that of fig. 20 in the paper mentioned.

Monoclinic-prismatic.

$$a : b : c = 1,5589 : 1 : 0,4073.$$

$$\beta = 68^\circ 30' / 4.$$

All forms previously observed were met with again; their relative development was also almost the same, only $q = [011]$ was appreciably larger here. New forms are: $r = [401]$, well developed and yielding good reflexes; and $s = [410]$, very narrow, but lustrous.

Angles:

	<i>Observed:</i>	<i>Calculated:</i>
$m : m = (110) : (\bar{1}\bar{1}0) =^*$	$110^\circ 50'$	—
$c : r = (001) : (\bar{4}01) =^*$	$57 36$	—

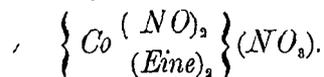
¹⁾ F. M. JAEGER, Zeits. f. Kryst. u. Miner. **39**. 564. (1904).

	Observed:	Calculated:
$m:c = (110):(001) =^*$	78 0	—
$m:b = (110):(010) =$	34 35	34°35'
$a:s = (100):(410) =$	19 44	19 56
$s:m = (410):(110) =$	35 31	35 29
$a:m = (100):(110) =$	55 25	55 25
$m:q = (110):(011) =$	60 48	60 54½'
$b:q = (010):(011) =$	69 20	69 14½'
$c:q = (001):(011) =$	20 40	20 45½'

No distinct cleavability was observed.

On [010] feebly dichroitic: for vibrations parallel to the c -axis, yellow-orange, for such perpendicular to them red-orange. The angle of extinction on [010] is about 60° with respect to the c -axis, in the acute angle of the axes a and c . The plane of the optical axes is probably [010].

§ 8. TRANS-DINITRO-DIETHYLENEDIAMINE-COBALTI-NITRATE. (*Croceo-salt*).



This compound was obtained from the mother-liquid of the corresponding *cis*-derivative, in the form of splendidly developed, reddish brown, very lustrous and transparent, little crystals. They are evidently identical with those prepared by WERNER, and previously described¹⁾; also in this case the angular values somewhat differ from those formerly measured. As a new form, $b = [010]$ was found. The external aspect of the crystals is that of hexagonally or

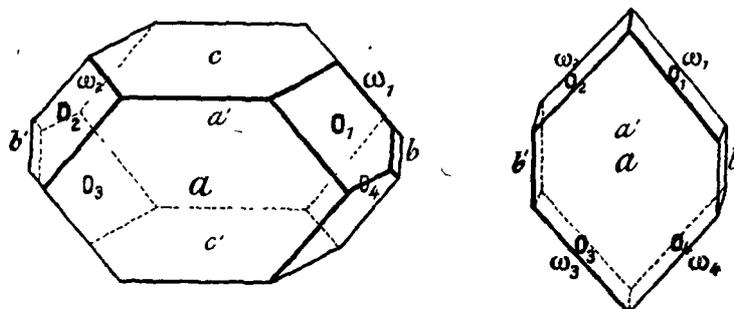


Fig. 6.

trans-Dinitro-diethylenediamine-Cobalti-Nitrate.

octogonally bordered, rather thick crystal-plates.

Monoclinic-prismatic.

$$a : b : c = 1,3040 : 1 : 1,0085 ;$$

$$\beta = 73^\circ 31' \frac{1}{4}.$$

¹⁾ F. M. JAEGER, Zeits. f. Kryst. u. Miner. 39. 565. (1904).

Forms observed: $a = [100]$, predominant and splendidly reflecting; $c = [001]$, smaller, often completely absent, but very lustrous; $b = [010]$, small, well reflecting; $o = [111]$, somewhat broader than $\omega = [\bar{1}11]$, perfectly reflecting. The external habit is flattened parallel to $[100]$, with a slight elongation parallel to the b -, or the c -axis.

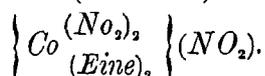
Angles:		Observed:	Calculated:
$a : \omega = (\bar{1}00) : (\bar{1}11) = *$		70°13'	—
$o : \omega = (\bar{1}11) : (\bar{1}11) = *$		77 30	—
$b : o = (010) : (111) = *$		55 54	—
$\omega : \omega = (\bar{1}11) : (\bar{1}11) =$		83 53	83°52'
$b : \omega = (010) : (\bar{1}11) =$		48 4	48 4
$o : \omega = (111) : (\bar{1}11) =$		57 26	57 35
$a : o = (100) : (111) =$		52 40	52 12
$a : c = (100) : (001) =$		73 58	73 31½
$c : o = (001) : (111) =$		45 12	44 59
$c : \omega = (001) : (\bar{1}11) =$		57 22	57 22
$o : o = (111) : (\bar{1}11) =$		69 12	69 12

No distinct cleavability was observed.

The crystals are distinctly dichroitic: on a for vibrations parallel to the c -axis: orange-yellow, for those perpendicular to them: lemon-yellow. The optical axial plane is $[010]$; one optical axis is almost perpendicular to a . Extremely strong dispersion, with $\rho < v$.

§ 9. RACEMIC CIS-DINITRO-DIETHYLENEDIAMINE-COBALTI-NITRITE.

(Flavo-salt).



Dark coloured crystals, which in their external aspect, are highly analogous to those of the corresponding *trans*-derivative. They are very beautifully developed, and possess constant angular values.

Monoclinic-prismatic.

$$a : b : c = 0,7382 : 1 : 0,9094;$$

$$\beta = 82^\circ 57'.$$

Forms observed: $m = [110]$, and $b = [010]$, large and very lustrous; $o = [111]$, large, perfectly reflecting; $\omega = [\bar{2}23]$, small but well reflecting; $c = [001]$, small, giving good reflexes. The external habit is prismatic parallel to the c -axis, and commonly somewhat flattened parallel to $[010]$. Occasionally $[010]$ is absent, in other cases, however, the same is true for $[\bar{2}23]$.

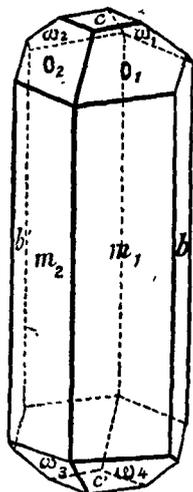


Fig. 7.
Racemic cis-Dinitro-
diethylenediamine-Cobalti-
Nitrite.

20*

Angles:	Observed:	Calculated:
$m : m = (110) : (\bar{1}\bar{1}0) = *$	72°27'	—
$c : m = (001) : (110) = *$	84 19	—
$o : o = (111) : (\bar{1}\bar{1}1) = *$	59 38	—
$b : m = (010) : (110) =$	53 49	53°46'½
$c : \bar{\omega} = (001) : (\bar{2}23) =$	48 34	48 24½
$c \cdot o = (001) : (111) =$	56 46	56 51
$o : m = (111) : (110) =$	38 41	38 50
$\omega : m = (\bar{2}23) : (\bar{1}10) =$	35 35	35 54½
$b : o = (010) : (111) =$	60 10	60 11
$b : \omega = (010) : (\bar{2}23) =$	63 37	63 38
$\omega : \omega = (\bar{2}23) : (\bar{2}23) =$	52 49	52 44

No distinct cleavability was found.

In contrast with the water-containing crystals of the *trans*-derivative, these crystals do *not* manifest any trace of change. They are distinctly dichroitic: on [010] orange-red for vibrations parallel to the *c*-axis, for such as are perpendicular to them: blood-red. The angle of extinction on *b* includes 33° with the direction of the *c*-axis, in the quadrant of the acute angle *a* : *c*.

§ 10. TRANS-DINITRO-DIETHYLENEDIAMINE-COBALTI-NITRITE (*Croceo*-salt).

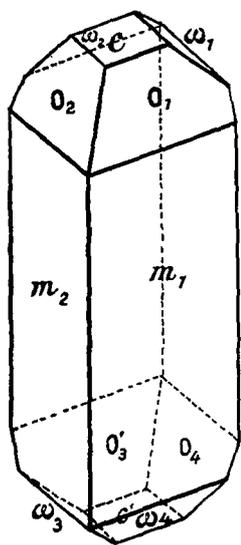
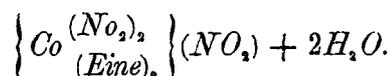


Fig. 8
Trans-Dinitro diethylenediamine-
Cobalti-Nitrite.

Big, splendidly developed, dark brown crystals which, however, soon lose their water of crystallisation, becoming gradually orange-yellow, most rapidly on the faces of the prism.

Monoclinic-prismatic.

$$a : b : c = 1,0458 : 1 : 1,7995 ;$$

$$\beta = 68^\circ 33' \frac{1}{2}.$$

Forms observed: $m = [110]$, predominant and very lustrous; $o = [111]$, large and giving good reflexes, like $c = [001]$, which is much smaller than m ; $\omega = [225]$, very small, and often absent. Notwithstanding the different angular values there exists a striking analogy in aspect and development of these crystals, and those of the anhydrous *cis*-derivative.

Angles:	Observed:	Calculated.
$c : o (001) : (111) =^*$	$54^{\circ}57'$	—
$o : o (111) : (\bar{1}\bar{1}) =^*$	$72\ 31$	—
$o . m (111) : (110) =^*$	$50\ 17$	—
$c : m (001) : (110) =$	$74\ 41$	$74^{\circ}49'$
$m : m (110) : (\bar{1}\bar{1}0) =$	$91\ 30$	$91\ 32$
$c : o (001) : (\bar{2}\bar{2}5) =$	$50\ 59$	$51\ 5$
$o . m (\bar{2}\bar{2}5) . (\bar{1}\bar{1}0) =$	$23\ 42$	$23\ 44$

A distinct cleavability was not found.

The crystals are dichroitic in a way analogous to that found in the case of the *cis*-derivative. On *m* is the angle of extinction oblique.

§ 11. From a solution containing both the *cis*- and *trans*-derivatives, crystals of the form shown in fig. 9 were deposited, which imitate in a striking way the aspect of the *cis*-derivative. In contradiction with those of this substance, however, the crystals of this kind do *not* decay, nor do they lose any water of crystallisation. Moreover, they have often rather oscillating angular values in the zone of the prism, and uneven faces. Their dichroism is analogous to that observed with the pure *cis*-, or *trans*-compounds.

Monoclinic-prismatic.

$a . b . c = 1,0169 : 1 : 0,9030$, $\beta = 66^{\circ} 16'$.

Forms observed: $m = [110]$ predominant and lustrous; $o = [111]$, large, giving good reflexes; $b = [010]$, much smaller than m ; $c = [001]$, small, but well measurable. The external form is prismatic towards the *c*-axis.

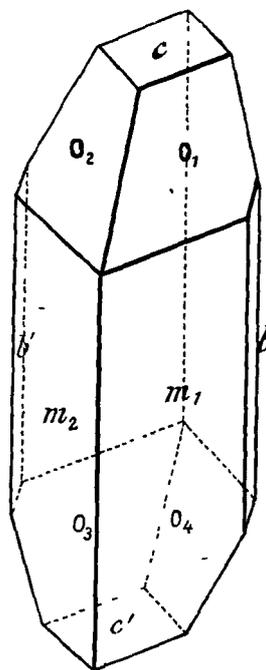


Fig 9.

cis- + *trans*-Dinitro-diethylene-diamine Cobalt-Nitrite.

Angles	Observed	Calculated
$c\ m = (001) (110) =^*$	$72^{\circ}52'$	—
$b\ m = (010) (110) =^*$	$47\ 3$	—
$o\ o = (111) (\bar{1}\bar{1}) =^*$	$64\ 29\frac{1}{2}$	—
$m\ m = (110) (\bar{1}\bar{1}0) =$	$85\ 58$	$85^{\circ}54'$
$c\ o = (001) (111) =$	$48\ 50$	$48\ 26\frac{1}{2}$
$o\ m = (111) (110) =$	$57\ 55$	$58\ 18$
$b\ o = (010) (111) =$	$57\ 47$	$57\ 45\frac{1}{4}$

No distinct cleavability was observed.

Notwithstanding the striking analogy in form, a distinct and real difference in the angular values and parameters is found to exist; the ratio $a:b$ is analogous to that of the *trans*-compound, while for $b:c$ exactly the same is true with respect to the *cis*-derivative. It is difficult to make sure whether here a double-compound of the isomeric salts is present, or a mixed-crystal between them. The fact that the angular values are somewhat fluctuating, and that the faces often reflect irregularly, might be looked upon as an argument of the greater probability of the last mentioned supposition. In any case, the peculiar crystallonomical analogy, and the intermediate shape of these crystals between those of the components, are highly remarkable phenomena, perhaps explicable by the *only feeble morphotropic influence* of NO_2 -groups in general.

It is worth drawing attention, moreover, to the fact that all the *cis*-Diethylenediamine-derivatives here studied, have *monoclinic* symmetry, however not that of the group C_2 . Probably there will be salts of this particular symmetry amongst the optically-active components of these racemic salts.

§ 12. Finally we give here a description of RACEMIC TRIETHYLENEDIAMINE-ZINC-CHLORIDE, the fission of which is also attempted in this laboratory.

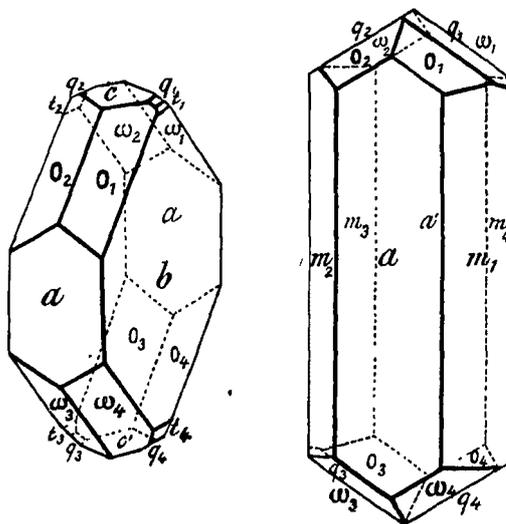
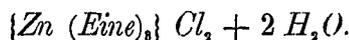


Fig. 10.
Tri-ethylenediamine-Zinc-Chloride.

Beautiful, colourless, very lustrous and transparent crystals, which allow very exact measurements. The substance was prepared from $ZnCl_2$ and *ethylenediamine* in slight excess; it was recrystallised from water. Analysis gave: 20% *Cl*, corresponding with a content of 2 molecules of water.

Monoclinic-prismatic.

$$a : b : c = 0,9238 : 1 : 0,6299;$$

$$\beta = 86^{\circ}33'.$$

Forms observed: $b = [010]$, commonly predominant and highly lustrous, occasionally totally absent; $a = [100]$, well-developed and always present; $o = [111]$, yielding splendid reflexes; $m = [350]$, lustrous, and when present, rather large; $c = [001]$, small, often absent, giving somewhat dull reflexes; $q = [011]$ and $t = [031]$, very dimly reflecting; $\omega = [\bar{1}11]$, highly lustrous and well-developed.

The external form is that of hexagonally bordered, thick plates parallel to $[010]$, or that of short prisms parallel to the c -axis.

<i>Angles:</i>	<i>Observed:</i>	<i>Calculated:</i>
$a : c = (100) \cdot (001) =^*$	86 33	—
$b \cdot b = (010) \cdot (111) =^*$	63 11	—
$a : \omega = (\bar{1}00) \cdot (\bar{1}11) =^*$	62 12 $\frac{1}{2}$	—
$o : o = (111) \cdot (\bar{1}\bar{1}\bar{1}) =$	53 44	53 $^{\circ}$ 44'
$\omega : \omega = (\bar{1}\bar{1}\bar{1}) \cdot (\bar{1}\bar{1}\bar{1}) =$	56 16	56 16
$b : \omega = (010) \cdot (\bar{1}\bar{1}\bar{1}) =$	61 52	61 52
$o : \omega = (\bar{1}\bar{1}\bar{1}) \cdot (\bar{1}\bar{1}\bar{1}) =$	59 50	—
$a : o = (100) \cdot (111) =$	57 58	57 49
$c \cdot b = (001) \cdot (011) =$	32 1	32 9 $\frac{2}{3}$
$q : t = (011) \cdot (031) =$	29 51	29 55
$t : b = (031) \cdot (010) =$	27 53	27 55 $\frac{1}{2}$
$a : m = (100) \cdot (350) =$	55 0	55 47
$m \cdot m = (350) \cdot (\bar{3}\bar{5}0) =$	67 58	68 16

No distinct cleavability was found.

On $[010]$ is the angle of extinction 11° with respect to the c -axis; the plane of the optical axes is probably $[010]$.

*Laboratory for Inorganic and Physical Chemistry of the
University, Groningen, Holland.*

Mathematics. — “*On Elementary Surfaces of the third order*”.
 (Second communication). By B. P. HAALMEYER. (Communicated
 by Prof. BROUWER).

(Communicated in the meeting of June 30, 1917).

§ 4. *If A is cusp in one and not more than one plane α , then α is tangent plane.*

Let α be cuspidal tangent and K_1 and K_2 the branches meeting at A . The Jordan theorem for three dimensional space tells us that within any vicinity of A the branches K_1 and K_2 are connected by a set of points I and by another set II, both sets belonging to F^3 . Again I and II have no points in common and are the continuous (1,1) representations of plane regions I_1 and II_1 which have the character of Jordan regions in the vicinity of the point A_1 corresponding to A . Inside a finite neighbourhood of A all points of F^3 belong to $I + II + K_1 + K_2$. Let EF be a linesegment in α crossing both branches K_1 and K_2 . Suppose I and II were situated on the same side of α . If a parallel linesegment converges from that side towards EF , it would end up by having at least two points in common with I and also two with II: a contradiction. Hence I and II lie on different sides of α , for instance I above and II below α .

Let β be a plane through A not containing the cuspidal tangent α . A cannot be cusp in β ($\beta \neq \alpha$), and the results of § § 1 and 3 show that A cannot be isolated or double point in β . Hence A is in β ordinary point or point of inflexion. On the line of intersection of α and β , A counts double in α hence according to the theorem of p. 117—118, A also counts double on that line in β and this excludes the possibility that A is point of inflexion in β . Thus only remains the possibility that A is ordinary point in β and the line of intersection with α is tangent because A counts double on this line.

Thus has been proved that in any plane not containing the cuspidal tangent in α the point A is ordinary point with tangent in α .

Remains to consider a section of F^3 in a plane β ($\beta \neq \alpha$) through the cuspidal tangent α . Let b be a line through A in β ($\beta \neq \alpha$). We consider a sequence of planes β_1, β_2, \dots through b and converging towards β . The lines of intersection of α and $\beta_1, \beta_2, \dots, \beta$ are respectively denoted by a_1, a_2, \dots, a (all passing through A). In

every plane β_n the line α_n is ordinary tangent at A . It is easy to show that in the vicinity of A the curves in all these planes lie on the same side of α . However this result is not wanted: we merely take a component sequence of planes in which the curves depart from A on the same side of α , let us say above α .

The point A divides the cuspidal tangent α in two semilines, let α' be the one departing from A in the same direction as the cuspidal branches and α'' the other. The corresponding semilines on the converging lines we denote by $\alpha_1', \alpha_2', \dots$ and $\alpha_1'', \alpha_2'', \dots$.

In every plane β_n a branch departs from A above α in the direction of α_n'' . The reasoning used for the examination of a section in a plane through a tangent at a double point shows here that in β the limiting branch departs from A above α in the direction of α'' . The line α has only A in common with F^3 and considering A cannot be double point or cusp in β , the only remaining possibility is that A is point of inflexion in β with α for tangent.

This completes the proof that α is tangent plane.

§ 5. *If A is cusp in two different planes, then A is exceptional point.*

In § 1 it was shown if A is isolated in a plane α , then α is tangent plane or A is exceptional point. In case α is tangent plane it was found that A is *ordinary point* in every plane except α . Hence when A is known to be *cusp* in some planes, and if we want to show that A is exceptional point, then it suffices to prove the existence of a plane in which A is isolated.

Point A is cusp in two different planes. We consider two assumptions: that the two cuspidal tangents *coincide* or *do not coincide*.

First assumption. A is cusp in the planes α and β and the line of intersection α of these planes is the common cuspidal tangent. Let γ be a plane through A not containing the line α .

In α the point A counts double on the line of intersection of α and γ , hence, according to the theorem of page 117—118, A also counts double on that line of intersection in γ . The same holds for the line of intersection of β and γ . Hence in γ two different lines exist on which A counts double, and from this follows that A is in γ either cusp, double point or isolated point.

If A were cusp in γ , then A would be cusp in two planes α and γ and the cuspidal tangents would not coincide. This case shall be dealt with later on, when the second possibility is assumed.

Hence to show that A is isolated in γ it only remains to prove that A cannot be double point in γ .

Let c be an arbitrary line through A in γ , not situated in α or β . Let the plane γ revolve round c . If in any position of γ the point A is isolated then our object is attained. The alternative is that A is double point in all planes through c except the plane through c and a . The foregoing results (p. 113—114) show that the only way to escape immediate contradiction is to assume A cusp in the plane through c and a . But c was an arbitrary line through A in γ only subjected to the condition not to be situated in α or β , hence every plane through a would show a cusp in A and the reasoning given on page 108 shows that then A would be isolated in every plane not containing a .

Second assumption: The cuspidal tangents do not coincide. The line of intersection a of the planes α and β , in which A is cusp, cannot be cuspidal tangent in either of these planes, because a has, except A , another point in common with F^3 . Hence the case indicated in fig. 6 includes all possibilities. Let $BEFC D$ be a plane $\perp a$.

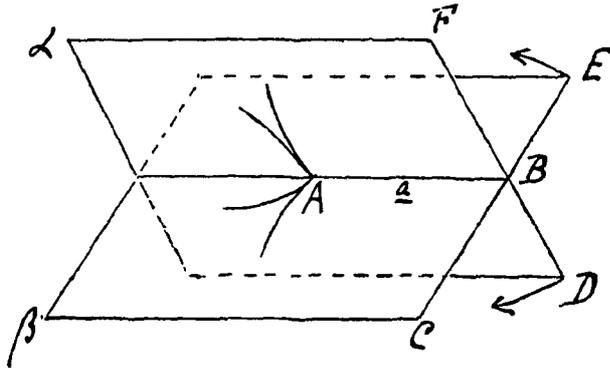


Fig. 6.

The semiplanes aE and aD contain no points of F^3 inside a certain finite neighbourhood of A . On p. 104—105 it was shown that if A is isolated in a plane α , then on one side of α there is a finite neighbourhood of A containing no points of F^3 . The demonstration was entirely based on the analysis situs, hence it is of no consequence whether the semiplanes in which α is divided by a line through A happen to make an angle of 180° with each other or any other angle (\neq zero). Applying this to the case of fig. 6 it follows that there exists a finite neighbourhood of A containing no points of F^3 inside that part of space situated between the semiplanes aE and aD and in which the semiplanes aF and aC are not situated (in the semiplanes aF and aC branches meet at A , so in this angle between aE and aD the point A is certainly not isolated).

Now let the semiplane aE revolve round a towards aF and aD towards aC as indicated by the arrows. For aE there is either a last position in which A is, or a first in which A is not isolated. Let this be aE_1 . In the same way aD_1 for aD . If the angle between aE_1 and aD_1 , in which aF and aC are situated, is $< 180^\circ$, then at once planes can be found in which A is isolated. Thus it remains to consider the cases in which the angle is $\geq 180^\circ$.

In every semiplane through a , in which A is not isolated, two branches must meet at A , because if there was only one, the prolongation of this branch would be situated in the complimentary semiplane, and these two branches would be connected inside any vicinity of A , on both sides of this plane, hence through a there would be no semiplanes at all in which A is isolated.

For this reason, if the angle between aE_1 and aD_1 were $> 180^\circ$, then there would be a finite angle inside which every plane through a has a double point in A . Let γ be a plane *inside* this angle. The semiplanes through a in which A is cusp are supposed to lie *underneath* γ . If γ be turned round a in either direction, A at first remains double point. In γ four branches depart from A , successively AP , AQ , AR and AS . Let a lie between AP and AS and by consequence also between AQ and AR . Let b be a line through A in γ between AP and AQ , hence also between AR and AS . Lastly let β be an arbitrary plane through b . In β two branches arrive at A from *above* γ , because *above* γ , AP is connected with AQ and AR with AS . The alternative that *above* γ , AQ is connected with AR and AS with AP , is excluded, because in the planes through a in which A is cusp, the branches meet in A from below γ .

Now the two branches in β meeting at A from above γ cannot form a cusp in A , because in that case, A could at the utmost be isolated in only one semiplane through a . On the other hand the branches in β meeting at A cannot form an ordinary point at A with b for tangent, because then we could turn γ round a to a position γ' in such a way that the line of intersection of γ' and β would have three different points in common with the curve in β . But in γ' the point A would remain double point (provided the rotation is small enough) hence this line of intersection of γ' and β would have at least four points in common with the curve in γ' : a contradiction.

In β two branches arrive in A from above γ , but we found that in β the point A can neither be cusp nor ordinary point with b for tangent, hence A must be double point in β . β however, was an arbitrary plane through b hence *every* plane through b would have

a double point in A and this has been shown on page 114 to be impossible.

It only remains to consider the case that the angle between the semiplanes aE_1 and aD_1 is equal to 180° . Above it was shown that in every *semi*plane through a in which A is not isolated, two branches must meet at A hence in the plane formed by aE_1 and aD_1 there are four possibilities:

1. A is double point.
2. A is ordinary point with a for tangent.
3. A is cusp.
4. A is isolated.

To complete the demonstration of the existence of a plane in which A is isolated, we shall show successively that 1, 2 and 3 lead to contradictions.

1. Let γ be the plane of aE_1 and aD_1 . From the double point A four branches depart in this plane, successively: AP , AQ , AR and AS . The line a lies again between AS and AP , hence also separates AQ from AR . The semiplanes α and β , in which A is cusp are again supposed to lie below γ . In the complementary semiplanes A is isolated hence *above* γ , AP is connected with AQ and AR with AS , *below* γ , AS with AP and AQ with AR . These last two connections are via the branches meeting at the cusps in α and β . Let d be a line in γ through A , separated from a by the branches RAP and QAS , and let σ be an arbitrary plane through d . In plane σ two branches meet in A from above γ . Both these branches have d for tangent, because A is isolated in *every* semiplane through a *above* γ . Hence in σ , A is ordinary point with d for tangent. In the vicinity of A the curve in σ lies *above* γ , hence *below* γ the point A is isolated in σ . This however holds for any position of σ (through d), but then it is impossible that the branches meeting at A in α (or β) are connected inside every neighbourhood of A with the branches meeting at A in γ .

2. Let γ again be the plane of aE_1 and aD_1 . In this plane A is ordinary point with a for tangent. The semiplanes with cusp in A are again supposed to lie underneath γ . Let d be a line in γ through A having three different points in common with F^* and let σ be a plane through d ($\neq \gamma$). In every semiplane through a above γ , A is isolated and in every semiplane through a below γ , A is not isolated, hence if a semiplane turning round a converges from below towards the semiplane of γ in which A is isolated then in these semiplanes ovals, passing through A and having a for

tangent will contract towards A . This means that in the plane σ the point A counts at least double on d , but d has two other points in common with F^3 : a contradiction.

3. A is cusp γ with b ($\neq a$) for tangent. The original semiplanes α and β , in which A is cusp are again supposed to lie below γ . Semiplanes through a converging from below towards the semiplane of γ , in which A is isolated, again show ovals through A with a for tangent and contracting towards A . Let c be a line in γ through A ($\neq a$ and $\neq b$). The contracting ovals show that c is tangent at A in every plane ($\neq \gamma$). Besides in all these planes A is ordinary point because c has still another point in common with F^3 . c is an arbitrary line in γ through A ($\neq a$ or $\neq b$), hence in every plane through A (except those through a or b) the curve is, in the vicinity of A , situated below γ and the tangents at A all lie in γ . Let us now consider one of the original semiplanes with cusp in A , for instance α . Applying the same reasoning given on p. 115—116 it is found that every line through A in α (except a and the cuspidal tangent in α) must be tangent at A in every plane passing through that line (except α). But this contradicts the result obtained above that in every plane through A (except those through a and b), A is ordinary point with tangent in γ .

§ 6. *Through A passes at least one plane in which A is either isolated, double point or cusp.*

Let A be ordinary point in two different planes, such that the tangents a and b in A do not coincide. In the preceding pages it has been shown that when A counts double on a line in a plane, then A also counts double on that line in any other plane. From this follows that in the plane through a and b , A counts double on both these lines, hence in that plane A is either isolated, double point or cusp. Remains to prove that through an arbitrary point A of F^3 pass two planes in which A is ordinary point with non-coinciding tangents. Except isolated points, double points, cusps and ordinary points there are only points of inflexion. We begin by showing that not all planes through A can have a point of inflexion at A .

Let a be a line through A which has still another point in common with F^3 , and thus can never be tangent at a point of inflexion. Suppose every plane through A shows a point of inflexion at A . In every semiplane through a departs from A a convex arch, situated at first either above or below the tangent at A (at the outset it was assumed that no line through A belongs entirely to F^3).

Now we obtain a contradiction if we can show that none of these semiplanes in which the convex arch departs *above* (*below*) the tangent in A can be limiting element of a sequence of semiplanes in which the convex arch departs *below* (*above*) the tangent.

Let the semiplanes $\alpha_1, \alpha_2, \alpha_3, \dots$ converge towards α . Let the corresponding semitangents be b_1, b_2, b_3, \dots, b . In $\alpha_1, \alpha_2, \alpha_3, \dots$ the convex arches are assumed to depart below b_1, b_2, b_3, \dots , and in α above b . The lines b_1, b_2, b_3, \dots have at least one limiting line b' through A in α . There are three a priori possibilities: b' can be situated above b , below b or can coincide with b .

First case. Let b'' be a semiline through A between b and b' , having a second point B in common with the convex arch departing from A in α (fig. 7). Let β'' be the plane through $b'' \perp \alpha$. Let the lines of intersection of β'' and $\alpha_1, \alpha_2, \alpha_3, \dots$ be respectively $b''_1, b''_2, b''_3, \dots$. From b_1, b_2, \dots we choose a component sequence: $b_{n_1}, b_{n_2}, b_{n_3}, \dots$ having b' for sole limiting element. Corresponding sequences are $\alpha_{n_1}, \alpha_{n_2}, \alpha_{n_3}, \dots$ and $b''_{n_1}, b''_{n_2}, b''_{n_3}, \dots$. For n_1 large enough the semi-

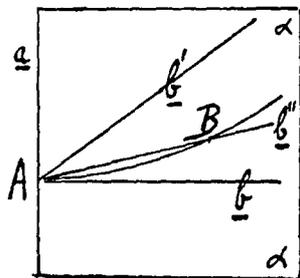


Fig. 7.

lines b_{n_1}, b_{n_2}, \dots (converging towards b') are respectively situated above $b''_{n_1}, b''_{n_2}, b''_{n_3}, \dots$

(converging towards b'').

In α_{n_1} a branch departs from A between b_{n_1} and b''_{n_1} , in α_{n_2} a branch departs from A between b_{n_2} and b''_{n_2} etc. None of these branches can cross $b_{n_1}, b_{n_2}, b_{n_3}, \dots$ (respectively) because these lines as tangents at the point of inflexion A have no other points in common with F^s . Hence in order that in the limiting semiplane α no branch departs from A between b' and b'' it is unavoidable that in the converging planes the branches cross $b''_{n_1}, b''_{n_2}, b''_{n_3}, \dots$ at points converging towards A . But all the lines $b''_{n_1}, b''_{n_2}, \dots$ are situated in one plane β'' , hence in this plane b'' is tangent in A . Then however, it is impossible that A is point of inflexion in β'' , because b'' has, except A , another point B in common with F^s .

Second case. Possibly the line α has, below A , one or two other points in common with F^s . Let C be the nearest. Again b_{n_1}, b_{n_2}, \dots represents a sequence of semi-lines having b' for sole limiting element. In $\alpha_{n_1}, \alpha_{n_2}, \dots$ curves depart from A below b_{n_1} etc. and to the right hand side of α . These curves cannot recross b_{n_1} etc. because these lines have only A in common with F^s , hence in the lower angle between α and b_{n_1} etc. these curves connect A either with the line at infinity

or with C or with the third point of F^3 on a , situated beyond C . Then however, for every q such that $AC > q > 0$ there must exist a point P of F^3 in the limiting plane, such that $AP = q$ and this point P must be situated either on b or a or in the lower angle between b and a . Thus, once more a contradiction is obtained.

Third case. This case is treated in entirely the same way as the second.

It has been shown that a plane through A exists in which that point is not a point of inflexion. Let α be this plane. If in α the point A is not isolated, double point or cusp, the only remaining possibility is that A is ordinary point in α . Let a be the tangent at A in α . a has, besides A , another point C in common with F^3 . When α revolves round a , the point A continues to count double and C to count single on α . Assuming that in no plane through a the point A is isolated, double point or cusp, it follows that in every plane through a , A is ordinary point with a for tangent. Now when α revolves round a and if we consider both semiplanes in which a divides α , it is obvious that at least once a semiplane in which A is isolated must be limiting element of a sequence of semiplanes in which convex arches are situated, passing through A and having a for tangent. Let α' be this semiplane and $\alpha'_1, \alpha'_2, \alpha'_3, \dots$ a converging sequence. In order that A be isolated in the semiplane α' , it is unavoidable that the curves passing through A in $\alpha'_1, \alpha'_2, \alpha'_3, \dots$ are ovals contracting towards A (it must be understood that the converging sequence is started far enough). Let b be a line in α' through A having two other points B and C in common with F^3 . Let β be the plane through $b \perp \alpha'$, and let b_1, b_2, b_3, \dots be the lines of intersection of β and $\alpha'_1, \alpha'_2, \alpha'_3, \dots$ respectively. Every line b_1, b_2, \dots intersects the oval in the corresponding plane at a second point, different from A . When the ovals contract, these points converge towards A . Hence in plane β the line b would be tangent at A , but this is impossible, because b has two other points B and C in common with F^3 . This completes the required demonstration.

Second part. Let A be ordinary point in a plane α and a ordinary line of intersection through A in α .

Theorem 1: If a sequence of lines in R_3 converges towards line a , then points of F^3 on these lines converge towards A .¹⁾

¹⁾ This theorem and its demonstration hold also when A is situated on a line of F^3 , provided this line does not lie in α .

Let AB and AC be the branches arriving at A in α and $B'C'$ a linesegment crossing both arches AB and AC . The JORDAN theorem for three dimensions shows that a double connection exists between the branches AB and AC by means of two sets of points I and II, having no points in common. If I and II were situated on the same side of α then a parallel linesegment converging from that side towards $B'C'$ would end up by having at least two points in common with I and also two with II: an impossibility. Hence I and II lie on different sides of α and inside any neighbourhood of A points of F^3 exist on both sides of α .

The vicinity of A on F^3 is the (1,1) continuous representation of the vicinity of a point in a plane. From this follows that inside any finite neighbourhood of A the points of R_3 which are not situated on F^3 , belong to either of two regions G_1 and G_2 , which regions are not connected within that finite neighbourhood of A . The common boundary of these regions F^3 has JORDAN character. Inside any vicinity of A we found points of F^3 on both sides of α . Let A_1, A_2, \dots be a sequence of these points converging from above and A_1', A_2', \dots a sequence converging from below towards A . A_1 and A_1' can be joined by a single path, belonging entirely to G_1 and by another belonging to G_2 . In the same way A_2 and A_2' etc. By going far enough in the sequence it follows from the Unbewalltheit that these paths can be kept inside an arbitrarily small neighbourhood of A . Each path connects a point above α with a point below α , hence in α points of both G_1 and G_2 exist inside any vicinity of A . From this follows that in α the region on one side of the convex arch BAC belongs to G_1 and that on the other side to G_2 .

Let D and E be points on line α on different sides of A . D belongs to G_1 , E to G_2 . Round D a finite sphere b_1 exists, all internal points of which belong to G_1 and round E a sphere b_2 containing points of G_2 only.

Now let the linesequences a_1, a_2, \dots converge towards α . Let on these lines the points D_1, D_2, \dots converge towards D and E_1, E_2, \dots towards E . D_1, D_2, \dots end up by being internal to sphere b_1 and then certainly belong to G_1 . E_1, E_2, \dots become internal to b_2 and then belong to G_2 . Hence for n larger than some finite number the finite linesegment $D_n E_n$ of a_n carries at least one point of F^3 and these points can only converge towards A , because this is the only point of F^3 on the segment DE of α .

Theorem 2: If the planes $\alpha_1, \alpha_2, \dots$ converge towards α , then the section of F^3 in α consists of the limiting set of the sections in

α_n , or is composed of this limiting set together with an isolated point.

Because F^3 is a closed set, the section in α contains the entire limiting set of the sections in α_n .

From *theorem 1* follows that an ordinary point in α must be limiting point of the sections in α_n . For a point of inflexion in α this is proved in a strictly analogous way. That a double point or cusp in α is limiting point of the sections in α_n can easily be shown, if we remember the connection existing between the branches arriving at such a point. This connection has been treated in the *first part*.

Remains only a possible isolated point in α . That such a point need not be limiting point of the sections in α_n may be seen from examples of cubic surfaces.

Theorem 3: The tangent plane changes continuously with the corresponding point of F^3 .

Let the points A_1, A_2, \dots of F^3 converge towards A . If $\alpha_1, \alpha_2, \dots, \alpha$ are the corresponding tangent planes we have to show that $\alpha_1, \alpha_2, \dots$ converge towards α , and nothing but α . Suppose $\alpha_1, \alpha_2, \dots$ had a limiting plane β , different from α , but of course passing through A . Foregoing results show that A is in β either ordinary point or point of inflexion, hence anyway a line a through A in β can be chosen having three different points A, B , and C in common with F^3 . Let a_1, a_2, \dots be a linesequence respectively passing through A_1, A_2, \dots and situated $\alpha_1, \alpha_2, \dots$ and converging towards the line a in the limiting plane β (these lines a_1, a_2, \dots can be fixed in different ways by a simple condition). From *theorem 1* follows that for $n >$ some finite number the lines a_n carry points B_n and C_n of F^3 converging towards B and C respectively. The point A_n however counts double on any line in the tangent plane α_n , hence lines would be constructed having four points in common with F^3 : a contradiction.

Theorem 4: An elliptical¹⁾ point of F^3 can only be limiting point of elliptical points.

Let the points A_1, A_2, \dots of F^3 converge towards A . Corresponding tangent planes $\alpha_1, \alpha_2, \dots, \alpha$. Suppose A_n were for every n double point or cusp in α_n . Then in every α_n a branch would connect A_n

¹⁾ Points of F^3 which are in the tangent planes isolated, double points or cusps we call respectively elliptical hyperbolical and parabolical points. Except these F^3 can contain one exceptional point, the character of which has been dealt with in the *first part*.

with the line at infinity and in the limiting plane α the point A could not be isolated, because a sequence of connected sets of points each having breadth $>$ some finite value p cannot converge towards a single point.

Theorem 5: A hyperbolic point of F^3 can only be limiting point of hyperbolic points.

A_1, A_2, \dots converge towards A . Corresponding tangent planes $\alpha_1, \alpha_2, \dots, \alpha$. A is supposed to be hyperbolic. We shall show that if A_n is assumed to be elliptical or parabolical for every n , contradictory results are obtained.

The points of space inside a sufficiently small but finite vicinity of A which are not situated on F^3 belong to either of two regions G_1 and G_2 which are not connected inside that vicinity of A .

The results obtained when proving *theorem 1* show that if we move round a hyperbolic point in the tangent plane we alternately pass through G_1 and G_2 , to be more exact: twice we pass through G_1 and twice through G_2 . Moving round a parabolical point in the tangent plane we pass once through G_1 and once through G_2 . In the tangent plane of an elliptical point however, a finite surrounding of that point belongs entirely to only one of the two regions, for instance to G_1 . Hence an arbitrary line through an elliptical point in the tangent plane departs on both sides in the same region. This also holds for a parabolical point, provided we exclude the cuspidal tangent.

From the converging planes $\alpha_1, \alpha_2, \dots$ we choose a component sequence $\alpha_{n_1}, \alpha_{n_2}, \dots$ such that in each of these every line through A_{n_1}, A_{n_2}, \dots departs on both sides in the same region, for instance G_1 (again cuspidal tangents excluded). In the limiting plane α we choose two points B and C of G_2 diametrically situated with regard to A . Let b_1 and b_2 be spheres round B and C ; all internal points of which belong to G_2 . Let a be the line through C, A and B and a_{n_1}, a_{n_2}, \dots a line sequence respectively passing A_{n_1}, A_{n_2}, \dots and situated in $\alpha_{n_1}, \alpha_{n_2}, \dots$, converging towards α and containing no cuspidal tangents (again $\alpha_{n_1}, \alpha_{n_2}, \dots$ can be fixed by a simple condition). In the end the lines a_{n_1}, a_{n_2}, \dots will pass through the spheres b_1 and b_2 , but this means that a line through a point which counts double, departs on both sides of that point in G_1 and further on on both sides carries points of G_2 . Hence on both sides F^3 must be crossed again and lines would have been constructed carrying four points of F^3 .

Theorem 6: If a hyperbolic point moves continuously, then the tangents in the tangent plane change continuously also.

Let the hyperbolic points A, A_1, \dots converge towards the hyperbolic point A . Corresponding tangent planes $\alpha_1, \alpha_2, \dots, \alpha$. A sequence of tangents through A_1, A_2, \dots in $\alpha_1, \alpha_2, \dots$ cannot have for limit a line through A in α which is not tangent, for such a line would have, besides A , another point in common with the curve in α and *theorem 1* tells us that the converging lines would carry points of F^3 having this second point of intersection as limiting point. This, however, contradicts the assumption that the converging lines are tangents at double points converging towards A .

To prove *theorem 6* it only remains to show that the tangents at the double points in $\alpha_1, \alpha_2, \dots$ cannot converge to only one of the two tangents in α . Let a and b be the tangents in α and let us assume that the tangents in the converging planes $\alpha_1, \alpha_2, \dots$ have only a as limiting element. For increasing n the tangents in α_n form a diminishing angle tending towards zero. The part of α_n inside this decreasing angle converges to the line a only and considering a

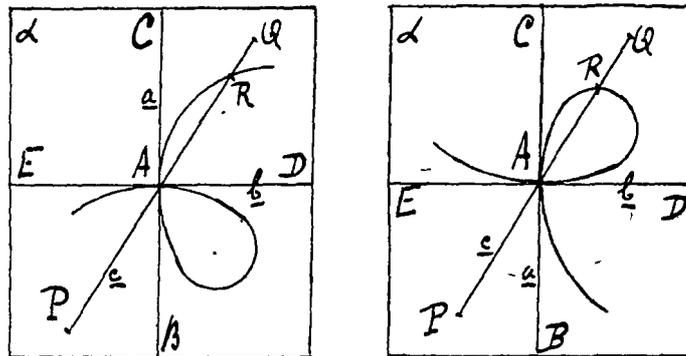


Fig. 8.

does not belong entirely to F^3 , it is unavoidable that for $n >$ some finite number the part of α_n inside the decreasing angle contains that part of the curve which is of the second order and besides this loop of the curve has the point A for sole limiting point (this "loop" can, of course be a projective oval, having one or two points in common with the line at infinity).

Besides the loop, two branches depart from A_n in the planes α_n , belonging to the part of the curve which is of the third order. Let $\alpha_1, \alpha_2, \dots$ contain a component sequence $\alpha_{n_1}, \alpha_{n_2}, \dots$ of planes in which these branches depart in the direction of the semitangents converging

towards the semiline AB . This implies no restriction, because with respect to the curve in α both possibilities indicated in fig. 8 are considered.

Let c be a line through A in α inside the angle EAB . This line has, besides A , another point in common with the curve in α . Let $c_{n_1} c_{n_2} \dots$ be a sequence of lines through $A_{n_1} A_{n_2} \dots$, respectively situated in $\alpha_{n_1} \alpha_{n_2} \dots$ and converging towards c . The points $P_{n_1} P_{n_2} \dots$ on these lines are supposed to have P for limiting point. Let $a_{n_1} a_{n_2} \dots$ be a sequence of tangents in $\alpha_{n_1} \alpha_{n_2} \dots$ and lastly we assume that the points $B_{n_1} B_{n_2} \dots$ on these lines converge towards B . (see fig. 8).

In α_{n_1} a branch departs from A_{n_1} between $A_{n_1} B_{n_1}$ and $A_{n_1} P_{n_1}$, in α_{n_2} a branch departs from A_{n_2} between $A_{n_2} B_{n_2}$ and $A_{n_2} P_{n_2}$ etc. These branches cannot cross the tangents $A_{n_1} B_{n_1}$ etc. again hence in order that in α no branch leaves A between AB and AP it is necessary that the branches in the converging planes cross $A_{n_p} P_{n_p}$ in points converging towards A_{n_p} . According to *theorem 1*, however, the lines c_{n_p} (of which $A_{n_p} P_{n_p}$ forms part) end up by carrying points of F^3 converging towards R and because A_{n_p} counts, double lines would exist having four points in common with F^3 .

The tangents at a double point divide their plane in two parts, respectively containing the loop of the curve and the part of the third order.

Theorem 7: If a hyperbolic point moves continuously, hence the tangent plane with tangents also changes continuously, then the parts of the tangent planes, containing the pieces of the third order, merge in each other and it follows that the same holds for the parts containing the loops. Besides the loop cannot switch round 180° .

$A_1 A_2 \dots$ converge towards A (all hyperbolic). Tangent planes $\alpha_1 \alpha_2 \dots \alpha$. The tangents in α_n form four angles round A_n , successively I_n, II_n, III_n and IV_n . These converge respectively towards I, II, III and IV in α . Suppose for every n the *principal branch* (that is the part of the third order) in α_n lies in $I_n + III_n$. This means that in α_n branches depart from A to both sides inside these angles, which are connected via the line at infinity. But then it is unavoidable that in the limiting plane α a branch departs in I and another in III, hence this part of α again contains the principal branch.

Suppose for every n the loop in α_n departs in II_n . In order that A be isolated in α in the angle II it is necessary that these loops contract towards A . Hence, in the end they cannot reach the line

at infinity and it follows that in a the point A must be isolated also in the angle IV. It follows that the oval cannot switch round 180° .

Theorem 8: If a sequence of hyperbolic points converges towards a parabolical point then both sets of tangents of the hyperbolic points converge exclusively towards the cuspidal tangent of the parabolical point. Besides the direction in which the principal branches (that is the parts of the third order) depart, cannot switch round 180° .

Let the hyperbolic points A_1, A_2, \dots converge towards the parabolical point A . Tangent planes $\alpha_1, \alpha_2, \dots, \alpha$. A line through A in α which is not cuspidal tangent has, besides A , an ordinary point B in common with the curve in α . *Theorem 1* shows that such a line can never be limit of tangents at double points converging towards A . This proves the first part of *theorem 8*. In the same way as when proving *theorem 6* we can show again that the loop in the converging planes lies inside the diminishing angle of the tangents and converges towards A .

In the case of *theorem 7* it was shown that the loop cannot switch round 180° , and it followed that the principal branch cannot change its direction discontinuously either. Here, however, the loop has disappeared in the limiting plane α and a new-proof is required that the principal branch cannot change its direction in discontinuous fashion.

Let AC be the cuspidal semitangent in α departing in the same direction as the cuspidal branches and AB the other half. Suppose in the converging planes the principal branch departs from A_n in the direction of the semitangents converging towards AB , but in α in the direction AC . Let b be a line through A in α ($\neq BC$) and b_1, b_2, \dots a sequence of lines converging towards b respect. situated in $\alpha_1, \alpha_2, \dots$ and passing through A_1, A_2, \dots .

The principal branches depart in α_n from A_n to both sides inside the increasing angles of the tangents. These branches do not cross the tangents again, but each goes in its own angle to the line at infinity. Besides they depart in directions converging towards AB . In order that in α no branches depart from A to that side of b on which AB is situated it is necessary that both branches in α_n (for n large enough) cross the lines b_n (converging towards b) on both sides of A_n at points converging towards A . However, on every line b_n the point A_n counts double, hence lines would have been constructed having four points in common with F^3 .

Theorem 9: If A is double point in plane α and if a point

departs from A along the principal branch in α , then at first the loops in the corresponding tangent planes will cross plane α .

Let us consider a sequence of points on arch CA (fig. 9) converging towards A . Provided we start close enough to A all these points are hyperbolic (theorem 5). We assume that the loops do *not* cross plane α and we select a component sequence of points such that the corresponding loops all arrive from the same side of α for instance from above. Let this sequence of points be A_1, A_2, \dots . Tangent planes $\alpha_1, \alpha_2, \dots$.

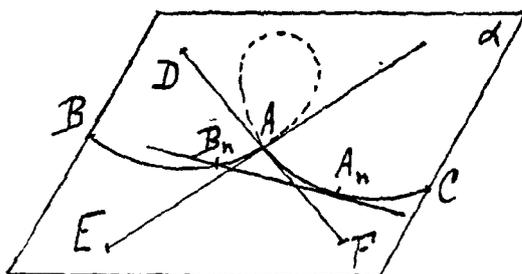


Fig. 9.

The tangent to AC in A_n intersects arch AB in B_n . For increasing n , B_n converges towards A . Plane α_n contains line $A_n B_n$. Let $A_n D_n$ be the semitangent in α_n which converges towards AD . Let us consider in α_n that part of the plane inside angle $D_n A_n B_n$. For increasing n no principal branch in α_n can continue to depart inside this angle, because the principal branches depart from A_n in directions converging towards AE and AF . B_n , however, belongs to the principal branch, as we assumed that the loop does not cross α . This principal branch which crosses $A_n B_n$ at B_n , cannot connect B_n with A_n inside angle $B_n A_n D_n$, but on the sides of this angle B_n is the only point of F^3 , because A_n counts double on $A_n B_n$ and triple on $A_n D_n$, hence it is unavoidable that inside angle $B_n A_n D_n$ this branch connects B_n with the line at infinity. Angle $B_n A_n D_n$, however, converges towards the semiline AD and B_n towards A . It follows that line AD would belong entirely to F^3 : a contradiction. This completes the proof of theorem 9.

Remark: When a point departs from A along the principal branch in α the tangent can be divided in a front half and a back half. The preceding proof shows that at first the loop departs inside that angle of the tangents, in which the back half of the tangent in α is situated. We shall indicate this briefly by saying that at first the loop trails behind.

Theorem 10: Round a parabolical point a finite surrounding exists in the tangent plane containing hyperbolical points only (except of course the original parabolical point itself).

Let A be parabolical point, a tangent plane and a cuspidal tangent. The points A_1, A_2, \dots on arch BA converge towards A . Corresponding tangent planes a_1, a_2, \dots . The lines of intersection of a and a_1, a_2, \dots are respectively a_1, a_2, \dots . These lines are tangents in a converging towards a . The points of intersection of a_1, a_2, \dots and arch AC we indicate by C_1, C_2, \dots . These points converge towards A . (Fig. 10).

Let b_1, b_2, \dots be lines respectively situated in a_1, a_2, \dots passing

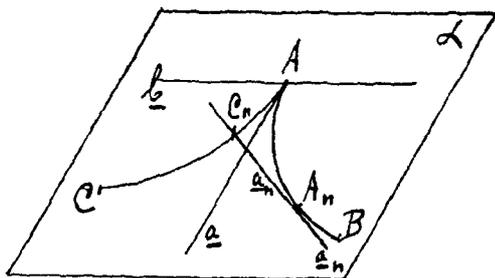


Fig 10

through A_1, A_2, \dots and perpendicular to a_1, a_2, \dots . These lines b_1, b_2, \dots converge towards $b \perp a$ in a . Now let us assume all points A_1, A_2, \dots were elliptical or parabolical. In no case the lines b_n can continue to be cuspidal tangents at A_n in a_n for even if A_n continued parabolical the cuspidal tangents would converge towards a (this follows again from *theorem 1*). Hence for n larger than some finite number the line b_n has, except A_n , another point in common with F^3 which counts single.

b_n divides the corresponding plane a_n in two semiplanes. We consider the one that does not contain C_n . These semiplanes converge towards the top one of those in which b divides a (fig. 10). If A_n is parabolical, then for n large enough the cuspidal branches depart in the semiplane of a_n which does *not* contain C_n , because the branches departing from A_n cannot switch round 180° in the limiting case (this is shown in a way analogous to that used for *theorem 8* where hyperbolical points converged towards a parabolical point).

Hence for n large enough no branch departs from A_n in the semiplane of a_n containing C_n . But C_n lies on the curve in a_n , and b_n carries besides A_n , only one singly counting point of the curve. But A_n is elliptical or parabolical, hence the curve in a_n (with possible exception of A) is connected. From this follows that C_n must be

connected with the line at infinity in the corresponding *semiplane* of α_n .

Passing on to the limit the *semiplane* of α_n containing C_n converges towards the top *semiplane* of α (fig. 10) and C_n converges towards A . But then it is unavoidable that a branch departs from A in the top *semiplane* of α (including line b). Hence a contradiction is obtained and it has been shown that the points A_1, A_2, \dots end up by being hyperbolical.

Theorem 11: If a surface F^3 contains no straight line, it cannot exist.

JUEL has shown¹⁾ that a non-degenerated elementary curve of the third order contains *one* and only one point of inflexion if that curve has a double point or cusp and that otherwise the curve has *three* and only three points of inflexion. We consider an arbitrary plane section of F^3 . If this section contains no straight line it has at least one point of inflexion. This point can be hyperbolical or parabolical. In the latter case we can, according to *theorem 10*, find hyperbolical points in the corresponding tangent plane. Hence in any case a hyperbolical point of F^3 can be found. Let this be A with α for tangent plane. We do not consider the loop of the curve in α , but only the principal branch. This branch has, according to JUEL, one and only one point of inflexion B . We consider two points A' and A'' , departing from A in opposite directions along the principal branch and meeting again at the point of inflexion B , after moving continuously along the curve. *Theorem 9* shows that the loops of A' and A'' , at first cross α and besides we found that at first they trail behind. Now in this state of affairs no change is possible before A' and A'' meet again at B : The tangents at a double point change continuously (*theorem 6*), hence only at a point of inflexion can they pass through α . Besides the loop cannot switch round 180° or change into a principal branch (*theorem 7*). Lastly it is impossible that on the way from A to B the point A' (or A'') changes its character, for this can only happen via a first parabolical point. Then, however, the angle between the tangents, inside which the loop is situated, would tend towards zero, and considering the loop crosses α all the time, the limiting position of the tangents would be situated in α and this would mean a cusp or point of inflexion in α , because the above mentioned limiting line coincides with the cuspidal tangent (*theorem 8*). Hence A' and A'' arrive at the point of inflexion B both hyperbolical with the loops crossing α and trailing behind.

¹⁾ Proc. Danish Acad. loc. cit. § 5.

Theorem 4 shows that B cannot be elliptical, hence B is parabolical or hyperbolic. In the former case the points A' and A'' would (*theorem 8*) prescribe opposite directions for the cuspidal branches departing from B : a contradiction.

Remains the case that B is hyperbolic. Let a be the tangent at B in α . Now A' and A'' prescribe opposite directions for *that* branch of the loop in the tangent plane of B , which has a for tangent, (the loops trail behind and cannot switch round discontinuously). Hence once more a contradiction is obtained.

CORRIGENDUM.

In the first communication on this subject page 103 line 1 and 2, for: "twodimensional continuum" read "closed twodimensional continuum".

Chemistry. — “*The boiling point line of the system: hexane-nitrobenzene.*” By Dr. E. H. BÜCHNER. (Communicated by Prof. HOLLEMAN).

(Communicated in the meeting of June 30, 1917).

On studying the experimental data available, it occurred to me that one may easily predict, whether a system of two partially miscible liquids will show a maximum in the vapour pressure curve or not. The following rule, indeed, may be enunciated: when the difference of the boiling points of the two substances is less than 100° , a maximum pressure is found; when the boiling points differ more than 100° , no maximum occurs in the p, x -curve. Of course, this limit is not perfectly sharp; yet, the deviations are remarkably few. I have been able to find only three systems ¹⁾, which may really be considered exceptions to the rule, as one observes a maximum, although the boiling points differ from 110° to 120° .

This made me sufficiently trust in the rule to predict with its help the behaviour of systems not yet investigated, and to expect, for instance, in the system *n*-hexane-nitrobenzene (boiling points resp. 69° and 210°) a p, x -curve, continually descending from the hexane side. This is particularly interesting, because a research by KOHNSTAMM and TIMMERMANS ²⁾, in connexion with a rule given by VAN DER WAALS, would lead to the conclusion that the p, x -curve must have a maximum.

These authors, indeed, reckon the systems, which consist of nitrobenzene and a hydrocarbon, among the group: “splitting up of the plait”, whereas VAN DER WAALS has shown that splitting up of a plait is only possible, if a minimum critical temperature occurs in the system (which is equivalent to a maximum in the vapour pressure curve). KOHNSTAMM and TIMMERMANS, it is true, expressed themselves with some reserve. While they were able to observe experimentally the minimum temperature in the plaitpoint curve of the system decane-nitrobenzene, they were prevented in doing the same for hexane-nitrobenzene by the appearance of solid nitrobenzene.

¹⁾ Cf. BAKHUIS ROOZEBOOM, *Heterogene Gleichgewichte*, zweites Heft, II (in the press).

²⁾ These Proceedings, 15, November 1912.

They only ascertained that the value of $\frac{dt}{dp}$ is negative, continually decreasing, however, in absolute amount: it falls namely from $-0^{\circ},0164$ to $-0^{\circ},0031$. In analogy with decane-nitrobenzene and petroleum-nitrobenzene¹⁾ they concluded the system hexane-nitrobenzene also to belong to the type: splitting up of the plait. Since, however, according to VAN DER WAALS, this goes necessarily together with the existence of a maximum pressure, we get obviously in defiance of the rule enunciated above, which requires no maximum. One of the three statements, therefore, must be wrong; I thought it, accordingly, of some interest to investigate experimentally, if a maximum exists or not.

Instead of the vapour pressure curve one may as well determine the boiling point line, which is more convenient. The question then becomes whether the boiling line exhibits a minimum or not.

The determinations were carried out in Professor SMITS' apparatus, formerly described²⁾; the substances used were carefully dried and fractionated. The results of the measurements are joined in the table below, and represented moreover in the figure.

As appears most clearly from the figure, there is no question of a minimum; the curve shows, on the contrary, the shape, often found in systems with limited miscibility above the critical solution point³⁾. A comparatively quick rise of short duration is followed by a very slow increase of the boiling temperatures over an extensive area⁴⁾; an inflexion point occurs and finally the curve rises very steeply to the boiling point of pure nitrobenzene.

This result fully agrees with my expectation; the question now arises how KOHNSTAMM and TIMMERMANS' determinations may be made to tally with it. It seems to me most likely that the system belongs to the type "retrogression", as the authors mentioned previously believed themselves also. We have, then, only to remark the particularity that the plaitpoint curve does not ascend regularly from the critical endpoint, but rises in the beginning slowly, afterwards more steeply. Thereagainst no objection, indeed, can be raised; although in the single system that is fully investigated (methylethylcetone-water), a uniform rise is observed, the known

1) For this system too, one gets in conflict with my rule; but it must not be forgotten, that petroleum itself is already a mixture, and that we have, thus, no binary system.

2) These Proceedings, April 1917

3) In our system 19.2° : TIMMERMANS, Zeitschr. phys. Chem. 58, 186, 1908.

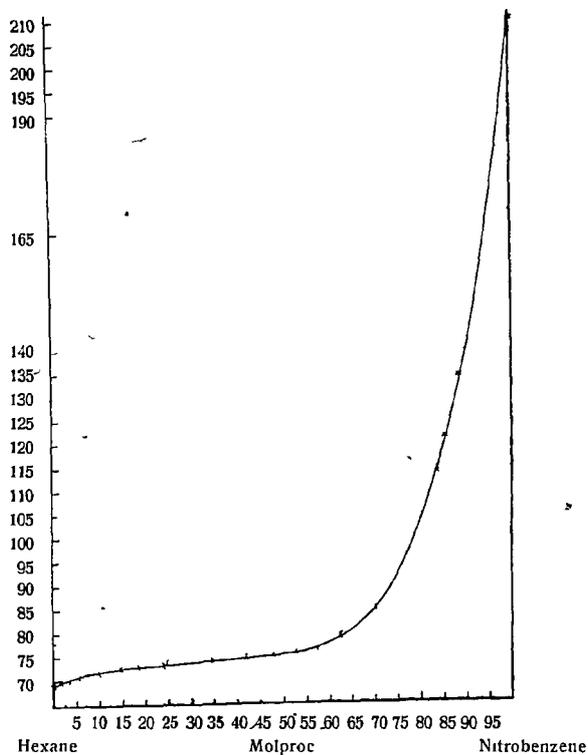
4) Nearly coinciding with the region of limited miscibility.

Boiling points hexane-nitrobenzene at a pressure of 76 cm.

Composition in mol.proc. nitrobenzene	Boiling point
0	69.0
1.6	69.7
3.5	70.0
5.7	70.7
7.5	71.3
10.0	71.7
14.6	72.3
18.5	72.8
24.0	73.3
24.8	73.55
34.4	74.1
41.7	74.9
47.6	75.3
52.7	75.7
53.0	75.9
57.6	76.3
62.5	79.3
70.2	85.1
83.5	114
85.4	121.5
88.5	134.5
100	210

data regarding the other systems are so scanty as not to allow of any positive assertion on the course of the curves. The shape, which, in our system, I consider probable, may even happen to be the most usual.

A further conclusion from this investigation is that systems, one component of which is a member of a homologue series, need not belong to the same type of demixtion phenomena. If we pass from decane to hexane, the limited miscibility remains, it being connected above all things with the chemical nature of the components, but



the type of the vapour pressure (resp. boiling) curves does change; with regard hereto the increasing difference in volatility of the two substances is of dominating importance.

It need not be argued that *a fortiori* no maximum pressure occurs in systems with the lower members of the series, e.g. pentane and butane¹⁾; these too will belong to the type retrogression. This is the more remarkable, because now the type: splitting up of the plait with a negative value of $\frac{dt}{dp}$, which was already considered rare on theoretical grounds, loses the greater part of its few representatives.²⁾ KOHNSTAMM's earlier opinion that this type would hardly ever occur seems therefore to be right, in spite of his later experiments which made him withdraw his statement.

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¹⁾ As has been found, indeed, for isopentane by KONOWALOW.

²⁾ Cf. e.g. NIEUWKAMP's review, dissertation Amsterdam 1915

Physiology. — "*Photography of the fundus of the human eye*". By
Prof. I. K. A. WERTHEIM SALOMONSON.

(Communicated in the meeting of April 27, 1917).

Since the discovery of the ophthalmoscope by HELMHOLTZ, disclosing the interior of the living human eye, many different attempts have been made to keep a permanent record of the aspect of the retina on a photographic plate. This proved to be much more difficult than viewing the background of the eye. The greatest difficulty was caused by the reflexes given off on the surface of the cornea and the anterior and posterior surface of the lens. Different ways have been tried to get rid of these reflexes and after more or less successful attempts by BAGNÉRIS, GUILLOZ, GERLOFF and others, DIMMER succeeded in obtaining satisfactory results. Shortly afterwards THORNER and also WOLFF, working on different lines, showed photographs of the living human retina which were nearly as good as those of DIMMER. His photographs are generally excellent.

Of the eyes of animals NICOLAËW was also successful in obtaining good negatives. But his method did not yield satisfactory results with the human eye, the fundus of which is infinitely more difficult to photograph than the animal fundus.

For practical purposes as yet only DIMMER's and perhaps WOLFF's method have to be considered. But DIMMER's method necessitates a costly instrumentarium, requiring much room and skilled assistance. I do not know of its being used outside his own clinic, except by a very few specialists (e. g. Hess.).

The different methods for obtaining a reflexless image of the fundus have been ably discussed by GULLSTRAND, who gave a clear and critical review of the general and special conditions necessary for getting clearly defined ophthalmoscopic images, free from any reflex. Finally his results were embodied in his large demonstration-ophthalmoscope, constructed by ZEISS, which shows the ophthalmoscopic appearance of the human eye with less difficulty, more extensively with a higher magnification and yet more clearly than any other instrument of the same kind. As yet this instrument cannot be used for photographic purposes. But it seemed to me that it

might possibly be rendered suitable for such. After a few preliminary trials I had an instrument made for me, differing in many respects from the original one.

The Nernstlamp was discarded and was replaced by a lamp of greater intrinsic brilliancy. The arrangement of the illumination-tube was slightly changed so as to allow a relatively greater part of the light reaching the eye.

In the ZEISS instrument the image of the Nernst filament is projected upon a slit and by means of a second condenser into the pupil of the eye. The light, after leaving the second condenser is deflected by a glass plate, making an angle of 45° with the axis of the tube. The optical system for viewing the fundus looks through this glass plate. With this construction about 8.5% of the light leaving the second condenser is projected into the eye and 91.5% of the light leaving the eye reaches the objective of the viewing-tube. I placed the glass-plate so as to make an angle of 65° with both tubes, which allowed about 21% of the light to enter the eye and 79% to reach the observing eye. In this way the amount of light falling on the photographic plate was about doubled.

The Nernstlamp has an intrinsic luminosity which I measured as of 3.1 Hefnercandles per square millimeter. By the use of a specially constructed halfwattlamp of low voltage I got an intrinsic brilliancy of nearly 29 units per square millimeter. A suitable small camera having been adapted to the instrument I got, after a few failures, usable negatives of a diameter of 26 to 30 millimeters, showing about 27 degrees of the fundus and covering an area of $4\frac{1}{2}$ times the diameter of a normal optic disc.

The negatives were sometimes good, though very often blurred, owing to the long exposure of 0.4 to 0.5 of a second. I have tried to get better results with a small arclamp of about 5 amperes but without much success. Though the intrinsic intensity was 3 times greater, the area was notably smaller. With an entirely modified construction and with an arclamp of 25—30 amperes better results might be expected as the exposure might have been reduced to $\frac{1}{8}$ of a second. As the angle of view was also rather small and could only be enlarged by a complete reconstruction of the apparatus, I have kept the instrument as it was, and have tried to get more satisfactory negatives in quite another way.

With the indirect ophthalmoscopy we can entirely eliminate the reflexes on the cornea and the lens by following GULLSTRAND'S method. But we always retain two reflexes on the ophthalmoscope lens. These do not hinder visual observation as they are rather small and

by slight movements of the ophthalmoscope lens can always be removed from any part of the real image of the fundus.

But their presence is an absolute hindrance to photography. They cause the appearance on the negative of one or two large spots, covering its central part and having a diameter of nearly $\frac{1}{3}$ of the whole negative. The brightness of these reflexes is several hundred times larger than that of the image of the fundus. I have tried in many different ways to eliminate these reflexes and have found that they could be reduced so as to be almost invisible by means of two small screens.

In accordance with this principle I constructed a new photographic ophthalmoscope. The diameter of the negative is 40 mm. The retina is photographed with a magnification of 4.7 times, over an angle of 33 degrees, giving an image with a diameter of about $5\frac{1}{2}$ times as large as the normal optic disc. The small arclamp of 4 to 5 Amperes with which the instrument is fitted allows of exposures of $\frac{1}{14}$ of a second, though this may be reduced to $\frac{1}{20}$ of a second in some cases. However as the reflex time for the orbicular muscle reflex is much longer there is no advantage in further reduction of the time of exposure. The exposures are short enough to give sharp negatives even in a case of nystagmus.

The quality of the negatives is generally sufficient. They are sharply defined. Generally the middle part is more strongly impressed than the marginal parts, as was to be expected. Yet direct enlargements or prints can nearly always be made without any retouching.

The whole apparatus, which will be fully described elsewhere can be used for both eyes without any alteration except the ordinary focussing. The dimensions are only slightly larger than those of the GULLSTRAND-ZEISS demonstration-instrument. Its use is not much more difficult than the making of an ordinary photograph with a studio-camera.



Fig. 1.
Normal fundus.

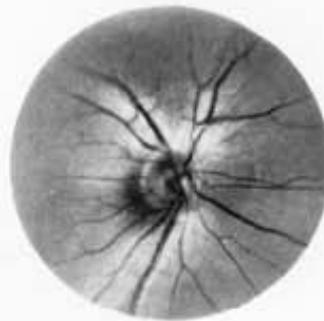


Fig. 2.
Normal fundus.

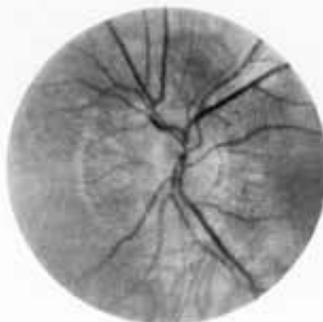


Fig. 3.
Normal fundus with chorooidal vessels.

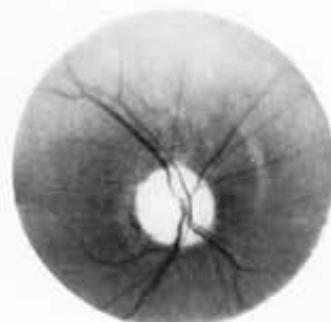


Fig. 4.
Secondary atrophy of the optic nerve.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

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- J. J. VAN LAAR: "Idem VI. The Alkali Metals" (Communicated by Prof. H. A. LORENTZ), p. 505.
- A. SMITS and J. GILLIS: "On Milk-Sugar". I. (Communicated by Prof. S. HOOGWERFF), p. 520.

Mathematics. — “On hyperelliptic integrals of deficiency $p = 2$, reducible by a transformation of order $r = 4$.” By Prof. J. C. KLUYVER.

(Communicated in the meeting of Sept. 29, 1917).

The conditions that an hyperelliptic integral of deficiency $p = 2$ is reducible to an elliptic integral by a transformation of order $r = 4$, have been assigned by BOLZA ¹⁾, who used direct algebraic methods and also by IGEL ²⁾, who based his deductions on the transformation of the double thetas. I will show that the geometry of a linear system of conics affords the means to solve the problem, and that geometric considerations enable us to add some results to those previously obtained ³⁾.

Let the integral be of the form

$$\int \frac{X dx}{\sqrt{\psi_1 \psi_2 \psi_3}},$$

where X is a linear quantic and ψ_1, ψ_2, ψ_3 are binary quadrics of the variable $x = x_1 : x_2$, then the integral is reducible under the following three conditions:

1. There are three quadrics ξ_1, ξ_2, ξ_3 , each of which is a perfect square, such that the quartics $\xi_1 \psi_1, \xi_2 \psi_2, \xi_3 \psi_3$ are linearly connected. Otherwise stated, these quartics are elements of an involution J of order 4.

2. The involution J contains an element T^2 , a quartic being a perfect square.

3. The numerator X of the integral has a determinate form depending on ψ_1, ψ_2, ψ_3 .

In fact, supposing the first and the second of these conditions to be fulfilled, we can take in J any two elements whatever R_1 and R_2 , and k_1, k_2, k_3, h being certain constants, we have

$\xi_1 \psi_1 = R_1 - k_1 R_2$, $\xi_2 \psi_2 = R_1 - k_2 R_2$, $\xi_3 \psi_3 = R_1 - k_3 R_2$, $T^2 = R_1 - h R_2$, then putting

$$t = \frac{R_1}{R_2},$$

¹⁾ Math. Ann., Bd. 28, p. 447.

²⁾ Monatshefte für Math. u. Phys., II, p. 157.

³⁾ For a summary of the researches on reducible Abelian integrals see: W. C. Posr, Dissertation, Leyden, 1917.

we get

$$dt = \frac{1}{R_2^2} (R_1 R_1' - R_2' R_1) dx,$$

$$\sqrt{(t-k_1)(t-k_2)(t-k_3)(t-h)} = \frac{T}{R_2^2} \sqrt{\xi_1 \xi_2 \xi_3 \psi_1 \psi_2 \psi_3}$$

and hence

$$\frac{dt}{\sqrt{(t-k_1)(t-k_2)(t-k_3)(t-h)}} = \frac{dx}{\sqrt{\psi_1 \psi_2 \psi_3}} \times \frac{(R_1 R_1' - R_2' R_1)}{TV \sqrt{\xi_1 \xi_2 \xi_3}}.$$

Now the sextic $(R_1 R_1' - R_2' R_1)$ is evidently divisible by the quintic $TV \sqrt{\xi_1 \xi_2 \xi_3}$, therefore the given integral is reducible, if we take

$$X = \frac{(R_1 R_1' - R_2' R_1)}{TV \sqrt{\xi_1 \xi_2 \xi_3}}.$$

Thus it is seen that the reducibility of the integral in the first instance depends upon the existence of the involution J , and on the possibility of determining the quadrics ξ_1, ξ_2, ξ_3 . The investigation of the involution J and of its characteristic properties may be conducted as follows.

With three binary quadrics

$$\psi_1 = a_0 x^2 + 2a_1 x + a_2, \quad \psi_2 = a_0' x^2 + 2a_1' x + a_2', \quad \psi_3 = a_0'' x^2 + 2a_1'' x + a_2''$$

six common invariants are associated. As such we get in the first place the discriminants

$$A_{11} = 2(a_0 a_2 - a_1^2), \quad A_{22} = 2(a_0' a_2' - a_1'^2), \quad A_{33} = 2(a_0'' a_2'' - a_1''^2)$$

and further the harmonic invariants

$$A_{23} = (a_0' a_2'' + a_0'' a_2' - 2a_1' a_1''), \quad A_{31} = (a_0'' a_2 + a_0 a_2'' - 2a_1'' a_1),$$

$$A_{12} = (a_0 a_2' + a_0' a_2 - 2a_1 a_1').$$

The three quadrics themselves are connected by the identical relation

$$\begin{vmatrix} A_{11} & A_{12} & A_{31} & \psi_1 \\ A_{12} & A_{22} & A_{23} & \psi_2 \\ A_{31} & A_{23} & A_{33} & \psi_3 \\ \psi_1 & \psi_2 & \psi_3 & 0 \end{vmatrix} = 0,$$

which I write in the form

$$K \equiv a\psi_1^2 + b\psi_2^2 + c\psi_3^2 + 2f\psi_2\psi_3 + 2g\psi_3\psi_1 + 2h\psi_1\psi_2 = 0.$$

Now this relation between binary quadrics can also be conceived as the equation in trilinear coordinates ψ_1, ψ_2, ψ_3 of a conic K , and since each of the coordinates is a quadric in x , this variable procures a parametric representation of the curve. From the same point of view any homogeneous polynomial $F(\psi_1, \psi_2, \psi_3)$ on the

one side is a binary quantic in x , on the other side it represents a curve in the plane of the conic K . An arbitrary quadric, for instance, can always be thrown into the form $h_1\psi_1 + h_2\psi_2 + h_3\psi_3$, and therefore it represents a right line meeting the conic K in two points, at which the parameter x is equal to either of the roots of the quadric $h_1\psi_1 + h_2\psi_2 + h_3\psi_3$. In particular, since the quadrics ξ_1, ξ_2, ξ_3 , are perfect squares, the right lines ξ_1, ξ_2, ξ_3 , are tangents of K with the points of contact, say, A_1, A_2, A_3 . In this way each element of the involution J corresponds with a conic and the involution J itself defines a linear system S of conics, such that the system is determined by three of its elements. Evidently the system S thus constructed must contain: the conic K , the three pairs of right lines $\xi_1\psi_1, \xi_2\psi_2, \xi_3\psi_3$ and lastly the double line T . Since S contains a double line, it is not a wholly general system. Its Jacobian breaks up into the right line T and into a conic H . The Jacobian passes through every point of contact of two conics belonging to S , hence the conic H passes through the points A_1, A_2, A_3 , and meets K in a fourth point A_4 . The tangents to K at the points A_1, A_2, A_3 , i.e. the right lines ξ_1, ξ_2, ξ_3 , and also the tangent ξ_4 at the point A_4 intersect H again respectively in the points B_1, B_2, B_3, B_4 . The latter points, lying on the Jacobian, are the centres of degenerate conics $\xi_1\psi_1, \xi_2\psi_2, \xi_3\psi_3$ and of a fourth degenerate conic $\xi_4\psi_4$, and thus we have proved that the involution J besides the three elements $\xi_1\psi_1, \xi_2\psi_2, \xi_3\psi_3$ each having a double root, necessarily must contain a fourth element $\xi_4\psi_4$ that has the same peculiarity.

In a certain sense the tangent ξ_4 considered as a binary quadric is directly connected with the reducible integral. Let us seek for the points in which the conic K is touched by any conic of the system S . If R_1 and R_2 are two arbitrary elements of S , the equation of the system is

$$R_1 + \lambda R_2 + \mu K = 0.$$

In order to find the values of the parameter x at the points of contact, we must again conceive R_1 and R_2 as binary quartics and the required parametric values are the roots of the sextic

$$(R_2 R_1' - R_2' R_1) = 0.$$

Now, as was said before, the points of contact in question are the points in which K meets the Jacobian. Hence the roots of the sextic are the parametric values of x at the points A_1, A_2, A_3, A_4 and at the points of intersection of K with the right line T . Therefore the sextic is the product of the five quantities $\sqrt{\xi_1}, \sqrt{\xi_2}, \sqrt{\xi_3}, \sqrt{\xi_4}$

and T , and the numerator X of the integral, which we have found to be

$$\frac{(R_2 R_1' - R_2' R_1)}{TV \xi_1 \xi_2 \xi_3},$$

is identical with the linear quantic $\sqrt{\xi_4}$.

Obviously, we may now conclude that as soon as the given integral is reducible, there are three other integrals of deficiency $p = 2$ connected with the involution J , i.e. the integrals

$$\int \frac{\sqrt{\xi_1}}{\sqrt{\psi_2 \psi_3 \psi_4}} dx, \quad \int \frac{\sqrt{\xi_2}}{\sqrt{\psi_1 \psi_3 \psi_4}} dx, \quad \int \frac{\sqrt{\xi_3}}{\sqrt{\psi_1 \psi_2 \psi_4}} dx,$$

which can be reduced to elliptic integrals. Moreover, it will be evident that the transformation of the four integrals will be effected by one and the same transformation formula, and we may notice that likewise the integral

$$\int \frac{T}{\sqrt{\psi_1 \psi_2 \psi_3 \psi_4}} dx$$

of deficiency $p = 3$ becomes elliptic by that transformation.

In order to find how the involution J can be constructed from the given quadrics ψ_1, ψ_2, ψ_3 , I will proceed with the analytical investigation of the system S . It is always possible by adjoining suitable constant factors to the quadrics ξ_1, ξ_2, ξ_3 to ensure the identical relation

$$\sqrt{\xi_1} + \sqrt{\xi_2} + \sqrt{\xi_3} = 0,$$

and hence the relation

$$\xi_1^2 + \xi_2^2 + \xi_3^2 - 2\xi_2 \xi_3 - 2\xi_3 \xi_1 - 2\xi_1 \xi_2 = 0,$$

an identity in the variable x that denotes at the same time the conic K in the trilinear coordinates ξ_1, ξ_2, ξ_3 .

The point A_1 on K , the coordinates of which in the system ξ_1, ξ_2, ξ_3 are $(0, 1, 1)$, has its conjugate with respect to the system S at the point A'_1 where the tangent ξ_1 of K meets the double line T of the system.

Supposing T to have the equation

$$T \equiv L\xi_1 + M\xi_2 + N\xi_3 = 0, \quad \dots \dots \dots (1)$$

this point A'_1 has the coordinates $(0, -N, M)$, hence the coefficients of the equation

$$A\xi_1^2 + B\xi_2^2 + C\xi_3^2 + 2F\xi_2\xi_3 + 2G\xi_3\xi_1 + 2H\xi_1\xi_2 = 0,$$

representing any conic of S , underly the condition

$$BN - FM + F(N - M) = 0,$$

or

$$F = B \frac{N}{M-N} - C \frac{M}{M-N}$$

In like manner the points A_1 and A'_2 , A_2 and A'_1 , are conjugate points of S , therefore we have also

$$G = C \frac{L}{N-L} - A \frac{N}{N-L}$$

$$H = A \frac{M}{L-M} - B \frac{L}{L-M}$$

and the equation of the system itself may be written in the form

$$A\xi_1 \left[-\xi_1 - \frac{2M}{L-M} \xi_2 + \frac{2N}{N-L} \xi_3 \right] + B\xi_2 \left[\frac{2L}{L-M} \xi_1 - \xi_2 - \frac{2N}{M-N} \xi_3 \right] + C\xi_3 \left[-\frac{2L}{N-L} \xi_1 + \frac{2M}{M-N} \xi_2 - \xi_3 \right] = 0.$$

Since S contains the three degenerate conics $\xi_1\psi_1$, $\xi_2\psi_2$, $\xi_3\psi_3$, it is seen that the expressions between brackets in the above equation denote the right lines ψ_1 , ψ_2 , ψ_3 , and we may write

$$\left. \begin{aligned} P_1\psi_1 &= \left[-\xi_1 - \frac{2M}{L-M} \xi_2 + \frac{2N}{N-L} \xi_3 \right], \\ P_2\psi_2 &= \left[\frac{2L}{L-M} \xi_1 - \xi_2 - \frac{2N}{M-N} \xi_3 \right], \\ P_3\psi_3 &= \left[-\frac{2L}{N-L} \xi_1 + \frac{2M}{M-N} \xi_2 - \xi_3 \right], \end{aligned} \right\} \dots \dots (2)$$

where P_1, P_2, P_3 are determinate constants.

From these equations we deduce, always using the coordinates ξ_1, ξ_2, ξ_3 , the coordinates of the points B_1, B_2, B_3 , the centres of the conics $\xi_1\psi_1, \xi_2\psi_2, \xi_3\psi_3$.

Putting

$$L(M-N) = q_1, \quad M(N-L) = q_2, \quad N(L-M) = q_3, \quad (3)$$

so that the constants q_1, q_2, q_3 are related by the equation

$$q_1 + q_2 + q_3 = 0,$$

we find for the coordinates of B_1, B_2, B_3 respectively $(0, q_2, q_3), (q_1, 0, q_3), (q_1, q_2, 0)$. Incidentally we may remark that at the points B_1, B_2, B_3 the right lines ξ_1, ξ_2, ξ_3 are touched by the conic

$$K_1 \equiv q_1^2 \xi_1^2 + q_2^2 \xi_2^2 + q_3^2 \xi_3^2 - 2q_2q_3 \xi_2\xi_3 - 2q_3q_1 \xi_3\xi_1 - 2q_1q_2 \xi_1\xi_2 = 0,$$

and at the same time we conclude that the equation of the conic H , that forms part of the Jacobian, must be

$$H \equiv q_1\xi_1^2 + q_2\xi_2^2 + q_3\xi_3^2 + q_1\xi_2\xi_3 + q_2\xi_3\xi_1 + q_3\xi_1\xi_2 = 0.$$

For plainly this conic passes through the points A_1, A_2, A_3 and also through B_1, B_2, B_3 .

The equations of the tangent ξ , and of the right line ψ , remain

to be found, and to this end I consider the pencil of quartic curves

$$\lambda H^2 + \xi_1 \xi_2 \xi_3 \xi_4 = 0.$$

These curves have the right lines $\xi_1, \xi_2, \xi_3, \xi_4$ as bitangents and the eight points of contact are obviously the points $A_1, A_2, A_3, A_4, B_1, B_2, B_3, B_4$. Now the product KK_1 is a quartic curve that passes through 14 of the 16 fixed points that are common to the curves of the pencil. For K touches the bitangents at A_1, A_2, A_3, A_4 and K_1 has contact with ξ_1, ξ_2, ξ_3 at the points B_1, B_2, B_3 . Hence the curve KK_1 belongs to the pencil, K_1 touches ξ_4 at the point B_4 , and there is a certain value λ_1 of λ such that

$$\lambda_1 H^2 + \xi_1 \xi_2 \xi_3 \xi_4 \equiv \mu KK_1$$

It is readily seen that $\lambda_1 = 1$, that we must have $\mu = 1$, and from

$$\xi_1 \xi_2 \xi_3 \xi_4 \equiv KK_1 - H^2$$

we find

$$\xi_4 \equiv (q_3 - q_1)(q_1 - q_2) \xi_1 + (q_1 - q_2)(q_2 - q_3) \xi_2 + (q_2 - q_3)(q_3 - q_1) \xi_3 = 0. \quad (4)$$

Putting

$$\psi_4 = \mu_1 \xi_1 + \mu_2 \xi_2 + \mu_3 \xi_3,$$

we write down that $A_1(0,1,1)$ and $A_1'(0, -N_1, M)$ are conjugate points with respect to the conic $\xi_4 \psi_4$. Thus we find the relation

$$\frac{\mu_3}{-3M + \frac{1}{M}(MN + NL + LM)} = \frac{\mu_2}{-3N + \frac{1}{N}(MN + NL + LM)}$$

and a similar relation is obtained by means of the conjugate points A_2 and A_2' . In this way it appears that the right line ψ_4 will be denoted by

$$\psi_4 = -3T + \left(\frac{\xi_1}{L} + \frac{\xi_2}{M} + \frac{\xi_3}{N} \right) (MN + NL + LM). \quad (5)$$

In the preceding we took for granted that it was possible to represent one and the same conic K in two different systems of coordinates by the two equations

$$K \equiv a\psi_1^2 + b\psi_2^2 + c\psi_3^2 + 2f\psi_2\psi_3 + 2g\psi_3\psi_1 + 2h\psi_1\psi_2 = 0, \quad (6)$$

$$K \equiv \xi_1^2 + \xi_2^2 + \xi_3^2 - 2\xi_2\xi_3 - 2\xi_3\xi_1 - 2\xi_1\xi_2 = 0, \quad (7)$$

the ψ -coordinates depending on the ξ -coordinates as is indicated by the equations (2), and we have now to examine if these two equations are really consistent.

Here it is noteworthy that, after introducing certain constants f_1, g_1, h_1 , the lefthand side of equation (6) becomes

$$\psi_1 [a\psi_1 + (h - h_1)\psi_2 + (g + g_1)\psi_3] + \psi_2 [(h + h_1)\psi_1 + b\psi_2 + (f - f_1)\psi_3] + \psi_3 [(g - g_1)\psi_1 + (f + f_1)\psi_2 + c\psi_3],$$

and that the lefthand side of equation (7) can be written

$$-(P_1 \xi_1 \psi_1 + P_2 \xi_2 \psi_2 + P_3 \xi_3 \psi_3).$$

The equations (6) and (7) therefore have the same meaning, as soon as we have

$$\frac{P_1 \xi_1}{a\psi_1 + (h-h_1)\psi_2 + (g+g_1)\psi_3} = \frac{P_2 \xi_2}{(h+h_1)\psi_1 + b\psi_2 + (f-f_1)\psi_3} = \frac{P_3 \xi_3}{(g-g_1)\psi_1 + (f+f_1)\psi_2 + c\psi_3} \dots \dots \dots (8)$$

and it is only when these relations hold that either of the equations (6) and (7) is a direct consequence, of the other.

To simplify somewhat the notation I put

$$\alpha = \frac{M+N}{M-N}, \quad \beta = \frac{N+L}{N-L}, \quad \gamma = \frac{L+M}{L-M}, \dots \dots \dots (9)$$

the new constants α, β, γ being related by the equation

$$(1 + \alpha)(1 + \beta)(1 + \gamma) + (1 - \alpha)(1 - \beta)(1 - \gamma) = 0,$$

or by

$$1 + \beta\gamma + \gamma\alpha + \alpha\beta = 0, \dots \dots \dots (10)$$

and consequently instead of (2) we may write

$$\left. \begin{aligned} P_1 \psi_1 &= -\xi_1 + (1 - \gamma) \xi_2 + (1 + \beta) \xi_3, \\ P_2 \psi_2 &= (1 + \gamma) \xi_1 - \xi_2 + (1 - \alpha) \xi_3, \\ P_3 \psi_3 &= (1 - \beta) \xi_1 + (1 + \alpha) \xi_2 - \xi_3. \end{aligned} \right\} \dots \dots \dots (11)$$

Comparing now the two sets of equations (8) and (11), we observe that (11) defines a homographic transformation expressing the quantities $P\psi$ in the quantities ξ , and that the inverse transformation is given by (8).

Writing down the determinant

$$\begin{vmatrix} -1 & 1 - \gamma & 1 + \beta \\ 1 + \gamma & -1 & 1 - \alpha \\ 1 - \beta & 1 + \alpha & -1 \end{vmatrix}$$

of the first transformation and also the determinant

$$\begin{vmatrix} \frac{a}{P_1^2} & \frac{h+h_1}{P_1 P_2} & \frac{g-g_1}{P_2 P_1} \\ \frac{h-h_1}{P_1 P_2} & \frac{b}{P_2^2} & \frac{f+f_1}{P_2 P_3} \\ \frac{g+g_1}{P_2 P_1} & \frac{f-f_1}{P_2 P_3} & \frac{c}{P_3^2} \end{vmatrix}$$

of the inverse transformation, in which I have interchanged lines and columns, a known proposition says that the elements of the latter determinant are proportional to the corresponding minors of the former. Nine ratios therefore are equal to one and the same

quantity λ , and so we have the equations

$$\lambda = \frac{b}{P_2^2 \beta^2} = \frac{c}{P_3^2 \gamma^2} = \frac{f+f_1}{P_2 P_3 (2+\alpha-\beta-\gamma+\beta\gamma)} = \frac{f-f_1}{P_2 P_3 (2-\alpha+\beta+\gamma+\beta\gamma)},$$

from which we infer

$$\frac{f-V\sqrt{bc}}{P_2 P_3} = \frac{f+V\sqrt{bc}}{P_2 P_3 (1+\beta\gamma)},$$

or

$$1 + \beta\gamma = \frac{f+V\sqrt{bc}}{f-V\sqrt{bc}}.$$

Similarly we obtain

$$1 + \gamma\alpha = \frac{g+V\sqrt{ca}}{g-V\sqrt{ca}},$$

$$1 + \alpha\beta = \frac{h+V\sqrt{ab}}{h-V\sqrt{ab}},$$

and then by equation (10)

$$2 = \frac{f+V\sqrt{bc}}{f-V\sqrt{bc}} + \frac{g+V\sqrt{ca}}{g-V\sqrt{ca}} + \frac{h+V\sqrt{ab}}{h-V\sqrt{ab}}. \dots (12)$$

Thus it appears that the reducibility of the given hyperelliptic integral implies the relation (12) between the invariants common to ψ_1, ψ_2, ψ_3 , and conversely as soon as these invariants, with a suitable determination of the surds, satisfy the relation (12) the involution \mathcal{J} can be realised, and the given integral will degenerate.

Supposing that the condition (12) is fulfilled, we have

$$\lambda = \frac{a}{P_1^2 \alpha^2} = \frac{b}{P_2^2 \beta^2} = \frac{c}{P_3^2 \gamma^2} = \frac{f}{P_2 P_3 (2+\beta\gamma)} = \frac{g}{P_2 P_1 (2+\gamma\alpha)} = \frac{h}{P_1 P_2 (2+\alpha\beta)} = \frac{f_1}{P_2 P_3 (\alpha-\beta-\gamma)} = \frac{g_1}{P_3 P_1 (-\alpha+\beta-\gamma)} = \frac{h_1}{P_1 P_2 (-\alpha-\beta+\gamma)}, \quad (13)$$

and

$$\alpha P_1 V\sqrt{bc} = \beta P_2 V\sqrt{ca} = \gamma P_3 V\sqrt{ab} \dots (14)$$

From these equations the constants $\alpha, \beta, \gamma, P_1, P_2, P_3, L, M, N, q_1, q_2, q_3$ can be successively evaluated, we can find the quantities $\xi_1, \xi_2, \xi_3, \xi_4, T, \psi_1$ and finally the transformation that reduces the integral.

To illustrate the method described, I will consider a numerical example. Let the given integral be

$$\int \frac{X dx}{\sqrt{(5x^2 - 12x + 4)(5x^2 - 2x + 2)(7x^2 - 6x + 2)}}$$

that is, let us assume

$$\psi_1 = 5x^2 - 12x + 4, \quad \psi_2 = 5x^2 - 2x + 2, \quad \psi_3 = 7x^2 - 6x + 2.$$

Calculating the invariants, we have

$$\frac{A_{11}}{-16} = \frac{A_{22}}{9} = \frac{A_{33}}{5} = \frac{A_{23}}{9} = \frac{A_{31}}{1} = \frac{A_{12}}{9},$$

$$\lambda = \frac{a}{4} = \frac{b}{9} = \frac{c}{25} = \frac{f}{-17} = \frac{g}{-8} = \frac{h}{4}.$$

Now we may take

$$\lambda = \frac{\sqrt{bc}}{-15} = \frac{\sqrt{ca}}{-10} = \frac{\sqrt{ab}}{6}$$

and with this determination of the surds we get

$$\frac{f + \sqrt{bc}}{f - \sqrt{bc}} = 1 + \beta\gamma = 16, \quad \frac{g + \sqrt{ca}}{g - \sqrt{ca}} = 1 + \gamma\alpha = -9, \quad \frac{h + \sqrt{ab}}{h - \sqrt{ab}} = 1 + \alpha\beta = -5.$$

The sum of the three fractions is equal to 2, therefore the integral is reducible. At the same time we have found

$$\beta\gamma = 15, \quad \gamma\alpha = -10, \quad \alpha\beta = -6,$$

or

$$\alpha^2 = 4, \quad \beta^2 = 9, \quad \gamma^2 = 25,$$

so that we have either

$$\alpha = 2, \quad \beta = -3, \quad \gamma = -5,$$

or

$$\alpha = -2, \quad \beta = 3, \quad \gamma = 5.$$

Two sets of values for the constants α, β, γ being admissible, we infer that the given quadrics ψ_1, ψ_2, ψ_3 allow us to us build up two entirely distinct involutions J , and instead of a single reducible integral of the given form, two such integrals are possible. This is obviously in accordance with the known proposition that, as soon as an integral belonging to an algebraic function of deficiency $\nu = 2$ is reducible, that function possesses a second degenerate integral.

I will take up the case

$$\alpha = 2, \quad \beta = -3, \quad \gamma = -5.$$

Then we have from (14) and from (13)

$$\frac{P_1}{1} = \frac{P_2}{-1} = \frac{P_3}{1},$$

$$\frac{a}{4} = \frac{f_1}{-10} = \frac{g_1}{0} = \frac{h_1}{1}$$

hence from (8)

$$\frac{\xi_1}{4\psi_1 - 8\psi_2} = \frac{-\xi_2}{8\psi_1 + 9\psi_2 - 7\psi_3} = \frac{\xi_3}{-8\psi_1 - 27\psi_2 + 25\psi_3},$$

or

$$\frac{\xi_1}{x^2} = \frac{\xi_2}{(x-1)^2} = \frac{\xi_3}{1},$$

$$\frac{\sqrt{\xi_1}}{x} = \frac{\sqrt{\xi_2}}{1-x} = \frac{\sqrt{\xi_3}}{-1}.$$

Now equations (9) and (3) give

$L = 2$, $M = 3$, $N = 1$, $q_1 = 4$, $q_2 = -3$, $q_3 = -1$
and then by equations (1), (4) and (5) we find
 $T = \text{const.}(5x^2 - 6x + 4)$, $\xi_4 = \text{const.}(7x - 2)^2$, $\psi_4 = \text{const.}(35x^2 - 64x - 16)$

The elements $\xi_1\psi_1$, $\xi_2\psi_2$, $\xi_3\psi_3$, $\xi_4\psi_4$, T^2 of the involution J being known, we may put for instance

$$t = \frac{\xi_1\psi_1}{\xi_2\psi_2} = \frac{x^2(5x^2 - 12x + 4)}{(x-1)^2(5x^2 - 2x + 2)}$$

and obtain consequently

$$\begin{aligned} \frac{t}{x^2(5x^2 - 12x + 4)} &= \frac{1}{(x-1)^2(5x^2 - 2x + 2)} = \frac{1-t}{(7x^2 - 6x + 2)} = \\ &= \frac{375t - 32}{(7x-2)^2(35x^2 - 64x - 16)} = \frac{8-3t}{(5x^2 - 6x + 4)^2}. \end{aligned}$$

The above transformation now will reduce four integrals of deficiency $p = 2$, connected with the involution J , and we may write down at once

$$\begin{aligned} \int \frac{(7x-2) dx}{\sqrt{(5x^2 - 12x + 4)(5x^2 - 2x + 2)(7x^2 - 6x + 2)}} &= -\frac{1}{\sqrt{2}} \int \frac{dt}{\sqrt{t(1-t)(8-3t)}}, \\ \int \frac{dx}{\sqrt{(5x^2 - 12x + 4)(5x^2 - 2x + 2)(-35x^2 + 64x + 16)}} &= \sqrt{2} \int \frac{dt}{\sqrt{t(32-375t)(8-3t)}}, \\ \int \frac{(x-1) dx}{\sqrt{(5x^2 - 12x + 4)(7x^2 - 6x + 2)(-35x^2 + 64x + 16)}} &= \\ &= -\sqrt{2} \int \frac{dt}{\sqrt{t(1-t)(32-375t)(8-3t)}}, \\ \int \frac{x dx}{\sqrt{(5x^2 - 2x + 2)(7x^2 - 6x + 2)(-35x^2 + 64x + 16)}} &= \\ &= \int \frac{dt}{\sqrt{(1-t)(32-375t)(8-3t)}} \end{aligned}$$

the constants $-\frac{1}{\sqrt{2}}$, etc. at the right hand sides being easily found by observing, that for small values of x we must have $t = x^2$.

As I have remarked before, the same transformation will also reduce an integral of deficiency $p = 3$, connected with the involution J .

In fact, we have

$$\begin{aligned} \int \frac{(5x^2 - 6x + 4) dx}{\sqrt{(5x^2 - 12x + 4)(5x^2 - 2x + 2)(7x^2 - 6x + 2)(-35x^2 + 64x + 16)}} &= \\ &= \sqrt{2} \int \frac{dt}{\sqrt{t(1-t)(32-375t)}}. \end{aligned}$$

Again, if we had used the second set of admissible values for α, β, γ ,

$$\alpha = -2, \quad \beta = 3, \quad \gamma = 5,$$

we should have found successively

$$\begin{aligned} \frac{P_1}{1} = \frac{P_2}{-1} = \frac{P_3}{1}, \quad \frac{a}{4} = \frac{f_1}{10} = \frac{g_1}{0} = \frac{h_1}{-4}, \\ \frac{\xi_1}{4\psi_1 + 8\psi_2 - 8\psi_3} = \frac{\xi_2}{9\psi_2 - 27\psi_3} = \frac{\xi_3}{-8\psi_1 - 7\psi_2 + 25\psi_3}, \\ \frac{\xi_1}{(x-2)^2} = \frac{\xi_2}{(6x-3)^2} = \frac{\xi_3}{(5x-1)^2}, \\ \frac{\sqrt{\xi_1}}{x-2} = \frac{\sqrt{\xi_2}}{-6x+3} = \frac{\sqrt{\xi_3}}{5x-1}, \end{aligned}$$

$$L = 3, \quad M = 2, \quad N = 6, \quad q_1 = -12, \quad q_2 = 6, \quad q_3 = 6.$$

$$T = \text{const.} (25x^2 - 16x + 4), \quad \xi_4 = \text{const.} \xi_1, \quad \psi_4 = \text{const.} \psi_1.$$

Now we may apply the transformation

$$t = \frac{\xi_1 \psi_1}{\xi_2 \psi_2} = \frac{(x-2)^2 (5x^2 - 12x + 4)}{(6x-3)^2 (5x^2 - 2x + 2)},$$

whence we have

$$\begin{aligned} \frac{9t}{(x-2)^2 (5x^2 - 12x + 4)} &= \frac{9}{(6x-3)^2 (5x^2 - 2x + 2)} \\ &= \frac{9(1-t)}{(5x-1)^2 (7x^2 - 6x + 2)} = \frac{32 - 27t}{(25x^2 - 16x + 4)^2} \end{aligned}$$

and we shall obtain

$$\int \frac{(x-2)dx}{\sqrt{(5x^2 - 12x + 4)(5x^2 - 2x + 2)(7x^2 - 6x + 2)}} = \frac{1}{6} \int \frac{dt}{\sqrt{t(1-t)(32-27t)}},$$

where the constant $\frac{1}{6}$ is found by observing that $x = 2 + \delta$ implies $t = \frac{4}{7} \delta^2$.

The involution J , in this case, is somewhat special, because we have now

$$\psi_4 = \psi_1, \quad \xi_4 = \xi_1.$$

In the corresponding system S the points A_1 and A_4 coincide, and the right line ψ_1 passes through A_1 . Hence of the four reducible integrals of deficiency $p = 2$ in the general case connected with the involution J , three degenerate here at once into ordinary logarithmic integrals. The integral

$$\int \frac{T dx}{\sqrt{\psi_1 \psi_2 \psi_3 \psi_4}},$$

in the general case of deficiency $p = 3$, reduces here to an elliptic integral of the third kind, but the transformation indicated above effects still a further reduction, and we obtain another logarithmic integral.

In fact, we shall have

$$\int \frac{(25x^2 - 16x + 4)dx}{(5x^2 - 12x + 4)\sqrt{(7x^2 - 6x + 2)(5x^2 - 2x + 3)}} = \frac{1}{6} \int \frac{dt}{t\sqrt{1-t}}.$$

As I remarked in the beginning, the principal condition for the reducibility has been given by BOLZA and by IGEL. I will now show that the invariant relations they deduced, may be derived without difficulty from the results obtained here.

BOLZA and IGEL both introduce the anharmonic ratios $\lambda_{23}, \lambda_{31}, \lambda_{12}$, formed by the roots of each pair of the quadrics ψ_1, ψ_2, ψ_3 .

The anharmonic ratio λ_{23} , formed by the roots of ψ_2 and ψ_3 , is given by the equation

$$\frac{(\lambda_{23} - 1)^2}{A_{22}A_{33}} = \frac{(\lambda_{23} + 1)^2}{A_{23}^2},$$

and putting

$$\mu_1 = \frac{\sqrt{\lambda_{23} + 1}}{\sqrt{\lambda_{23} - 1}}, \quad \sqrt{\lambda_{23}} = \frac{\mu_1 + 1}{\mu_1 - 1},$$

the constant μ_1 is related to the invariants A_{22}, A_{33}, A_{23} by the equation

$$\frac{2\mu_1}{\sqrt{A_{22}A_{33}}} = \frac{\mu_1^2 + 1}{A_{23}}.$$

Now we have

$$\frac{A_{22}}{ca - g^2} = \frac{A_{33}}{ab - h^2} = \frac{A_{23}}{gh - af}$$

and hence by equations (13)

$$\frac{A_{22}}{2P_2^2\beta(s-\beta)} = \frac{A_{33}}{2P_2^2\gamma(s-\gamma)} = \frac{A_{23}}{-P_2P_3(2\beta\gamma + as)},$$

where s stands for $\alpha + \beta + \gamma$.

In this way we get

$$\frac{\mu_1}{\sqrt{\beta\gamma(s-\beta)(s-\gamma)}} = \frac{\mu_1^2 + 1}{-(2\beta\gamma + as)} = \frac{\mu_1^2 - 1}{as} = \frac{\mu_1^2}{-\beta\gamma}$$

and we may take

$$\mu_1 = -\sqrt{\frac{\beta\gamma}{(\alpha + \beta)(\gamma + \alpha)}},$$

Similarly we obtain

$$\mu_2 = \frac{\sqrt{\lambda_{31} + 1}}{\sqrt{\lambda_{31} - 1}} = -\sqrt{\frac{\gamma\alpha}{(\beta + \gamma)(\alpha + \beta)}},$$

$$\mu_3 = \frac{\sqrt{\lambda_{12} + 1}}{\sqrt{\lambda_{12} - 1}} = -\sqrt{\frac{\alpha\beta}{(\gamma + \alpha)(\beta + \gamma)}}.$$

and we infer

$$\frac{\mu_2 \mu_3}{\mu_1} = -\frac{\alpha}{\beta + \gamma}.$$

Hence we have between μ_1, μ_2, μ_3 the set of relations

$$\begin{aligned} \alpha \mu_1 + \beta \mu_2 \mu_3 + \gamma \mu_1 \mu_3 &= 0, \\ \alpha \mu_3 \mu_1 + \beta \mu_2 + \gamma \mu_3 \mu_1 &= 0, \\ \alpha \mu_1 \mu_2 + \beta \mu_1 \mu_2 + \gamma \mu_3 &= 0, \end{aligned}$$

and by eliminating α, β, γ , we obtain as the invariant relation between the quadrics ψ_1, ψ_2, ψ_3 BOLZA's equation

$$\begin{vmatrix} 1 & \mu_3 & \mu_2 \\ \mu_3 & 1 & \mu_1 \\ \mu_2 & \mu_1 & 1 \end{vmatrix} = 1 - \mu_1^2 - \mu_2^2 - \mu_3^2 + 2\mu_1\mu_2\mu_3 = 0.$$

When this relation is satisfied for any one of the possible determinations of the constants μ_1, μ_2, μ_3 , the quadrics ψ_1, ψ_2, ψ_3 are apt to build up a degenerate integral.

As we have

$$\sqrt{\lambda_{23}} = \frac{\mu_1 + 1}{\mu_1 - 1} = \frac{(\mu_1 + 1)^2}{(\mu_1^2 - 1)},$$

we have also

$$\sqrt[3]{\lambda_{23}\lambda_{31}} = \frac{(\mu_1 + 1)(\mu_2 + 1)}{\sqrt{(\mu_1^2 - 1)(\mu_2^2 - 1)}}.$$

Now it follows from BOLZA's equation that

$$(\mu_1^2 - 1)(\mu_2^2 - 1) = (\mu_1\mu_2 - \mu_3)^2$$

and since

$$\mu_3 = -\frac{\alpha + \beta}{\gamma} \mu_1 \mu_2, \quad \mu_1 \mu_2 - \mu_3 = \frac{s}{\gamma} \mu_1 \mu_2,$$

we get

$$\sqrt[3]{\lambda_{23}\lambda_{31}} = \frac{\gamma(1 + \mu_1 + \mu_2 + \mu_1\mu_2)}{s\mu_1\mu_2} = \frac{\gamma}{s} + \frac{1}{s\mu_1\mu_2\mu_3} \{\gamma\mu_2\mu_3 + \gamma\mu_3\mu_1 - (\alpha + \beta)\mu_1\mu_2\}.$$

Writing out similar expressions for $\sqrt[3]{\lambda_{12}\lambda_{23}}$ and $\sqrt[3]{\lambda_{31}\lambda_{23}}$, we find by adding them IGEL's equation

$$\sqrt[3]{\lambda_{12}\lambda_{31}} + \sqrt[3]{\lambda_{23}\lambda_{12}} + \sqrt[3]{\lambda_{31}\lambda_{23}} = 1.$$

Again, if for any one of the possible determinations of the surds this relation is satisfied, a degenerate integral can be constructed by means of the quadrics ψ_1, ψ_2, ψ_3 . Both the equations of condition given by BOLZA and by IGEL involve rather intricate surds, and I should say that they are less adapted for examining the reducibility of a given integral than the equation (12) deduced in this paper.

Chemistry. — “*On the Saponification of Fats.*” II. By Dr. J. P. TREUB. (Communicated by Prof. S. HOOGWERFF).

(Communicated in the meeting of June 30, 1917.)

§ 1. In a previous paper ¹⁾ equations were derived for the case that saponification takes place in emulsion, which equations indicate the quantities of glycerine and fatty acid present in free state after an arbitrary time.

These equations are:

$$g = 1 - \frac{2pq}{(2p-3)(q-3)} e^{-3kt} + \frac{3q}{(2p-3)(q-2p)} e^{-2pkt} - \frac{6p}{(q-3)(q-2p)} e^{-qkt}. \quad (1)$$

$$T = 1 - \frac{1+(2p-1)(q-2)}{(2p-3)(q-3)} e^{-3kt} + \frac{2(q-p)}{(2p-3)(q-2p)} e^{-2pkt} - \frac{2p}{(q-3)(q-2p)} e^{-qkt}. \quad (2)$$

Equation (1) represents: the fraction of the total number of molecules of glycerine, present after the time t in free state. (Relative concentration of the free glycerine after the time t).

Equation (2) expresses the relative concentration of the free fatty acid after the time t .

In these equations p and q represent: the increase of concentration of di- resp. monoglycerides at the surface of contact between fat- and waterphase, in consequence of the adsorption.

When the velocity constant k is not constant in reality (as in the saponification in emulsion, where the surface of contact between fat- and water phase constantly varies in size), the equations (1) and (2) have no physical meaning *each in itself*. When, however, we eliminate $k \times t$, which is possible for different numerical values of p and q , we arrive at equations of the general form $f(g, T) = 0$, which give the connection between the relative concentrations of free glycerine and free fatty acid for the assumed values of the adsorption constants p and q . As was proved ²⁾ these equations are independent of the variability of the constant of velocity k .

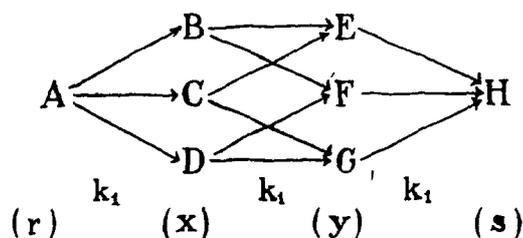
In the saponification in emulsion complications make, therefore, their appearance, which in some cases entirely cover the stagewise

¹⁾ These Proc. **20**, 35 (1916).

²⁾ loc. cit. 41.

course of the saponification (saponification in alkaline surroundings), and it is now of importance more closely to examine the ideal case, in which such complications do not appear.

Let us consider the saponification of triacetine in solution, and let us assume that the three ester-groups are perfectly equivalent¹⁾. Then the saponification takes place according to the following scheme:



In this A represents the triglyceride, B , C , and D the diglycerides, E , F , and G the monoglycerides and H glycerine. Let the number of molecules of each of these substances, present after a time t , be represented by r , x , y , and s , in which x and y indicate the number of molecules of the three di- resp. monoglycerides each taken separate, and let the constant of velocity at the splitting off of each fatty acid group be k_1 .

Then the equations of velocity are:

$$-\frac{dr}{dt} = 3k_1 r.$$

$$\frac{dx}{dt} = k_1 r - 2k_1 x,$$

$$\frac{dy}{dt} = 2k_1 x - k_1 y,$$

$$\frac{ds}{dt} = 3k_1 y.$$

Starting from a molecules of triglyceride, we may calculate from this that the number of molecules of the different stages present after a time t amounts to the values from column 2 of table 1.

The relative concentrations (fraction of the total possible number of molecules) of each of the glycerides is, therefore, represented by the values from column 3 of table 1. The sum of these relative concentrations is of course, always = 1.

When we now finally calculate the number of molecules of acetic acid (z) split off after the time t , we find from $z = 3(x + 2y + s)$:

$$z = 3a(1 - e^{-k_1 t}).$$

¹⁾ With regard to the validity of this assumption cf. § 3 and 4.

TABLE 1.

1	2	3
Glycerides	Number of molec. present after the time t .	Relat. concentrations after the time t
Triglyceride	$r = a \cdot e^{-3k_1 t}$	$v = e^{-3k_1 t}$
Diglyceride	$3x = 3a \cdot e^{-2k_1 t} (1 - e^{-k_1 t})$	$d = 3e^{-2k_1 t} (1 - e^{-k_1 t})$
Monoglyceride	$3y = 3a \cdot e^{-k_1 t} (1 - e^{-k_1 t})^2$	$m = 3e^{-k_1 t} (1 - e^{-k_1 t})^2$
Glycerine	$s = a \cdot (1 - e^{-k_1 t})^3$	$g = (1 - e^{-k_1 t})^3$

Where now $3a$ molecules of acetic acid are possible, the relative concentration T of the free acetic acid is:

$$T = 1 - e^{-k_1 t}$$

The two relative concentrations which are of most importance here, are those of the free fatty acid and of the free glycerine, viz.:

$$g = (1 - e^{-k_1 t})^3 \quad . \quad . \quad (3) \quad \text{and} \quad T = 1 - e^{-k_1 t} \quad . \quad . \quad (4)$$

from which follows:

$$g = T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or in words:

In case of stagewise saponification of an ester of a tri-valent alcohol (with equivalent OH groups) and a univalent acid, the relative concentration of the free alcohol, independent of time, is always equal to the third power of the relative concentration of the free acid, provided that no complications (as in case of saponification in emulsion), take place.

When we saponify an ester of a trivalent acid and a univalent alcohol, the reverse holds of course.

The equations (3) and (4) may be derived from (1) and (2) by putting $p = q = 1$.

We may now apply our considerations also to the opposite case, viz. the esterification of glycerine, with the equivalent quantity of acetic acid.

In this case the reaction is bimolecular, as the reaction velocity is not only dependent on the number of still unesterized OH groups, but also on the number of molecules of free fatty acid. When we, therefore, draw up equations of velocity as in the case of triglyceride saponification, i e. when in our equations we only express the number of free OH groups, which can become esterized, and *not* the number of acetic acid molecules available to bring about this

esterification, the velocity constant k_2 occurring in this equation¹⁾ will in reality not be constant, but vary with the acetic acid concentration, hence with the time.

The formulae for g and T , which we obtain by integration from these equations of velocity, will then have no physical meaning in themselves. If, however, $k_2 \times t$ is eliminated, which is always possible, the equation obtained gives the connection existing between g and T at any moment of the esterification, and that independent of the variation of k_2 .

The equations of velocity drawn up like this for the esterification run :

$$\begin{aligned} -\frac{ds}{dt} &= 3k_2 \cdot s, \\ \frac{dy}{dt} &= k_2 s - 2k_2 y, \\ \frac{dx}{dt} &= 2k_2 y - k_2 \cdot x \\ \frac{dr}{dt} &= 3k_2 \cdot x, \end{aligned}$$

from which after integration and introduction of the relative concentrations, follows:

$$g = e^{-3k_2 t}, \text{ and } T = e^{-k_2 t}, \text{ and therefore } g = T^3$$

We see, therefore, that $g = T^3$ holds both for the reaction in saponifying sense and for that in esterizing sense. It follows from this that when the two reactions take place at the same time (i. e. when an equilibrium sets in) $g = T^3$ holds likewise.

This may be proved as follows:

For the reaction of equilibrium holds:

$$\frac{dg}{dT} = \frac{dg_1 + m dg_2}{dT_1 + m dT_2},$$

when $\frac{dg_1}{dT_1}$ refers to the reaction in saponifying sense, and $\frac{dg_2}{dT_2}$ to the reaction in esterizing sense, in which m is a quantity varying with the time.

Because at any moment:

$$\frac{dg_1}{dT_1} = \frac{dg_2}{dT_2} = 3T^2$$

also

¹⁾ We shall denote here and later the velocity constant in saponifying sense by k_1 , that in esterizing sense by k_2 .

$$\frac{dg}{dT} = 3T^2,$$

independent of the value of m .

As further the equilibrium reaction begins at the same point as one of the finishing reactions (viz. $g = T = 0$, or $g = T = 1$), the equation $g = T^3$ must hold also for the equilibrium reaction:

$$g = T^3.$$

If the saponification did *not* take place stagewise, but if triacetine directly split up into glycerine and acetic acid, then $1/n$ of the acetic acid would be present in free state, when $1/n$ of the glycerine was split off, so that in this case the relative concentrations of glycerine and acetic acid would be equal to each other. For the esterification of equivalent quantities of glycerine and acetic acid the same thing holds of course.

The comparison of the relative concentrations of initial resp. final products furnishes, therefore, a direct quantitative proof whether or no a reaction takes place in stages.

§ 2. The case of the saponification of triacetine in aqueous solution is not easy to study experimentally on account of the difficulty to determine the free glycerine here quantitatively.

Esters, for which free alcohol and free acid is easier to determine, are the fats. Glycerine is soluble in water, the glycerides of the higher fatty acids are hardly so, no more than these fatty acids themselves, so that the split off glycerine will be easily separated from it.

The slight solubility in water of the higher glycerides, however, involves that most of the saponification processes do not take place in solution, but in emulsion.

A procedure, however, that takes place in solution at least partially, is the so-called sulphuric acid saponification.

VAN ELDIK THIEME¹⁾ has isolated the lower glycerides in this method of saponification, which quantitatively proves the stagewise course of the reaction.

The method comes to this: 5—10% strong sulphuric acid is added to the fat, which is heated to 120° or higher. The action of the acid is allowed to continue for some time, then the reaction product is led into boiling water, and the formed emulsion is boiled, till the required degree of decomposition is attained.

During the first phase of the process the reaction takes place in solution. The action of the sulphuric acid is here twofold: 1 the

¹⁾ Thesis for the Doctorate, Delft 1911. J. f. pr. Chem. (2) 85 284 (1912).

strong acid acts saponifying; and 2 it attacks the double binding of the oleic acid present, in consequence of which this is partially found back after the operation is over (saponification in emulsion and distillation), as iso-oleic acid, which is solid at the ordinary temperature. Accordingly this method of saponification is applied, when a yield of solid fatty acid as high as possible is desired.

In order to examine the stagewise course of the saponification with strong sulphuric acid quantitatively, it is necessary to start from a saturate triglyceride in order to avoid this complication. A suitable material is the trilaurine (to be prepared from Tangkallak-fat by re-crystallisation from alcohol), the same triglyceride that was used by VAN ELDIK THIEME

After repeated futile attempts to isolate the partially saponified fat without further saponification in emulsion taking place, the following method was applied:

5 grammes of trilaurine were carefully weighed in a glass beaker of 250 cc. It was carefully melted, a certain quantity of strong sulphuric acid was added, and everything was thoroughly mixed. Then the glass beaker was covered by a watch glass, and left for some time either in a drying oven, or at room temperature, during which the stirring was several times repeated.

After the fixed time had elapsed, the beaker was cooled in ice, and in order to separate glycerine and sulphuric acid from the glycerides and the fatty acid, as much pounded ice was added as was necessary to keep the temperature under 0° C. After mixing, ether was added and it was all brought into a cock-funnel. After shaking and separation of the layers ¹⁾ the water layer was poured off as sharply as possible, and collected for the determination of the quantity of free glycerine.

The ether layer was rinsed with alcohol in a flask and titrated with alcoholic KOH to fix the quantity of split off fatty acid. In this titration a little sulphuric acid is always also titrated. This was gravi-metrically determined after evaporation of ether and alcohol, decomposition of the soap with hydrochloric acid, and removal of the fatty acids with ether, and then deducted.

The glycerine water was repeatedly shaken with ether to remove traces of glycerides, then boiled till all the ether (and alcohol originating from the ether) had again been removed. Then the glycerine was determined by oxidation with potassium bichromate of known strength,

¹⁾ If a sufficient quantity of sulphuric acid is present a good separation is obtained in a few minutes.

and retitration with sodium thiosulphate according to STEINFELS' method¹.)

The results obtained thus are recorded in table 2 (curve A of the

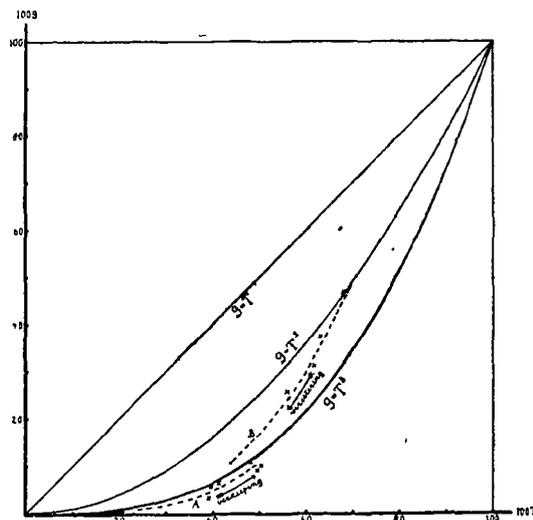


figure). The relative concentrations have here been both given in percentages. It appears that within a short time a state of equilibrium is reached, the situation of which varies with the concentration of the sulphuric acid.

T A B L E 2.
Saponification of Trilaurine.

1	2	3	4	5	6		7	8
					calculated	found		
Time of action (about)	Temperature	Strength of the H_2SO_4	Number of cc. H_2SO_4 to 5 gr. of trilaurine	100 T (found)	100 g.		Remarks	
1 uur	60°	91.5%	15	39.6	6.2	5.7		carbonization!
1 »	90	»	»	41.3	7.0	6.4		
2 »	95	»	»	54.0	15.8	(4.9)		
4 »	75	»	5.5	39.0	5.9	3.1		
3 »	75	95%	0.25	15.35		—		
1 »	60	»	40	49.4	12.1	8.9		
1 »	20	»	30	50.4	12.8	10.0		
15 min.	20	»	20	48.1	11.15	10.7		

¹) Seifens. Ztg. 42 721 (1915).

Somewhat less split off glycerine was always found than corresponds with $g = T^3$. The deviation is slight, but on an average more than the error of observation. In § 3 the importance of this will be further set forth.

As, on account of the setting in of the equilibrium, only a small region could be examined in the saponification, it was tried to complete the found curve by starting from equivalent quantities of glycerine and laurinic acid, and esterizing this in strong sulphuric acid. The procedure was here quite identical with the preceding case, instead of 5 grams of trilaurine 4.705 grams of laurinic acid and 0.710 gram of glycerine were now weighed.

The results obtained in this way are collected in table 3 (curve B of the figure).

It appears that in the esterification always more free glycerine is present than corresponds with $g = T^3$, and the more as the esterification has proceeded less far.

It is now the question: how are the deviations found in the saponification and the esterification, to be accounted for?

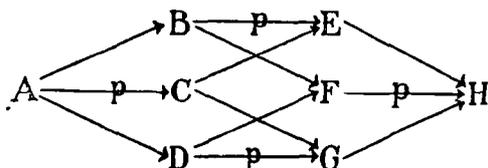
T A B L E 3.
Esterification of laurinic acid with glycerine

1	2	3	4	5	6	7	8
Time of action (about)	Temperature	Strength of the added H_2SO_4	Number of cc. H_2SO_4 to 4.705 gr. laurinic acid and 0.710 gr. of glycerine.	100 T found	100 T^3	100 g found	100 T_2
5 hours	20°	95%	20	43.8	8.4	10.6	19.2
1 "	"	"	"	55.9	17.45	25.8	31.25
20 min.	"	"	"	61.75	23.5	31.3	38.1
10 "	"	"	"	63.1	25.1	37.3	39.8
5 "	"	"	"	67.9	31.3	46.9	46.1

§ 3. Shortly after I had obtained the results recorded in tables 2 and 3 I imagined the question to be as follows: In virtue of the fact that secondary esters are on the whole more slowly saponified than primary ones it is natural to expect that the middle ester group of the triglyceride will also be slower to react than the two others. We may then expect in the saponification that $g < T^3$. If on the other hand laurinic acid with glycerine is esterized, the secondary alcohol group will probably also in this case react more slowly.

It seemed explicable to me therefore that in the esterification reversely $g > T^3$ was found. On second thoughts the latter, however, appeared to be entirely erroneous.

Let us first study the saponification of the triglyceride, and let the velocity constant of the saponification of the secondary ester-group be $= p \cdot k_1$, those of the two primary ester-groups $= k_1$. Then we obtain the following scheme:



In the calculation of the relative concentrations of the different mono- and di-glycerides we must now bear in mind that these concentrations are *not* mutually equal.

We now find that after the time t :

$$g = (1 - e^{-\nu k_1 t}) (1 - e^{-k_1 t})^2 \dots \dots \dots (6)$$

$$T = 1 - \frac{1}{3} e^{-\nu k_1 t} - \frac{2}{3} e^{-k_1 t} \dots \dots \dots (7)$$

If in these equations we substitute $p = 1$, we of course find back the equations (3) and (4).

It is now the question: what is the situation of the curve $f(g, T) = 0$, when $p \geq 1$, with regard to the curve $g = T^3$.

For $p \geq 1$ we have according to (6):

$$g = (1 - e^{-k_1 t})^2 \cdot (1 - e^{-\nu k_1 t}) = (1 - e^{-k_1 t})^3 \cdot \frac{1 - e^{-\nu k_1 t}}{1 - e^{-k_1 t}}$$

or

$$g = (1 - e^{-k_1 t})^3 \cdot \left\{ 1 + \frac{e^{-k_1 t} - e^{-\nu k_1 t}}{1 - e^{-k_1 t}} \right\} \dots \dots \dots (8)$$

Further:

$$T = 1 - \frac{2}{3} e^{-k_1 t} - \frac{1}{3} e^{-\nu k_1 t} = 1 - e^{-k_1 t} + \frac{1}{3} (e^{-k_1 t} - e^{-\nu k_1 t}),$$

or

$$T = (1 - e^{-k_1 t}) \left\{ 1 + \frac{1}{3} \frac{e^{-k_1 t} - e^{-\nu k_1 t}}{1 - e^{-k_1 t}} \right\} \dots \dots \dots (9)$$

If we now put the fraction:

$$\frac{e^{-k_1 t} - e^{-\nu k_1 t}}{1 - e^{-k_1 t}} = \Delta,$$

in which, therefore Δ is positive or negative according as p is greater or smaller than unity, the following equation follows from (8):

$$g = (1 - e^{-k_1 t})^3 \cdot (1 + \Delta) \dots \dots \dots (10)$$

and from (9)

$$T = (1 - e^{-k_1 t}) (1 + \frac{1}{3} \Delta)$$

or

$$T^3 = (1 - e^{-k_1 t})^3 (1 + \frac{1}{3} \Delta)^3 \dots \dots \dots (11)$$

From (10) and (11) follows:

$$\frac{g}{T^3} = \frac{1 + \Delta}{(1 + \frac{1}{3} \Delta)^3} = \frac{1 + \Delta}{1 + \Delta + \frac{1}{3} \Delta^2 + \frac{1}{27} \Delta^3} \dots \dots \dots (12)$$

This fraction is always < 1 , also when Δ is negative, because the third power term can never preponderate. The latter is easily proved as follows:

If $\Delta < 0$, it is required for the preponderance of the 3rd power term that:

$$-\frac{1}{27} \Delta^3 > \frac{1}{3} \Delta^2, \text{ hence } \Delta < -9,$$

hence:

$$e^{-k_1 t} - e^{-pk_1 t} < -9 + 9e^{-k_1 t},$$

or

$$8e^{-k_1 t} + e^{-pk_1 t} > 9,$$

and this can never be fulfilled, because $e^{-k_1 t}$ and $e^{-pk_1 t}$ are always smaller than 1.

It follows therefore from what precedes that when p deviates from the value 1, no matter whether $p > 1$, or < 1 , always *less* glycerine will be liberated during the saponification than corresponds with $g = T^3$.

§ 4. Let us now consider the esterification which proceeds according to the same scheme. Then we find:

$$g = e^{-(p+2)k_2 t} \dots \dots \dots (13)$$

and

$$T = \frac{1}{3} e^{-pk_2 t} + \frac{2}{3} e^{-k_2 t} \dots \dots \dots (14)$$

We now put the question: what is for values of $p \geq 1$ the situation of the $f(g, T) = 0$ determined by (13) and (14) with regard to the curve $g = T^3$.

We find from (13) and (14) in the same way as before:

$$g = e^{-3k_2 t} \cdot \left\{ 1 + \frac{e^{-pk_2 t} - e^{-k_2 t}}{e^{-k_2 t}} \right\} \dots \dots \dots (15)$$

and

$$T = e^{-k_2 t} \cdot \left\{ 1 + \frac{1}{3} \frac{e^{-pk_2 t} - e^{-k_2 t}}{e^{-k_2 t}} \right\} \dots \dots \dots (16)$$

Let us put the fraction:

$$\frac{e^{-pk_2 t} - e^{-k_2 t}}{e^{-k_2 t}} = \Delta,$$

in which Δ is now positive or negative according as p is smaller or greater than unity. Then follows again from (15) and (16):

$$\frac{g}{T^3} = \frac{1 + \Delta}{(1 + \frac{1}{3}\Delta)^3} < 1 \dots \dots \dots (12)$$

We see therefore that also in the esterification g is always $< T^3$, when p departs from the value 1, as here too $\Delta < -9$ is impossible.

When now equilibrium sets in, the reactions in saponifying and esterizing sense take place simultaneously. When one ester group deviates from the two others, every change in either direction leads to a relation $g < T^3$, in other words $g < T^3$ holds also here for the reaction of equilibrium.

When we shortly sum up what precedes, it appears that:

Both in the saponification of triglycerides and in the esterification of equivalent quantities of glycerine and fatty acid the relative concentration of the free glycerine is equal to or smaller than the third power of the relative concentration of the free fatty acid, according as the different groups are equivalent or not, provided no further complications (as e. g. in the saponification in emulsion) take place.

The situation of the experimentally determined curve A (see the figure) under the curve $g = T^3$, can therefore have been caused either by a saponification of the secondary ester group that proceeds more rapidly and by one that proceeds less rapidly compared with the primary ester groups.

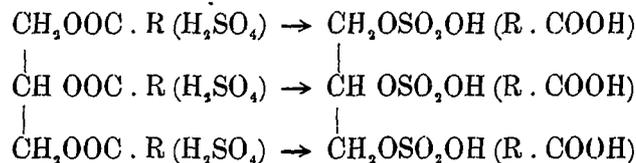
It is, however, natural to assume that the latter is the case.

§ 5. After the foregoing it is clear that the experimentally determined curve B of the figure can never find its explanation in inequivalence of the ester groups; accordingly there must be another reason that causes g to be $> T^3$ in the esterification. This reason is probably the bivalence of the sulphuric acid which serves as medium.

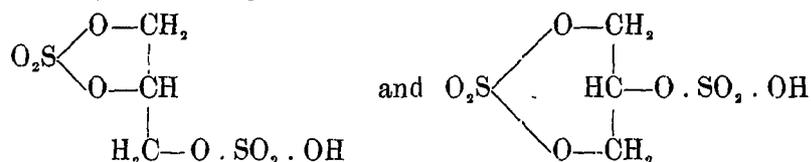
To realise this let us first inquire a little more closely into the process of saponification:

When trilaurine is put in contact with sulphuric acid, addition compounds are formed. The sulphuric acid is very loosely bound in these compounds, in water it is immediately split off again. The binding between sulphuric acid and laurinic acid may perhaps be most fitly compared with that between water and salt in a salt hydrate. However this may be, the saponification may now be imagined as follows:

The sulphuric acid bound to an estergroup, expels the laurinic acid from it under formation of glycerine sulphuric acid, so that, finally glycerine trisulphuric acid is formed. This may be expressed as follows:

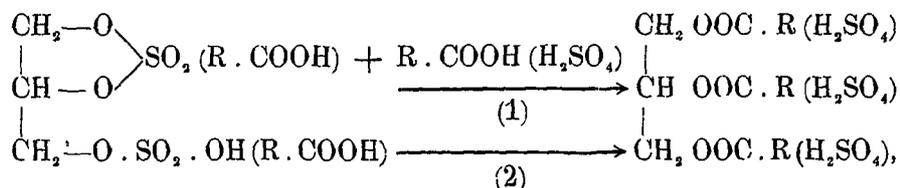


What takes place now on the other hand in case of esterification in sulphuric acid surroundings? When glycerine, laurinic acid, and sulphuric acid are mixed the glycerine will immediately be bound with the sulphuric acid, but certainly not *only* glycerine trisulphuric acid will be formed then. When a molecule of sulphuric acid combines with one of the alcohol groups of the glycerine, the chance is great that the free acid group of the sulphuric acid still combines with a second alcohol group of the same glycerine molecule, and that we therefore get the compounds:



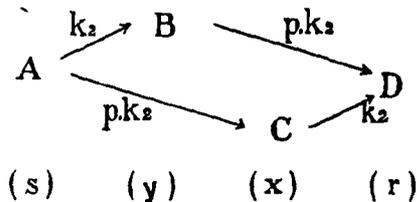
i.e. sulphates of glycerine mono sulphuric acid.

We may imagine the esterification of these sulphates as follows:



i.e. the two OH groups that are bound to one molecule of H_2SO_4 are esterized at the same time.

Let us now examine what relation there will be between the relative concentrations of free glycerine and free laurinic acid. Let us put the "constant of velocity" = pk_2 for reaction (1), and k_2 for reaction (2), we obtain the following scheme for the esterification:



In this A represents the glycerine, which can be converted to monoglyceride B with a "velocity constant" k_2 , and into diglyceride C with a "velocity constant" pk_2 . Either of these can be converted into triglyceride D with the given "constants of velocity".

When we now determine the equations of velocity, then p and k_2 occur in them, which are both variable:

$$-\frac{ds}{dt} = (p + 1)k_2 \cdot s,$$

$$\frac{dy}{dt} = k_2 \cdot s - pk_2 \cdot y,$$

$$\frac{dx}{dt} = pk_2 \cdot s - k_2 \cdot x,$$

$$\frac{dr}{dt} = k_2 \cdot x + pk_2 \cdot y.$$

We may, however, put p and k_2 constant during a short period from the beginning of the reaction, and ascertain the form of $f(g, T) = 0$ at the end of this short period.

As was already discussed before, k_2 does not occur in this last function, from which follows that $f(g, T) = 0$ is independent of the value and of the variations of k_2 . It is now, however, the question whether the factor p can likewise be eliminated, or whether it remains in the equation. In the former case $f(g, T) = 0$ is also independent of p , in the latter case it is not. It is, of course, directly to be seen that the factor p will certainly have influence, and can, therefore, not be eliminated.

This, however, causes the relation holding at the end of the short period that p is considered constant, to change if the reaction progresses. From this results that the found $f(g, T) = 0$ does not hold throughout the course of the reaction, but only represents a curve which may be serviceable as an orientation whether $g > T^3$ is possible at the supposition made.

Moreover when equilibrium comes near, the reaction in opposite sense begins to exert more and more influence. In view of the fact that the sulphates considered are esterized to glycerides, but are not restored to their original form by the opposite reaction, it is clear that at last the same equilibrium is reached as in the saponification of triglyceride.

It is, therefore, now the question: is there an initial value of p to be found by means of which the curve B found experimentally is to be explained.

Integration of the equations of velocity yields for the relative concentrations of free glycerine and free fatty acid after the very short time t :

$$g = e^{-(p+1)k_2t} \dots \dots \dots (17)$$

and:

$$T = \frac{1}{3} \{ 2e^{-pk_2t} + e^{-k_2t} \} \dots \dots \dots (18)$$

from which:

$$T = \frac{1}{3} \left\{ 2 \frac{p}{2g^{p+1}} + \frac{1}{g^{p+1}} \right\} \dots \dots \dots (19)$$

Equation (19) gives for:

$$\begin{array}{lll} p = 1 & T = g^{1/2} & \text{or} \quad g = T^2 \\ p = 2 & T = \frac{1}{3} \{ 2g^{3/2} + g^{1/2} \} \text{ ,,} & g = \frac{1}{64} \{ \sqrt{1 + 24T} - 1 \}^2 \end{array}$$

When now the values found experimentally are compared with the values of column 8 of table 3 and with the curve $g = T^2$ of the figure, it appears that the experiment can be explained by the above reaction, if the initial value of p is $p \geq 1$.

The above should strictly speaking be completed with the determination of the quantity of "sulphate of glycerine mono sulphuric acid" formed when glycerine and sulphuric acid are mixed, which, however, will be exceedingly difficult to accomplish.

It is, therefore, only our intention to give a plausible explanation of the experimentally found curve B of the figure. Whether this explanation is perfectly correct may perhaps be decided by later experiments.

We see, therefore, that in the esterification of glycerine with fatty acid dissolved in strong sulphuric acid, complications are again met with, which cause a deviation from the ideal case.

Probably others than glycerine esters will be better adapted to realise this ideal case. It appears, however, from the above that it is exactly the deviations that often furnish valuable data about the mechanism of a reaction that takes place in stages.

In conclusion a few words about the second phase of the sulphuric acid saponification, viz. the boiling with water. When the reaction product of the first phase is made to flow into boiling water, a very fine emulsion is formed, the dispersity of which rapidly diminishes. The temporary fineness is caused by the presence of monolaurine, which greatly lowers the surface tension between water and fat.¹⁾ This is attended with adsorption of monolaurine at the surface of contact between fat and water (the place of reaction in saponification in emulsion), which causes it to be quickly saponified, and the dis-

¹⁾ TREUB l. c.

persity of the emulsion to decrease.¹⁾ A consequence of this is that in the initial stage of the second phase a considerable separation of glycerine takes place.

In the saponification in emulsion the relation between the relative concentrations of free fatty acid and free glycerine is now determined by the adsorption of the lower glycerides at the surface of contact between fat and water. In this case the three ester groups of the triglyceride may be taken as equivalent with very close approximation. The equation $T = \frac{1}{3}(g + g^{2/3} + g^{1/3})$, which is founded on this supposition, and which holds for the TWITCHELL-process, holds also at the end of the second phase of the sulphuric acid saponification, when the water contains but little sulphuric acid (from 1 to 2%). If the acid content in the water is greater, then $T > \frac{1}{3}(g + g^{2/3} + g^{1/3})$.

S U M M A R Y.

The relation between the relative concentrations of free glycerine and free fatty acid was derived for the ideal case that tri-glyceride saponification takes place in solution, the ester groups are equivalent, and no complications present themselves.

It holds that the relative concentration of the free glycerine is at any moment equal to the third power of the relative concentration of the free fatty acid in case of stagewise saponification.

The same thing holds for the ideal case of esterification.

In the saponification of trilaurine with strong sulphuric acid only a very slight deviation was found, caused by the not perfect equivalence of the three ester groups. This is a direct and quantitative proof of the stagewise course of the reaction.

In the esterification of equivalent quantities of laurinic acid and glycerine dissolved in strong sulphuric acid deviations were found, which are probably caused by the action of the two-basic sulphuric acid.

Gouda, May 1917.

*Laboratory of the Royal Stearine
Candle Works "Gouda".*

¹⁾ In treating fats, containing unsaturated acids, with strong sulphuric acid at high temperature, compounds are formed that keep up the dispersity of the emulsion during a longer time.

Terrestrial magnetism. — “Do the forces causing the diurnal variation of terrestrial magnetism possess a potential?” By Miss ANNIE VAN VLEUTEN. (Communicated by Dr. J. P. VAN DER STOK).

(Communicated in the meeting of June 30, 1917).

1. In their analysis of the diurnal field of variation, SCHUSTER¹⁾ and FRIESCHE²⁾ assumed that this field possesses a potential, the necessity of this hypothesis not being proved a priori. For a test by means of integration along a closed curve on the surface sufficient data are still lacking, but another method enables us to inquire how far the horizontal forces can be deduced from one and the same function.

According to the Gaussian theory the potential of the terrestrial magnetic field is determined, when we know:

either the Northcomponent over the surface, or the Eastcomponent over the surface and the values of the force, directed North along a curve joining the two poles.

As in this case the forces are those causing the diurnal variation, hence completely periodical, the Eastcomponent on the surface alone is sufficient to determine the potential.

When for a number of points on the surface ΔX and ΔY are given, we can deduce from ΔX a function π_x representing the potential, if there exists such a function; in the same manner we can deduce from ΔY a function π_y and compare these two expressions.

2. From the diurnal variation at *Pavlovsk* (59°41' N. 30°29' E.); *Sitka* (57°3' N. 135°20' W.); *Irkoutsk* (52°16' N. 104°19' E.); *De Bilt* (52°6' N. 5°11' E.); *Cheltenham* (38°44' N. 76°51' W.); *Zi-ka Wei* (31°19' N. 121°2' E.); *Honolulu* (21°19' N. 158°4' W.); *Bombay* (18°54' N. 72°49' E.); *Buitenzorg* (6°35' S. 106°47' E.) and *Samoa* (13°48' S. 171°46' W.), all for the period 1906—1908, for each of the components a function has been deduced in this manner.³⁾

¹⁾ The Diurnal Variation of Terr. Magn. Phil. Trans. Vol. 180 (1889) A.

²⁾ Die Tagliche Periode der Erdm. Elemente St. Petersburg 1902

³⁾ This research is treated more at length in a thesis for the doctorate.

TABLE I.

SUMMER										
	g_1^1	h_1^1	g_2^1	h_2^1	g_3^1	h_3^1	g_4^1	h_4^1	g_2^2	h_2^2
π_x	- 1.70	2.96	-11.45	1.81	- 8.33	- 1.61	27.71	- 5.76	1.60	-4.36
π_y	- 6.42	- 1.89	- 3.02	18.58	-34.41	-29.77	46.67	29.88	-0.31	-3.36
WINTER										
π_x	6.36	- 0.61	-13.31	1.77	1.78	- 0.87	22.99	- 1.30	0.50	-0.51
π_y	1.34	- 7.19	- 2.17	23.88	-35.26	-37.11	55.97	37.94	-3.00	1.55
SUMMER										
	g_3^3	h_3^2	g_4^2	h_4^2	g_3^3	h_3^3	g_4^3	h_4^3	g_4^4	h_4^4
π_x	9.76	- 1.91	2.62	0.94	0.26	2.31	- 4.01	2.03	0.03	-0.43
π_y	11.63	- 4.02	1.22	- 0.86	0.44	1.59	- 4.44	3.11	-0.29	-0.36
WINTER										
π_x	10.11	- 1.53	- 3.05	1.96	- 0.53	0.73	- 4.27	1.73	0.26	-0.52
π_y	15.80	5.74	- 8.17	3.78	0.43	- 0.88	- 5.23	3.82	0.31	-0.22

g_n^m and h_n^m are the coefficients of the function P_n^m , which GAUSS used in his "Allgemeine Theorie des Erdmagnetismus", where :

$$\frac{V}{R} = \sum_{n=1}^{n=\infty} P_n$$

$$P_n = \sum_{m=1}^{m=n} (g_n^m \cos m \lambda + h_n^m \sin m \lambda) P_n^m$$

λ represents the geographical longitude, V the potential, R the radius of the earth, the functions P_n differing from the spherical harmonics only by a numerical factor.

It is worth notice that most of the coefficients in π_x are much smaller than those in π_y , whereas the sign is not always the same.

3. If we want to know what part of these differences may be ascribed to the choice of the sets of observations, we have first to find out how far these coefficients represent the results of observation.

In order to avoid disturbing influences as much as possible, we

used the diurnal variation on "quiet" days; in consequence of the use of the "international" quiet days the material for all the stations refers to the same days and therefore is as *homogeneous* as possible.

By means of the calculated values of g and h the FOURIER-coefficients for the diurnal variation were obtained for the places used in the calculation, and for the 10 stations an average deviation between calculated and observed amplitude (positive and negative values taken with the same sign) was found, amounting to

34% in the diurnal, 35% in the semi-diurnal period for ΔX
 20% " " " 16% " " " " " ΔY

4. For a determination of the harmonic coefficients at other places a *graphic* interpolation is the most suitable. The calculated points in the diagram are joined by a smooth curve, by means of which the coefficients for each intermediate latitude can be read off. Moreover we can decide how far observations made at stations situated outside the interval 60° N.—14° S. follow the curve of the calculated points.

A test in this manner gave satisfactory results and led to the following conclusions:

a. In the main the curves would show the same character if more stations had been used for the calculation.

b. The difference between π_2 and π_y cannot be completely attributed to insufficient observational material, i.o.w.: The forces causing the diurnal variation, taken as a whole, do *not* possess a potential, although it remains always possible to deduce part of these forces from a potential.

Terrestrial Magnetism. — “*On the question whether the internal magnetic field, to which the diurnal variation in terrestrial magnetism is partly ascribed, depends on induced currents.*”
By Miss ANNIE VAN VLEUTEN. (Communicated by Dr. J. P. VAN DER STOK).

(Communicated in the meeting of June 30, 1917.)

1. In 1889 SCHUSTER ¹⁾ suggested that the diurnal magnetic variation might be explained by a system of electric currents *exterior* to the earth, and currents induced *within* the earth by the former system.

Assuming that the conducting power of the earth increases with the depth, he found the results of his analysis of the horizontal and vertical forces in harmony with that hypothesis.

2. In 1902 FRITSCHÉ ²⁾ starting from other data expanded the potential of the diurnal field of variation in a series of spherical harmonics, and in 1912 STEINER ³⁾ examined whether these numbers contained a corroboration of SCHUSTER's idea.

It appeared that the mutual relations of the two parts of the potential corresponding to the external and the internal field did not correspond to the theory.

By taking into account also the magnetic permeability he could obtain a reasonable agreement for some of the terms but in general the above mentioned supposition was *not* confirmed.

3. In 1913 FRITSCHÉ ⁴⁾ published new values for the potential coefficients of the diurnal variation, using the same material as in 1902, except that of the polar stations, which seemed less reliable.

If we repeat STEINER's investigation by means of these values, these numbers are no more than the coefficients of 1902 in accordance with the supposition, that the internal field is caused by induced currents.

¹⁾ The Diurnal Variation of Terr. Magn. Phil Trans. Vol. 180 (1889) A.

²⁾ Die Tägliche Periode der Erdmagnetischen Elemente. St. Petersburg 1902.

³⁾ Die Bestimmung der Elemente des Erdmagnetismus und ihrer zeitlichen Aenderungen. Riga 1913.

⁴⁾ Ueber die tägliche Variation der erdmagnetischen Kraft. Met. Z.schr. 29 (1912).

TABLE II.

SUMMER.												
	External						Internal					
	<i>g</i>	<i>h</i>	<i>a</i>	ϵ	FRITSCHÉ (1913)		<i>g</i>	<i>h</i>	<i>A</i>	$\epsilon + \alpha$	FRITSCHÉ (1913)	
					<i>a</i>	ϵ					<i>A</i>	$\epsilon + \alpha$
P_1^1	-5.79	1.66	6.02	196°0'	3.96	171°35'	-1.73	-1.13	2.02	33°9'	4.24	245°19'
P_2^1	0.03	2.97	2.98	270 30	12.70	212 15	-7.26	7.22	10.24	224 50	5.19	187 52
P_3^1	-21.25	-4.70	21.76	167 32	1.85	206 1	-0.12	-10.99	10.99	90 37	5.47	78 24
P_4^1	29.53	4.89	29.93	350 36	7.63	17 19	7.66	7.18	10.5	316 51	6.55	298 8
P_2^2	0.50	-2.56	2.61	79 2	1.53	62 13	0.15	-1.30	1.31	83 23	1.67	89 19
P_3^2	8.11	-1.82	8.31	12 40	6.89	31 31	2.59	-1.15	2.83	23 56	2.65	13 46
P_4^2	0.74	0.64	0.98	319 16	3.41	348 0	1.18	-0.60	1.32	26 57	1.71	78 34
P_3^3	0.07	1.34	1.34	273 2	0.76	283 40	0 28	0.61	0.66	294 41	0.76	291 32
P_4^3	-3.26	1.64	3.64	206 42	3.39	214 4	0.97	0.94	1.38	223 50	0.89	216 21
P_4^4	-0.07	-0.32	0.33	101 13	0.27	145 43	-0.06	-0.07	0.10	130 34	0.20	182 52

WINTER.												
P_1^1	-0.84	-2.34	2.49	109°45'	5.77	20°28'	4 69	-1.56	4.94	18 23'	1.56	284°29'
P_2^1	1.99	6.75	7.04	286 27	12.92	204 36	-9.74	6.07	11.48	211 58	4.78	200 27
P_3^1	-20.88	9.51	22.95	155 30	5.17	326 2	4.14	9.48	10.34	66 25	5.15	47 31
P_4^1	33.04	10.71	34.74	342 2	5.88	351 0	6.44	7.60	9.97	310 16	4.96	273 35
P_2^2	-0.94	0.32	0.99	198 52	1.64	221 47	-0.31	0.20	0.37	213 1	0.61	216 18
P_3^2	8.80	-1.77	8 97	11 23	6.00	16 57	4.16	-1.87	4.56	24 12	3.98	25 48
P_4^2	-3.59	1.47	3.88	202 18	0.75	259 17	-2.02	1.40	2.46	214 46	3.02	209 22
P_3^3	-0.05	-0.08	0.09	121 10	0.72	48 58	-0.00	0.01	uncertain		uncertain	
P_4^3	-3.35	1 58	3.71	205 16	3.45	212 27	-1.40	1.19	1.84	220 19	1.60	229 19
P_4^4	0.24	-0.23	0.33	43 24	0.18	29 21	0.05	-0.14	0.15	70 50	0.08	330 15

4. With a view to different objections, that can be raised against SCHUSTER's calculation as well as against that of FRITSCHÉ, we thought it desirable once more to analyze the diurnal field of

variation, and to separate it into an external and an internal part. ¹⁾

The notation is the same as that of STEINER. Instead of the notation used by FRITSCHÉ in accordance with (GAUSS) where

$$\frac{V}{R} = \sum_{n=1}^{n=\infty} P_n$$

$$P_n = \sum_{m=1}^{m=n} (g_n^m \cos m \lambda + h_n^m \sin m \lambda) P_n^m,$$

λ representing the geographical longitude, V the potential, and R the radius of the earth, the functions P_n differing from the spherical harmonics only by a numerical factor, we put:

$$g_n^m \cos m \lambda + h_n^m \sin m \lambda = \begin{cases} a_n^m (\cos m \lambda + \varepsilon_n^m) & \text{for the external field.} \\ A_n^m (\cos m \lambda + (\varepsilon + \alpha)_n^m) & \text{,, ,, internal field.} \end{cases}$$

5. In Tab. III $c = \frac{A}{a}$ and α for each term represent the ratio of amplitudes and the phase-difference between those parts that correspond to the internal and external fields.

In the first column are given the values calculated for two limiting values of the specific resistance, in the second our results, in the third column the results of FRITSCHÉ's first calculation, in the fourth those deduced from his last publication. (The first and third column are taken from STEINER for the sake of comparison).

A comparison of the values shows that the newly calculated values are more regular than those of FRITSCHÉ, a fact especially demonstrated by the agreement between summer and winter.

With the exception of P_1^1 , P_2^1 and P_4^2 the ratio c is situated between the limits calculated from theory, somewhat closer however to that corresponding to the smallest ρ .

The phasedifference α is negative for the first four terms, positive for the other ones; all differences are smaller than those resulting from theory, but approaching to the limit corresponding to the smallest resistance.

The regularities in the terms of higher order are in favour of SCHUSTER's idea, but the fact that the principal terms P_1^1 and P_2^1 do not correspond to the theory indicates, that the cause of the diurnal variation certainly cannot be ascribed to nothing else but a system of currents exterior to the earth and currents within the earth induced by the former system.

¹⁾ Some details of this research, which will be treated more at length in a thesis for the doctorate, are given in the foregoing communication. For the potential from which part of the horizontal forces is to be deduced we took $\frac{1}{2}(\pi_x + \pi_y)$.

TABLE III.

	Calculated from Theory				FRITSCHÉ (1902)		FRITSCHÉ (1913)			
	I		II		III		IV			
	<i>c</i>	<i>α</i>	<i>c</i>	<i>α</i>	<i>c</i>	<i>α</i>	<i>c</i>	<i>α</i>		
P_1^1	$q = 3.7 \times 10^{14}$	0.03	85°	0.34	-163°	1.90	77°	1.07	74°	Summer
	$q = 3.7 \times 10^{12}$	0.40	13	1.99	-91	0.44	-89	0.27	-96	Winter
P_2^1	$q = 3.7 \times 10^{14}$	0.02	87	3.44	-46	0.36	-45	0.41	24	Summer
	$q = 3.7 \times 10^{12}$	0.47	22	1.63	-74	0.40	-26	0.37	-4	Winter
P_3^1	$q = 3.7 \times 10^{14}$	0.01	89	0.50	-77	1.51	-119	2.96	-128	Summer
	$q = 3.7 \times 10^{12}$	0.45	30	0.45	-89	1.13	25	1.00	81	Winter
P_4^1	$q = 3.7 \times 10^{14}$	0.01	89	0.35	-34	0.91	183	0.86	-79	Summer
	$q = 3.7 \times 10^{12}$	0.41	38	0.29	-32	1.39	182	0.84	-77	Winter
P_2^2	$q = 3.7 \times 10^{14}$	0.04	85	0.50	4	1.09	28	1.10	27	Summer
	$q = 3.7 \times 10^{12}$	0.52	15	0.38	14	0.37	-7	0.37	-5	Winter
P_3^2	$q = 3.7 \times 10^{14}$	0.02	87	0.34	11	0.30	-28	0.38	-18	Summer
	$q = 3.7 \times 10^{12}$	0.53	21	0.51	10	0.64	2	0.66	9	Winter
P_4^2	$q = 3.7 \times 10^{14}$	0.02	88	1.35	67	1.39	162	0.50	91	Summer
	$q = 3.7 \times 10^{12}$	0.51	27	0.63	12	2.61	50	4.01	-50	Winter
P_3^3	$q = 3.7 \times 10^{14}$	0.04	86	0.50	12	1.02	8	1.00	8	Summer
	$q = 3.7 \times 10^{12}$	0.56	17			0.36	39			Winter
P_3^3	$q = 3.7 \times 10^{14}$	0.02	87	0.37	17	0.31	-7	0.26	2	Summer
	$q = 3.7 \times 10^{12}$	0.55	22	0.50	15	0.47	19	0.46	17	Winter
P_4^4	$q = 3.7 \times 10^{14}$	0.03	86	0.30	29	0.72	41	0.75	37	Summer
	$q = 3.7 \times 10^{12}$	0.58	19	0.45	27	0.42	-47	0.44	-59	Winter

Physics. — “*The equation of state of an associating substance*”.
 By Prof. J. E. VERSCHAFFELT. Supplement N^o. 42a to the Commu-
 nications from the Physical Laboratory of Leiden. (Communi-
 cated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of June 30, 1917).

1. A few years ago it was pointed out by KOHNSTAMM and ORNSTEIN ¹⁾ that VAN DER WAALS' equation of state is not consistent with NERNST's thermodynamical theorem. Taking this theorem in the form which PLANCK ²⁾ has given it, viz. the entropy of a system in a condensed state at the absolute zero under its own vapour-pressure, i. e. under zero pressure, is zero, ³⁾ which means that the entropy-difference between this condition and any other (excepting the ideal gas-condition) is finite, the contradiction consists in the equation of state of VAN DER WAALS giving for $v = b$ (the limiting volume) a value of the entropy which is lower than that for any other volume by an infinite amount ⁴⁾.

This objection only applies, however, to the equation in its original form, i. e. with a , b , and R constant; for it is evident, that it must be possible by making these quantities change in a suitable manner to bring about not only a qualitative, but even a complete quantitative agreement between the equation of state and observation, and thus also with NERNST's theorem, if the latter is really in accordance with the experimental system of isothermals. In particular it will be clear that agreement with NERNST's theorem ⁵⁾ can be obtained

¹⁾ These Proceedings. XIII (2), p. 700. Comp. W. NERNST These Proceedings XIV (1) p. 201.

²⁾ Thermodynamik, 4e Aufl., 1913, p. 266.

³⁾ According to NERNST and PLANCK the entropy at the absolute zero should even be zero under any other pressure, i. e. should be independent of the pressure. Comp. however MAX B. WEINSTEIN Ann. d. Phys., (4), 52 (1917), p. 218; (4), 53 1917, p. 47. Vid. also PAUL S. EFSTEIN Ann. d. Phys., (4), 53 (1917), p. 76.)

⁴⁾ Indeed, according to v. D. WAALS $S_v - S_b = \int_b^v \left(\frac{\partial p}{\partial T} \right)_v dv = |R \log (v-b)|_b^v$.

The two further important inferences to be drawn from the theorem: $\left(\frac{\partial v}{\partial T} \right)_p = 0$ and $C_p = 0$ for the condensed state at $T = 0$, which seem to be confirmed by observations at low temperature, are not satisfied by this equation of state either.

⁵⁾ That is: $S_v - S_b$ can be made finite,

by making R approach zero at the same time as T in an appropriate manner. A variation of R of that nature for a definite amount¹⁾ of substance means that the molecules combine to aggregates (association)²⁾ or undergo a different process, which resembles the former very closely (quasi-association) and was repeatedly assumed by VAN DER WAALS³⁾ and his pupils⁴⁾ for the purpose of explaining the incomplete numerical correspondence between the original equation of state and the actual course of the isothermal. It was, however, always assumed, that only one kind of molecular aggregate was formed⁵⁾, whereas for R to fall to zero a much more complex association (or quasi-association) is required, viz. a process in which the molecular groups which are formed become more and more complex, according as the temperature falls, until finally at $T = 0$ the substance behaves as if consisting of only one molecule, at least at small volumes⁶⁾.

On this ground I have made an attempt to extend the theory of association by introducing the hypothesis, that instead of one special aggregate all possible molecular complexes are formed: double molecules, triple, quadruple, etc.⁷⁾ In this attempt I think I have succeeded, proceeding logically on the lines followed by VAN DER WAALS in his theory of "quasi-association or molecular aggregation"

1) R is only then a universal constant (the gas constant) when it refers to a gram mol of the substance. When the molecules form groups, the number of gram-mols in a given mass diminishes and R for that mass changes proportionally to that number.

2) Previously F. RICHARZ (ZS. f. anorg. Chem., 58 (1908) p. 356; (1908) p. 146) has explained the fall of the specific heat by association. Comp. also J. DUCLAUX, C.R. 155 (1912) p. 1015. The same hypothesis was shown by C. BENEDICKS (Ann. d. Phys., (4), 42 (1913) p. 133) to be capable of giving an explanation of PLANCK's law of energy distribution.

3) Continuität, II, p. 27. These Proceedings (1), p. 107 and 494.

4) J. J. VAN LAAR, ZS. f. physik. Chem., 31, (1899) p. 1; Arch. Teyler, (2), XI, 1908.

G. VAN RIJ, Proefschrift, Amsterdam, 1908.

5) This assumption was made for the sake of simplicity, although the probability of different molecular complexes being formed was recognised. (See for instance VAN DER WAALS, These Proceedings, XIII (1), p. 494).

6) Comp. H. KAMERLINGH ONNES and W. H. KEESOM Die Zustandsgleichung Encyklopädie der Mathematischen Wissenschaften, V, 10, p. 886. Suppl. 23 of the Comm. from the Phys. Lab of Leiden, p. 272

We shall not dwell on the difficulty which may be involved in imagining the state in which during the transition to the molecular condition of one solid lump the substance must have consisted of a small number of molecules.

7) This thought I developed many years ago for an associating substance such as water in the dissolved condition (Acad. Roy. de Bruxelles, Mém. cour., 1896).

(loc. cit.). The equation of state at which I have arrived in this manner is no longer incompatible with the requirements of NERNST'S theorem ¹⁾).

2. Let 1 gr. of the associating substance contain x_1 gr. of single molecules, x_2 gr. of double molecules, etc. in general x_n gr. of n -fold molecules ²⁾, so that $\sum x_n = 1$. The x_n grammes contain $\frac{x_n}{nM}$ gram-mols (M being the molar weight of the simple substance), so that there will be altogether $\frac{1}{M} \sum \frac{x_n}{n}$ gram-mols per gramme. If αM be the mean molar weight, α being the mean *degree of association*, the number of grammols per gramme will be $\frac{1}{\alpha M}$, so that

$$\frac{1}{\alpha} = \sum \frac{x_n}{n} \dots \dots \dots (1)$$

We now assume, that for M grms. of an arbitrary *unchanging* mixture of molecules of mean degree of association α , the equation of state has the form used by VAN DER WAALS:

$$p = \frac{R_x T}{v - b_x} - \frac{a_x}{v^2}, \dots \dots \dots (2)$$

where R_x does not represent the gas-constant R corresponding to a gram-mol, but $R_x = \frac{R}{\alpha}$ ³⁾. Moreover a_x and b_x are functions of the quantities x_n , b_x being also a function of v , whereas both a_x and b_x might in general be functions of the temperature; but on various grounds, which were fully discussed by VAN DER WAALS ⁴⁾, we shall not introduce the last-mentioned supposition.

We shall also for the sake of simplicity following VAN DER WAALS ⁵⁾ leave out a dependence of b on the quantities x_n , i. e. we assume

¹⁾ According to E. ARIÈS (Paris C. R. 164 (1917) p. 593) this theorem would be implied by the ordinary theorems of thermodynamics. This statement is incorrect, however, and is obviously due to the author unconsciously introducing suppositions which involve the theorem. As an instance he adheres to the identity of adiabatics and isentropics down to the absolute zero, although at that temperature $dQ = TdS = 0$ does not necessarily imply $dS = 0$. He also introduces in some well known relations such as HELMHOLTZ'S theorem transformations which are not in general mathematically allowable and therefore presuppose a special course of the thermodynamical functions at $T = 0$.

²⁾ n is supposed to assume all possible integral values from 1 to ∞ .

³⁾ See page 366, footnote 1.

⁴⁾ These Proceedings, XIII (1), p. 109; XIII (2), p. 1213.

⁵⁾ These Proceedings, XIII (1), p. 121.

that the volume of the molecules is not modified by the grouping of the molecules, which agrees with VAN DER WAALS'S manner of considering associated (or quasi-associated) molecules as "mere complexes of the simple molecules, which can be formed without further radical modifications in the structure of the molecules themselves".¹⁾

3. As to the quantity a_x VAN DER WAALS had originally²⁾ made some simplifying assumptions which resulted in this factor also becoming independent of the degree of association; later on³⁾ he made his theory independent of these special suppositions on the ground, that when molecular complexes are formed only a part of the cohesion can make itself felt as internal pressure. In order to conform to this view it is natural in our case to replace the form $a_x = a [(1-x) + kx]^2$ chosen by VAN DER WAALS in the case of only one kind of complex molecules by the more general form⁴⁾

$$a_x = a (\sum k_n x_n)^2 \dots \dots \dots (3)$$

where a is independent of the degree of association. In this manner we obtain an equation of the following form:

$$p = \frac{RT}{v-b} \sum \frac{x_n}{n} - \frac{a}{v^2} (\sum k_n x_n)^2 \dots \dots \dots (4)$$

which is a generalisation of the one assumed by VAN DER WAALS (l. c. p. 92)⁵⁾.

The coefficients k_n may no doubt be assumed to have definite numerical values, only depending on the ordinal number n ($k_1 = 1$).

¹⁾ These Proceedings, V (1902), p. 304. VAN LAAR on the other hand (Arch. Teyler, (2), XI, 1908) assumes, that the molecular volume does change (increases or diminishes) by association. This assumption is an essential one in his theory, as he derives from it the possibility of a coexistence of the vapour and liquid with a third (solid) phase (These Proceedings 1909—1911).

²⁾ Continuität II, p. 28. See also VAN RIJ and VAN LAAR (loc. cit.).

³⁾ These Proceedings, XIII (1), p. 119.

⁴⁾ This form is arrived at by assuming in general $a = \sum a_n x_n^2 + 2 \sum \sum a_{\mu\nu} x_\mu x_\nu$, and making the additional simplifying assumption $a^2_{\mu\nu} = a_\mu a_\nu$ (c.f. v. D. WAALS, loc. cit., p. 120).

⁵⁾ We might have retained the equation used by VAN DER WAALS, assuming that in it x represents that fraction of the substance which is present as complex, n -fold molecules, n being the mean complexity of all not-single molecules; the possibility of such a generalisation was pointed out by VAN DER WAALS himself, loc. cit., p. 494; n would then have to be considered as a function of v and T , connected with α by the relation:

$$\frac{1}{\alpha} = 1 - x + \frac{x}{n} = 1 - \frac{n-1}{n} x.$$

If all k were equal to 1, a_x would be equal to α and the equation would be

$$p = \frac{1}{\alpha} \frac{RT}{v-b} - \frac{a}{v^2} \dots \dots \dots (4')$$

If k_n were, equal to $\frac{1}{n}$, we should have

$$p = \frac{1}{\alpha} \frac{RT}{v-b} - \frac{a}{\alpha^2 v^2} \dots \dots \dots (4'')$$

A more general assumption would be that

$$k_n = 1 - \frac{n-1}{n} \epsilon \quad (0 < \epsilon < 1), \text{ so that } \sum k_n x_n = 1 - \frac{\alpha-1}{\alpha} \epsilon; \quad (5)$$

in that case²⁾:

$$p = \frac{1}{\alpha} \frac{RT}{v-b} - \frac{a\varphi(\alpha)}{v^2}, \text{ where } \varphi(\alpha) = \left(1 - \frac{\alpha-1}{\alpha} \epsilon\right)^2 \quad (5')$$

4. The manner in which b changes with v , independently of all association, has also been fully discussed by VAN DER WAALS. The law of dependence sketched out by him³⁾ may be very well represented by the following expression:

$$(b_\infty - b)(v - kb_\infty) = \frac{1}{4}(1-k)^2 b_\infty^2 \quad \text{or} \quad b = b_\infty - \frac{1}{4} \frac{(1-k)^2 b_\infty^2}{v - kb_\infty}, \quad (6)$$

where b_∞ is the value of b for an infinite volume, whereas at the smallest possible volume:

$$v_{lim} = b_{lim} = \frac{1}{2}(1+k)b_\infty, \text{ where } 0 < b_{lim} < b_\infty \text{ or } -1 < k < +1^4). \quad (6')$$

On this assumption as regards the relation between b and v the equation of state (5') becomes:

¹⁾ The special form proposed by VAN DER WAALS $a_x = a \left(1 - \frac{x}{2}\right)^2$ is arrived at by putting k_n ($n=1$) constant and equal to $\frac{1}{2}$; even at the highest degree of association ($x=1$) a_x would still be $\frac{1}{4}a$. It seems more natural, however, to assume that as n increases, k_n becomes smaller; if the diminution of k_n went so far, that it approached zero, a_x would ultimately become zero.

²⁾ Although a given mean degree of association may be obtained in an infinite number of ways, still according to the assumption (5) the cohesion (and thereby the equation of state for a given α) is no longer dependent on the special way in which the molecules are grouped.

If $\epsilon = \frac{1}{2}$, so that $\varphi(\alpha) = \frac{1}{4} \left(1 + \frac{1}{\alpha}\right)^2$, the limiting value of a_x will be equal to $\frac{1}{4} \alpha$, as according to VAN DER WAALS's assumption.

³⁾ These Proceedings, XV (2), p. 1131.

⁴⁾ If $k=1$, $b = \text{constant} = b_\infty$, as in the original equation of VAN DER WAALS. With $k=-1$ we should have $v_{lim} = b_{lim} = 0$.

$$p = \frac{RT}{\alpha} \frac{v - \frac{2k}{1+k} b_{lim}}{(v - b_{lim})^2} - \frac{a \varphi(\alpha)}{v^2} \dots \dots \dots (6'')$$

This would therefore be the equation of state of an associated substance of unchanging mean degree of association α . But we may also look upon this equation as referring to a substance undergoing a molecular transformation, if we consider α as a function of v and T expressing how the mean degree of association depends on volume and temperature. This is the function which we propose to determine.

5. But before proceeding to do this we shall first consider (6'') once more as the equation of state of a substance with constant α . The critical constants are found to be by the usual method

$$(v_k)_\alpha = K_1 b_\infty \quad (p_k)_\alpha = K_2 \frac{a}{b_\infty^2} \varphi(\alpha) \quad R(T_k)_\alpha = K_3 \frac{a}{b_\infty} \alpha \varphi(\alpha) \quad (7)$$

where the numerical coefficients K_1 , K_2 and K_3 , the so-called critical coefficients¹⁾, have values which change with k ²⁾. Hence:

$$(v_k)_\alpha = (v_k)_1 \quad (p_k)_\alpha = (p_k)_1 \varphi(\alpha) \quad (T_k)_\alpha = (T_k)_1 \alpha \varphi(\alpha)^2 \quad (7')$$

According to the above assumptions, therefore, the critical volume of all polymers would be the same; i. e. the same as that of the pure substance with the simplest molecules; the critical pressure would also remain constant, if ε were zero (equation 4'), and $T_{\alpha k}$ would then be proportional to α , whereas with $\varepsilon = 1$ (equation 4'') $p_{\alpha k}$ would be inversely proportional to α^2 , and $T_{\alpha k}$ inversely to α . With the more general form (5) it becomes somewhat less simple: $p_{\alpha k}$ is then found to diminish continually with increasing α , and $T_{\alpha k}$ first increases and afterwards also diminishes³⁾.

¹⁾ Vide H. KAMERLINGH ONNES and W. H. KEESOM, Die Zustandsgleichung, p. 703 (89).

²⁾ The following results are obtained:

$k = 1$	$b = b_\infty$	$K_1 = 3$	$K_2 = \frac{1}{27} = 0,0370$	$K_3 = \frac{3}{27} = 0,296$
$k = \frac{1}{2}$	$\frac{3}{4} b_\infty$	2,80	0,0408	0,368
$k = 0$	$\frac{1}{2} b_\infty$	2,32	0,0540	0,342
$k = -\frac{1}{2}$	$\frac{1}{4} b_\infty$	1,59	0,0952	0,422
$k = -1$	0	0	∞	1

³⁾ Although these relations are derived from a special form of the equation, it is quite possible that independently of it they may be at least approximately valid, in the same way as the law of corresponding states, although it was found by means of the original equation of state of VAN DER WAALS, is not bound to this particular one. But the necessary experimental data to test the equations (7') by experiment are not available.

⁴⁾ In the well known case of polymerisation acetaldehyde (C_2H_4O , $t_k = 188^\circ C$.)-paraldehyde ($C_6H_{12}O_3$; $t_k = 290^\circ C$) the relation (7') gives a correct result for the critical temperatures with $\varepsilon = \frac{1}{2}$ about; unfortunately the critical pressures and volumes of these substances are not known, so that a further test is impossible. However, it is doubtful, whether the above theory would be applicable to a chemical transformation of that kind.

From the equations (7) it also follows that

$$\frac{1}{\alpha} \frac{R(T_k)_\alpha}{(p_k)_\alpha (v_k)_\alpha} = \text{a constant}^1) \dots \dots \dots (7'')$$

6. We shall now consider the equation (4) as representing the

¹⁾ This constant, the critical virial-coefficient K_4 (vid. KAMERLINGH ONNES and KEESOM, loc. cit., p. 752 (138)), again has a value which changes with k . For

$k = 1$	$\frac{1}{2}$	0	$-\frac{1}{2}$	-1
$K_4 = \frac{8}{3} = 2,67$	2,69	2,73	2,80	3

The change of K_4 with k is seen to be comparatively small, and the relation which we have assumed between b and v does not raise the coefficient K_4 to the experimental value of 3.6 about, holding for the so-called normal substances, or the still higher value required by the associating substances; it is even doubtful, whether this could be attained with any other relation $b = \psi(v)$, unless a very special form were purposely chosen (comp. on this point VAN DER WAALS, These Proceedings, XIII (2), p. 1211; see also KAMERLINGH ONNES and W. H. KEESOM, loc. cit., p. 752) It is true that v. d. WAALS (Boltzmann-Festschrift, 1904, p. 305)

found the correct value of K_4 , by putting $b = b_\infty \left(1 - k \frac{b_\infty}{v}\right)$ and $k = \frac{8}{3}$, but it is easily seen, that this expression for b cannot hold down to small volumes: in fact for $v_{lim} = b_{lim}$ it gives an imaginary value.

In this connection it may be of interest to remark, that the author (vid. these Proceedings II, p. 558 and Arch. Néerl. d. sc. ex. et mat., (2), 650 1901) established a purely empirical form of the equation of state

$$p = p_1 + \mu \left(\frac{v_1 - b}{v - b} - 1 \right) + \alpha \left(\frac{v_1 - b}{v - b} - 1 \right)^n,$$

according to which

$$K_4 = \frac{RT}{p_k v_k} = n_k \left(1 - \frac{b}{v_k} \right);$$

where it appeared that approximately $n_k = 4$ and $b = 0,1 v_k$, which gives a value for K_4 agreeing well with the experimental value.

BATSCHINSKI (ZS. physik. Chem., 40 (1902) p. 629; Bull. soc. imp. nat. Moscou, 1903, p. 188) has made the relation (7'') with $K_4 = \frac{8}{3}$ the basis of a determination of the degree of association for associating substances, in particular for acetic acid at different temperatures, assuming that the degree of association varies with the temperature, but not with the volume (an assumption which is, however, in contradiction with the well known laws of dissociation and also with determinations of the vapour-density). By comparing the separate isothermals of the associating substance with the set of isothermals of a normal standard substance, BATSCHINSKI determines the critical constants appertaining to each isothermal and then calculates α by means of (7''). In this manner he finds, that the value of $(v_k)_\alpha$ is very much the same for all isothermals, whereas $(T_k)_\alpha$ diminishes a little towards the higher temperatures, whereby α also gets smaller and $(p_k)_\alpha$ increases in the same direction; this agrees in the main with what we have just derived about $(v_k)_\alpha$, $(p_k)_\alpha$ and $(T_k)_\alpha$ from the equation of state.

set of compressibility-curves for various mixtures at a given temperature and ask the question in what manner does the isothermal of the associating substance run through this set of curves, i. e. how does the degree of association vary with the volume at a given temperature? For the solution of this problem we shall follow the way given by VAN DER WAALS (loc. cit., p. 121): we first establish the expression for the free-energy of a given quantity (M grms) of a mixture with constant a and then write down the conditions that for every elementary change of condition (change of the molecular constitution) at constant temperature and volume the free-energy remains unchanged (the free-energy having a smallest value in the condition of equilibrium).

In our case the expression for the free-energy is ¹⁾

$$F = -RTf(v)\sum \frac{x_n}{n} - \frac{a}{v}(\sum k_n x_n)^2 + RT\sum \frac{x_n}{n} \log x_n + \sum E_n x_n - T\sum H_n x_n, \quad (8)$$

where E_n is the internal energy of M grms n -fold molecules in the ideal gas-state, H_n its entropy in volume 1 ²⁾; $f(v)$ stands for $\int \frac{dv}{v-b}$, so that according to § 4:

$$f(v) = \log(v - b_{lm}) \frac{1-k}{1+k} \frac{b_{lm}}{v - b_{lm}} \dots \dots \dots (8')$$

The condition $dF = 0$, connected with $\sum dx_n = 0$, by the usual method gives an infinite series of equations of the form

$$-\frac{RT}{n}f(v) - \frac{2a}{v}k_n \sum k_n x_n + \frac{RT}{n} \log x_n + \frac{RT}{n} + E_n - TH_n - \mu = 0 \quad (9)$$

The constant μ ³⁾ can be determined by the condition $\sum k_n = 1$. In order to make this summation possible it is necessary to make

¹⁾ It is only necessary to generalize the expression given by VAN DER WAALS (loc. cit., p. 121).

²⁾ E_n and H_n are functions of the temperature, connected by the relation $\frac{dE_n}{dT} = T \frac{dH_n}{dT} = C_n$, the specific heat of M gr. n -fold molecules in the ideal state at constant volume.

³⁾ Putting $Z = F + pv$ (thermodynamic potential) the equation may also be put in the form $\mu = \left(\frac{\partial Z}{\partial x_n} \right)_{p,T}$, which shows the indeterminate constant μ to represent the so called molecular thermodynamic potential of the n -fold molecules. Equations (9) thus express the law that in the condition of equilibrium the molar thermodynamic potential is the same for all the different kinds of molecules; this is a well-known theorem, which we might have used straight away to establish the equations (vid. for instance VAN LAAR, loc. cit.).

a suitable assumption about the manner in which E_n , H_n and k depend on n . The simplest supposition no doubt which we can make regarding E_n is, that in a union of M grms of simple molecules in the ideal gaseous state with nM grms of n fold molecules to form $(n+1)$ fold molecules a quantity of potential energy E is lost which is independent of n ¹⁾; on this assumption we have:

$$E_n = E_1 - \frac{n-1}{n} E, \dots \dots \dots (10)$$

and thus also, seeing that $\frac{dE_n}{dT} = T \frac{dH_n}{dT}$ ²⁾

$$H_n = H_1 - \frac{n-1}{n} H, \dots \dots \dots (10')$$

where E_1 and H_1 now refer to simple molecules³⁾. These equations are of the same form as that which was assumed above between k and n and which we shall again introduce here.

Equation (8) now leads to:

$$x_n = e^{-X-nY}, \dots \dots \dots (11)$$

where

$$X = \frac{E}{RT} - \frac{H}{R} + 1 - f(v) - \frac{2a}{RTv} \epsilon \left(1 - \frac{\alpha-1}{\alpha} \epsilon \right),$$

$$Y = \frac{E_1-E}{RT} - \frac{H_1-H}{R} - \frac{\mu}{RT} - \frac{2a}{RTv} (1-\epsilon) \left(1 - \frac{\alpha-1}{\alpha} \epsilon \right).$$

We thus find:

$$1 = \sum x_n = e^{-X} \cdot \sum e^{-nY} = e^{-X} \cdot \frac{e^{-Y}}{1-e^{-Y}}³⁾$$

so that

$$e^{-Y} = \frac{1}{1+e^{-X}}$$

and hence

¹⁾ This assumption which is tantamount to assuming an equal binding of all molecules in the complex, was made by me before (vid. Acad. Roy. de Belgique, Mém. cour., 1896, p. 54).

²⁾ $\frac{dE_1}{dT} = T \frac{dH_1}{dT} = C_1$ and also $\frac{dE}{dT} = T \frac{dH}{dT}$ (it will appear further on that E and H must be assumed to be also functions of the temperature). It follows that $C_n = C_1 - \frac{n-1}{n} \frac{dE}{dT}$ and also $C_\alpha = C_1 - \left(\frac{\alpha-1}{\alpha} \right) \frac{dE}{dT}$.

³⁾ Provided $e^{-Y} < 1$, which is confirmed by the result, at least unless $e^{-X} = 0$, or $X = \infty$, which is only the case at $T=0$ or at $v = v_{um}$.

$$x_n = \frac{e^{-X}}{(1 + e^{-X})^n} \dots \dots \dots (11)$$

Finally we obtain:

$$\frac{1}{\alpha} = \sum \frac{x_n}{n} = -e^{-X} \log \left[1 - \frac{1}{1 + e^{-X}} \right] = \frac{1}{e^X} \log [1 + e^X] \dots (12)$$

This is, therefore, the equation determining α as a function of v and T ; it actually gives for α values enclosed between 1 ($X = -\infty$) and infinity ($X = +\infty$)¹⁾. It is a fairly complicated relation, as X itself contains α ; but as $\frac{1}{\alpha}$ only changes between narrow limits, these limits themselves are not modified thereby and the law of change of X is moreover mainly determined by that of v and T .

The manner in which α changes with v and T is most easily understood by putting $k = 1$ and $\varepsilon = 0$, that is b independent of v and α_x independent of α . Expression (12) then reduces to

$$\frac{1}{\alpha} = \frac{v-b}{e^q} \log \left(1 + \frac{e^q}{v-b} \right) \dots \dots \dots (12')$$

where

$$q = \frac{E}{RT} - \frac{H}{R} + 1 \dots \dots \dots (12'')$$

is now only a function of the temperature. In this case it will be seen, that at a constant value of e^q , i. e. at constant temperature, $\frac{1}{\alpha}$ diminishes continually from 1 to 0, when v decreases from ∞ to b , so that along an isothermal α steadily increases from 1 ($v = \infty$) to ∞ ($v = b$). When the temperature falls towards $T = 0$ at constant volume the degree of association increases regularly up to $\alpha = \infty$, at least if E and H depend on the temperature in such a manner that at $T = 0$ $q = \infty$; similarly with rising temperature α falls towards unity, if q approaches $-\infty$; it will appear in § 10 that this must be so.

According to the law¹⁾ of dependence assumed between b and v the course of $f(v)$ (equation 8') remains in the main unchanged, so that the change of α with v and T also remains very much the

¹⁾ The following table shows the manner in which $\frac{1}{\alpha}$ changes with X :

$X = \dots$	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7..
$\frac{1}{\alpha} = \dots$	1	0,99	0,98	0,93	0,85	0,69	0,48	0,28	0,16	0,08	0,03	0,01	0..

same. The introduction in X (eq. 11) of the term depending on the cohesion ($\epsilon > 0$ and even $= 1$) will not produce any fundamental change in the relation.

8. We shall now consider equation (5) as the equation of state of a substance with molecular transformation. According to this equation the isothermals representing the compressibility obtain a shape which does not essentially differ from that of a substance without molecular transformation ($\alpha = \text{const}$). This is best recognized in the simplest case where $k = 1$ and $\epsilon = 0$, that is for equation (4') connected with (12'), when the equation of state would be:

$$p = \frac{RT}{e^q} \log \left(1 + \frac{e^q}{v-b} \right) - \frac{a}{v^2}; \quad \dots \quad (13)$$

the function $\frac{1}{e^q} \log \left(1 + \frac{e^q}{v-b} \right)$, which takes the place of $\frac{1}{v-b}$ in the original equation of state of VAN DER WAALS has in the main a similar course to the latter function, with which it coincides to a first approximation (large volume or small value of e^q , i. e. weak association): as v decreases from ∞ to b , the function increases steadily from 0 to ∞ , more slowly, however, than $\frac{1}{v-b}$. It follows that the isothermals of the associating substance intersect the normal set ($e^q = 0$), towards lower pressures (consequently towards lower temperatures), as v becomes smaller.

Again the change of b with v does not bring about an essential difference in this result. As regards a dependence of a on α , this again cannot modify the shape of the isothermals fundamentally; but it can have an important influence on the whole set of isothermals in the sense, that the possibility of neighbouring isothermals intersecting each other is not excluded, which might give rise to special phenomena. But it is not our intention to inquire into this further on this occasion.

9. Before going on let us for a moment longer consider equation (13), in which a and b are constants. The critical point, as determined by the conditions $\left(\frac{\partial p}{\partial v} \right)_T = 0$ and $\left(\frac{\partial^2 p}{\partial v^2} \right)_T = 0$, corresponds to a temperature which is given by

$$T_k = \frac{2a(1-u+\sqrt{1-u+u^2})(1+\sqrt{1-u+u^2})}{bR(2-u+\sqrt{1-u+u^2})^3}, \quad \dots \quad (14)$$

where

$$u = \frac{e^{q_k}}{b}, \quad q_k = \frac{E_k}{RT_k} - \frac{H_k}{R} + 1,$$

and to a volume

$$v_k = b(2 - u + \sqrt{1 - u + u^2}), \quad \dots \quad (15)$$

whereas equations (12') and (13') determine the critical degree of association α_k and the critical pressure p_k . Moreover

$$\frac{p_k v_k}{RT_k} = \frac{2 - u + \sqrt{1 - u + u^2}}{u} \log \left(1 + \frac{u}{1 - u + \sqrt{1 - u + u^2}} \right) - \frac{2 - u + \sqrt{1 - u + u^2}}{2(1 - u + \sqrt{1 - u + u^2})(1 + \sqrt{1 - u + u^2})}. \quad (16)$$

As u increases from 0 to ∞ (that is α_k from 1 to ∞), the expression (16) diminishes slowly but steadily from $\frac{2}{3}$ to 0. Now it is well-known, that for most (so-called normal) substances the value of $\frac{p_k v_k}{RT_k}$ is about .28, whereas for the so-called abnormal substances it is even smaller. According to (16) this might be explained by assuming, that even for the so-called normal substances association (or quasi-association) exists at the critical point, to such a degree that $u = 7$ about, giving $v_k = 1.5b$ and $\alpha_k = 5$.¹⁾

¹⁾ If a and b are functions of the volume this value will probably be considerably lowered (VAN DER WAALS, these Proceedings, XIII (2), 1257 etc.).

Similarly SCHAMES (Ann. d. Phys. (4), 39, (1912) p. 887; Verh. d. D. Physik. Ges. 15, (1913) p. 1017.) tries to explain the deviations of experiment from VAN DER WAALS'S original equation by association of simple to double molecules. He starts from equation (4'), in which, however he considers b and a as functions of α , in such a manner that $b = b_k \frac{\alpha_k}{\alpha}$ and $a = \alpha_k \frac{T_k}{T} \frac{\alpha - 1}{\alpha_k - 1}$; he thus establishes the equation

$$\left(v - b_k \frac{\alpha_k}{\alpha} \right) \left(p + \frac{\alpha - 1}{\alpha_k - 1} \frac{\alpha_k T_k}{v^2 T} \right) = \frac{RT}{a},$$

in which α changes from 1 to 2 according to a law which is not specified, as v decreases from ∞ to its smallest value. He further assumes the relations (7) (with $a = \alpha_k$ and $b_\infty = b_k$ and $\varphi(\alpha) = 1$), which involves the relation $\frac{RT_k}{p_k v_k} = \frac{8}{3} \alpha_k$. Owing

to these assumptions SCHAMES finds for $\frac{RT_k}{p_k v_k}$ the experimental value 3.6 by taking $\alpha_k = 1.4$ and for the smallest volume the value $\frac{1}{4} v_k$ instead of $\frac{1}{3} v_k$. The fact, that for the critical coefficient $\frac{T_k}{p_k} \left(\frac{\partial p}{\partial T} \right)_k$ he also obtains the experimental value 7 is

not due to his association-hypothesis, but is the consequence of the further fact, that he makes a change inversely as T (for this well-known rule vid. e.g. J. P. KUENEN, Die Zustandsgleichung etc., 1907, p. 194).

10. We now return to the more general equation of state (6''), where α has the value given by (12).

As at very low temperatures e^X becomes very large (infinite of infinitely high degree), it is easily seen that, provided v itself is not infinite,

$$\left(\frac{\partial v}{\partial T}\right) = 0 \text{ and even } \left(\frac{\partial^n v}{\partial T^n}\right) = 0.^{1)}$$

For the free energy by introducing (11) into (8) we find the expression:

$$F = -RT \log(1 + e^{-X}) - \frac{RT}{\alpha} - \frac{a}{v} \left[(1 - \varepsilon)^2 - \frac{\varepsilon^2}{\alpha^2} \right] + E_1 - E - T(H_1 - H), \quad (17)$$

and therefore, (for the sake of simplicity assuming α and b independent of T)²⁾,

$$S = - \left(\frac{\partial F}{\partial T}\right)_v = R \left[1 + e^{-X} \left(1 + \frac{E}{RT}\right) \right] \log(1 + e^{-X}) + R \left(1 + \frac{E}{RT}\right) X e^{-X} - \frac{2a}{v} \cdot \frac{E}{RT^2} \cdot \frac{\varepsilon^2}{\alpha} \left[\frac{1}{\alpha} - \frac{1}{1 + e^{-X}} \right] + H_1 - H \dots \quad (18)$$

At very low temperatures and moderately large volumes we thus have:

$$S = H_1 - H \text{ and } U = F + TS = E_1 - E - \frac{a}{v} (1 - \varepsilon)^2. \quad (19)$$

It will, therefore, be seen that at low temperature the entropy on the side of the condensed condition of matter is no longer a function of the volume (or of the pressure)³⁾, so that there can only be question of one specific heat

$$C = T \frac{dS}{dT} = T \frac{d(H_1 - H)}{dT} = \frac{d(E_1 - E)}{dT} \dots \quad (20)$$

¹⁾ This agrees with what may be derived from the theory of quanta at low temperatures (vid. e.g. P. LANGEVIN et M. DE BROGLIE: La théorie du rayonnement et les quanta, Paris, 1912, p. 284).

²⁾ Comp. VAN DER WAALS, these Proceedings, XIII (2), p. 1213.

³⁾ This follows also from the relation $\left(\frac{\partial S}{\partial p}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_p$, and therefore = 0;

similarly $\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T = 0$. This is again in accordance with modern views.

⁴⁾ In our equations E_1 and E are indeterminate functions of the temperature and we cannot, therefore, conclude from them that C approaches zero with T . It is clear why this is so. The dependence of C on the temperature is not solely determined by the equation of state of the system of separate molecules, but also by the internal mechanism of the molecule itself, that is at low temperature and small volume the internal mechanism of the amorphous-solid body consisting

We may choose the arbitrary constant occurring in the function $E_1 = \int_0^T C_1 dT$ such that at $T=0$ and $v=b$ the energy $U=0$. Further utilising the fact that at $T=0$ $C=0$, we can also choose the arbitrary constants of the functions $H_1 = \int_0^T \frac{C_1}{T} dT$ and $H = \int_0^T T \frac{dE}{dT} dT$ so as to make $S_0=0$. The functions E_1 , E , H_1 and H are then completely determined by the values of C_1 and C , except that H_1 and H contain another constant h which, however, occurs in the constant of the vapour-pressure formula, the chemical constant so-called (vid § 12), and is therefore determined by it.

Putting also :

$$C_1 = \frac{dE_1}{dT} = T \frac{dH_1}{dT} = C_0 + f_1(T), \dots \dots (21)$$

and similarly, in agreement with the preceding discussion ($C_{T=0}$ must be 0),

$$\frac{dE}{dT} = T \frac{dH}{dT} = C_0 + f_2(T) \dots \dots \dots (22)$$

it follows that

$$\left. \begin{aligned} E_1 &= E_0 + \frac{a}{b} + C_0 T + \int_0^T f_1(T) dT \\ E &= E_0 + C_0 T + \int_0^T f_2(T) dT \\ H_1 &= h + C_0 \log T + \int_0^T \frac{1}{T} f_1(T) dT \\ H &= h + C_0 \log T + \int_0^T \frac{1}{T} f_2(T) dT \end{aligned} \right\} \dots \dots \dots (23)$$

11. What are now the quantities determining the coexisting of one single molecule. Our equation cannot teach us anything about that mechanism; how the properties of the amorphous-solid condition arise by association is here left out of consideration.

phases at low temperatures, i. e. for infinitely low values of T ? They are determined by the relations $p_1 = p_2 = p_{coex}$ and $Z_1 = Z_2$ (the index 1 referring to the condensed condition, the index 2 to the dilute gaseous state) which for small values of T are capable of great simplifications. In fact at low temperatures v_1 differs infinitely little from the limiting volume b_{lim} , that is: $v_1 - b$ is infinitely small; α_1 is infinitely large; v_2 is infinite and p_{coex} infinitely small; assuming further that α_2 differs infinitely little from 1, as confirmed by the result, and neglecting infinitely small terms, the conditions of coexistence become:

$$p_{coex} = \frac{RT}{v_2} = \frac{RT}{\alpha_1} \left[\frac{1-k}{1+k} \frac{b_{lim}}{(v_1 - b_{lim})^2} + \frac{1}{v_1 - b_{lim}} \right] - \frac{a(1-\epsilon)^2}{b^2_{lim}}$$

and

$$RT \log(1 + e^{-X_1}) + \frac{a}{b_{lim}}(1-\epsilon)^2 = RT \log(1 + e^{-X_2}).$$

In order that α_1 may be infinite and α_2 may differ infinitely little from 1, according to (12) e^{X_1} must be infinite and e^{X_2} infinitely small; the second condition of coexistence becomes as follows

$$\log v_2 = \frac{E}{RT} - \frac{H}{R} + 1 + \frac{a}{RTb_{lim}}(1-\epsilon)^2 + \dots \quad (24)$$

hence

$$\log p_{coex} = \log RT - \frac{E}{RT} + \frac{H}{R} - 1 - \frac{a}{RTb_{lim}}(1-\epsilon)^2 + \dots \quad (25)$$

and

$$\alpha_2 = 1 + \frac{1}{2} e^{-\frac{a(1-\epsilon)^2}{RTb_{lim}}} + \dots \quad (26)$$

12. The heat of evaporation at low temperature is found to be (vid. equation 19)

$$\begin{aligned} \lambda &= T(S_2 - S_1) = RT \log v_2 + TH_1 - T(H_1 - H) = \\ &= \frac{a}{b_{lim}}(1-\epsilon)^2 + E_0 + (C_0 + E)T + \int_0^T f_2(T) dT + \dots \quad (27) \end{aligned}$$

Putting $\lambda_0 = \frac{a}{b_{lim}}(1-\epsilon)^2 + E_0$, i. e. the heat of evaporation at

¹⁾ This expression is also arrived at, if one starts from the relation $\frac{d \log p}{dT} = \frac{\lambda}{RT^2}$, which holds for low pressures, i. e. for low temperatures, or from the relation $\frac{d\lambda}{dT} = C_p - C$ repeatedly used by NERNST.

$T=0$, and $i = \log R + \frac{h}{R} - \frac{C_0}{R} - 1$, i. e. the chemical constant ¹⁾, equation (25) becomes,

$$\log p = -\frac{\lambda_0}{RT} + \frac{C_0 + R}{R} \log T + i + \frac{1}{R} \int_0^T \frac{1}{T} f_1(T) dT - \frac{1}{RT} \int_0^T f_2(T) dT + \dots \quad (25')$$

We thus find, as might be expected, a vapour-pressure formula of the form assumed by NERNST. ²⁾

13. The equation contains two indeterminate functions $f_1(T)$ and $f_2(T)$, the former being governed by the internal mechanism of the single molecule and determining the change of the specific heat C_1 with the temperature, while the latter depends upon the internal mechanism of the associated molecule and in connection with the former determines the change with T of the specific heat C of the condensed state. The fact that we are free to choose these functions as we like might give the impression as if the equation of state which we have deduced and which is independent of that internal mechanism, would be compatible with the properties of the amorphous-solid condition without any modification. Still this is clearly impossible: for it is evident that the pressure must also depend upon that internal mechanism ³⁾, and from this point of view something must be lacking in our equation of state.

It is, however, not impossible that it will be sufficient to make a small modification in the law of dependence of b ⁴⁾ in order to obtain the devised correspondence with the equation of state of the solid condition, and that by establishing the "equation of state of the molecule" ⁵⁾, not only of the single molecule, but also of the complex one, the object might be attained. Still, so long as the equation of state of the solid condition itself is not better founded than it is, it would be premature to go into this question any further.

¹⁾ I. W. CEDERBERG (Die thermodynamische Berechnung chemischer Affinitäten, Berlin, 1906, p. 25) puts $i = \log pk$; in our result this constant remains indeterminate.

²⁾ This is known not to be the case with the original equation of state (cf. e.g. PLANCK, Thermodynamik, p. 277).

³⁾ Comp. H. KAMERLINGH ONNES and W. H. KEESOM, loc. cit., p. 887 (273) etc. Vid. also MAX B. WEINSTEIN, Ann. d. Phys., (4) 51 (1916) p. 465; (4) 52 (1917) p. 203; (4) 52 (1917) p. 506.

⁴⁾ As an instance: whereas according to the previous assumptions the condensed state would be completely incompressible at $T=0$, the hypothesis of a change with pressure of the limiting volume b_{lm} would give the substance in that condition a certain degree of compressibility.

⁵⁾ See e.g. VAN DER WAALS, these Proceedings, III, p. 515, 571, 643.

14. In conclusion a remark may be added about the dilute gaseous condition. It follows from equation (11) that:

$$\frac{x_n}{x_1^n} = e^{X(n-1)}.$$

Representing by c_n the molecular concentration of the n -fold molecules, namely the number of gram-mols for unit of volume, we have $c_n = \frac{1}{v} \frac{x_n}{nM}$, and the above equation may be written as follows:

$$\frac{c_n}{c_1^n} = \frac{1}{n} (Mve^X)^{n-1} \quad \dots \quad (28)$$

For very large volumes this becomes

$$\frac{c_n}{c_1^n} = \frac{1}{n} (Me^{\rho})^{n-1} = K, \quad \dots \quad (28')$$

in other words, to a first approximation this ratio is independent of the volume; this is the well-known law of GULDBERG-WAAGE, as applied to the transformation of n -fold molecules into single ones. It further follows that

$$\frac{d \log K}{dT} = (n-1) \frac{dX}{dT} = -(n-1) \frac{E}{RT^2}, \quad \dots \quad (29)$$

the expression $-(n-1) E$ giving the heat effect of the transformation (VAN 'T HOFF's law).

Finally representing the total molecular concentration by c_m , so that $c_m = \frac{1}{v} \sum \frac{x_n}{nM} = \frac{1}{v} \cdot \frac{1}{\alpha M}$, we find from (12):

$$Mc_m = \frac{1}{ve^X} \log(1 + e^X) \quad \dots \quad (30)$$

For v very large and also e^X (strong association), we may write by approximation

$$Mc_m = \frac{1}{r} \log(1 + r\rho) \quad \dots \quad (30')$$

where r represents the density and $\rho = e_\rho$ a coefficient depending upon the temperature, that is: decreasing with rising temperature²⁾.

¹⁾ This relation (but in that case for the dissolved condition, ρ being the ordinary concentration by weight of the dissolved substance) was several years ago derived by me empirically for water from determinations of the molecular weight (cf. Acad. Roy. de Bruxelles, loc. cit., p. 20, 23 and 37).

²⁾ This is also confirmed by the experimental data (cf. Acad. Roy. de Bruxelles, loc. cit. p. 47). From the change of this coefficient with the temperature:

$$\frac{d \log r}{dt} = \frac{dX}{dT} = -\frac{E}{RT^2} \quad \text{I calculated (loc. cit., p. 61) the heat of dissociation } E \text{ of}$$

2 M grms of double molecules of water.

Chemistry. — “*Influence of different compounds on the destruction of monosaccharids by sodiumhydroxide and on the inversion of sucrose by hydrochloric acid II*”. By Dr. H. I. WATERMAN. (Communicated by Prof. J. BÖESEKEN).

(Communicated in the meeting of June 30, 1917).

In a previous communication¹⁾ it has been proved that in alkalic solutions amino acetic acid and α amino propionic acid behave about as one-basic acids, because they retard the destruction of glucose by alkali almost as much as an equivalent quantity of hydrochloric acid.

In acidic solution the said amino acids act about as monacidic alkali since they retard the inversion of sucrose by hydrochloric acid almost in an equal degree as the equivalent quantity of strong alkali.

It could be expected that other amino-acids with a greater number of atoms of carbon should in the same way show in alkalic solution strong acidic, in acidic solution strong basic properties as well. Experiment has confirmed this expectation.

The following α -aminoacids were examined:

$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$ α -aminobutyric acid
Molecular weight: 103.

$\begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \left\{ \text{CH} \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH} \right.$ α -aminoisovaleric acid
(valine).

Molecular weight: 117.

$\begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \left\{ \text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH} \right.$ α -aminoisocaproic acid
(leucine).

Molecular weight: 131.

Behaviour in alkalic solution.

The just mentioned aminoacids prevent the destruction of glucose by sodiumhydroxide as is proved by the following. A solution of 50 Gr. glucose in distilled water after being boiled was diluted to 1 Liter.

¹⁾ Chemisch Weekblad, 14, 119 (1917). These Proceedings, Vol. XX, p. 88, April 27, 1917.

From this solution 40 cm³. was taken with a pipette. I let it flow into a 50 cm³. flask, added a fixed quantity of the aminoacid in question to some of the flasks and added at the same time different volumes of a solution of sodium hydroxide of known strength.

Finally the liquids were diluted with H₂O to 50 cm³. and shaken thoroughly. The thus obtained solutions were placed in a thermostat with waterjacket (temperature 34°), the temperature of the liquid in the flasks therefore rising gradually. At the beginning of the experiment and later from time to time the polarisation and the intensity of colour of the solutions were determined under comparable circumstances. The results of these observations are found in table I. (See table on the following page).

From the results mentioned in this table it follows in the first place that the aminoacids in question practically do not influence the polarisation of glucose (polarisation of Nrs. 6, 7 and 8 at beginning).

After 3½ hours the polarisation has diminished most in the flasks that contained the largest quantity of NaOH (Nrs. 5 and 9 : + 4° 6 V.).

Although the added number of cm³. of the NaOH-solution with the Nrs. 6, 7 and 8 is equally great as that with the Nrs. 5 and 9, it follows from the table that the polarisation with 6, 7, and 8 has diminished only to respectively 6,5, 6,6, and 6,5.

This number is less than that of N^o. 3 to which 3 cm³. of the NaOH-solution had been added. We may therefore conclude that two milligram molecules of each of the aminoacids compensate the action of about 2 cm³. of 1,06 normal NaOH-solution. The intensity of colour too of Nrs. 6, 7, and 8 (after ± 21 and 6 × 24 hours) that lies between that of Nrs. 3 and 4 was herewith in agreement.

The α-amino compounds of butyric acid, isovaleric acid and isocaproic acid therefore behave in alkalic solution as about mono-basic acid.

Behaviour in acidic solution.

The inversion of sucrose by hydrochloric acid was likewise prevented by the said three α-aminoacids.

From the results united in table II^a and II^b especially from the polarisation at the beginning of the experiments it follows that these three aminoacids neither influence to an important degree the polarisation of sucrose nor change polarisation of the solution by their own optical activity.

Whilst the polarisation after addition of 5 cm³ 1,01 normal hydrochloric acid after 16½ hours (Table II^a) has lowered to respectively

T A B L E I.

Influence of γ -aminobutyric acid, α -aminoisovaleric acid and γ -aminoisocaproic acid on the destruction of glucose by alkali.

No.	Added	Number of cm ³ 1,06 Norm. NaOH-sol. added	Filled up to 50 cm ³ and placed in thermostat with watermantle (Temp. 34°)	Polarisation in grades VÉNIZKE (2 dm. tube)		Colour of the solution		
				At beginning of the experiment 1)	After $\pm 3\frac{1}{2}$ hours	After ± 21 hours	After $\pm 6 \times 24$ hours	
1	40 cm ³ . of a sol. containing glucose (50 Gr. gluc. to 1 Liter)	0		+ 11,5	+ 11,4	colourless	colourless	
2	id.	2		2)	+ 8,1	pale yellow	pale yellow	
3	id.	3		2)	+ 6,8	yellow	yellow	
4	id.	4		2)	+ 5,6	yellow brown	brown-yellow	
5	id.	5		+ 10,0	+ 4,6	deep yellow-brown	deep brown	
6	id.	206 milligram γ -aminobutyric acid (= 2 milligrammolecule)	5		+ 10,5	+ 6,5	} yellow, somewhat deeper than No. 3	} brown-yellow, paler than No. 4
7	id.	234 milligram α -aminoisovaleric acid (= 2 mgr. molecule)	5		+ 10,7	+ 6,6		
8	id.	262 milligram γ -aminoisocaproic acid (= 2 mgr. mol.)	5		+ 10,6	+ 6,5		
9	id.		5		+ 10,3	+ 4,6	deeper yellow-brown	deeper brown

+ 1,2 and + 2,5 (Nrs. 4 and 7) the addition of 2 milligrammolecules of α -aminobutyric acid and α -aminoisovaleric acid causes that in presence of the same quantity of hydrochloric acid the polarisation has diminished only to respectively + 12,2 and + 11,9 (Nrs. 5 and 6). From this results that the added quantities of these amino acids

1) Between the dilution to 50 cm³ and the determination of polarisation of course some time passes.

2) The polarisation was not determined; the results obtained would lie between that of No. 1 (+ 11,5) and those of Nrs. 5 and 9 (+ 10,0 and + 10,3) and would diminish gradually from No. 2 to No. 4 (Compare the results obtained before).

compensate the action of somewhat less than 2 cm³ of normal hydrochloric acid, which is demonstrated too by the observations made after 24, 40—41 and 72 hours.

Therefore they act about as monacidic alkali. From the observation after ± 89 hours it follows that finally the same end-situation is reached so that the stated influence of the amino acids cannot be ascribed to an accidental influence on the polarisation of fructose or glucose.

T A B L E IIb.
Influence of α-aminoisocaproic acid on the inversion of sucrose by hydrochloric acid.

N ^o .	Added	Number of cm ³ 1,01 Norm. HCl-sol. added	Polarisation in grades VENTZKE (2 dm. tube)			
			At beginning	After ± 3½ hours	After ± 20 hours	After ± 137 hours
1	50 cm ³ of a solution which contains 260 Gr. sucrose pro Liter	0	+ 49,6			
2	id.	3	+ 49,2 + 43,4	(24°,5)	+ 10,6	(23°,5) — 14,9 (24°)
3	id.	4	+ 49,4 + 41,7	(24°,5)	+ 4,0	(24°,5) — 14,9 (24°,5)
4	id.	5	+ 49,0 + 39,4	(25°)	— 1,0	(24°) — 15,2 (24°)
5	id.	5	+ 49,5 + 42,2	(24°,5)	+ 8,0	(24°) — 15,1 (24°)
6	id.	5	+ 49,1 + 39,4		— 0,9	— 15,1
7	id.	3	+ 49,2 + 42,7		+ 10,6	(23°,5) — 15,1 (24°)

Diluted to 100 cm³ and placed in thermostat (temp. 34°)

262 mgr. α-amino-isocaproic acid (= 2 milligr.mol.)

T A B L E II_a.Influence of γ -aminobutyric acid and α -aminoisovaleric acid on the inversion of sucrose by hydrochloric acid.

N ^o .	Added	Number of cm ³ 1,01 Normal HCl-solution added		Polarisation in grades VENTZKE (2 dm tube)											
				At begin- ning	± 16½ hours	± 24 hours	After 40—41 hours	± 72 hours	± 89 hours	Temp. of the pola- risation liquid	Temp. of the pola- risation liquid	Temp. of the pola- risation liquid	Temp. of the pola- risation liquid		
1	50 cm ³ of a solution which contains 130 Gr. sucrose pro 500 cM ³ .	0	Diluted with H ₂ O to 100 cm ³ and placed in thermostat (temp. 34°)	+ 49,6		Temp. of the pola- risation liquid		Temp. of the pola- risation liquid		Temp. of the pola- risation liquid		Temp. of the pola- risation liquid		Temp. of the pola- risation liquid	
2	id.	3		+ 49,3	+ 13,7	(23°)	+ 6,0	(25°,5)	- 5,9	(24°,5)	- 13,4	(23°,5)	- 14,5	(23°,5)	
3	id.	4		+ 48,9	+ 6,7	(23°)	- 0,5	(25°,5)	- 10,3	(25°)	- 14,7	(23°,5)	- 14,8	(24°)	
4	id.	5		+ 48,4	+ 1,2	(23°)	- 5,0	(25°,5)	- 12,6	(25°)	- 15,1	(23°,5)	- 15,1	(24°)	
5	id.	206 mgr. α -amino- butyric acid (= 2 milligr.molecule)		5	+ 48,7	+ 12,2		+ 4,5		- 7,1		- 14,1		- 14,8	
6	id.	234 mgr. α -amino- isovaleric acid (= 2 milligr.mol.)		5	+ 48,8	+ 11,9	(23°)	+ 4,3	(25°)	- 7,2	(24°,5)	- 14,0	(23°)	- 14,8	(23°,5)
7	id.			5	+ 48,6	+ 2,5		- 4,9		- 12,5		- 15,2		- 15,4	(23°)
8	id.			3	+ 49,0	+ 14,8	(22°,5)	+ 7,0	(24°)	- 5,5	(24°)	- 13,5	(23°)	- 14,4	

TABLE IIIa.

Influence of asparagine, glutamic acid and tyrosine on the destruction of glucose by alkali.

No.	Added	Number of cm ³ 1,06 Norm. NaOH- sol. added	Diluted to 50 cm ³ and placed in thermostat (temp. 34°)	Polarisation in grades VENTZKE (2 dm tube)		Colour of the liquid after ± 43 hours
				At begin- ning	After ± 3½ hours	
1	40 cm ³ of a sol. containing 50 Gr. gluc. p. L. 1)	0		+ 11,3	+ 11,2	colour- less
2	id.	2		+ 10,5	+ 8,0	pale yellow
3	id.	3		+ 10,3	+ 6,3	yellow
4	id.	4		+ 10,2	+ 5,2	brown- yellow
5	id.	5		+ 9,6	+ 4,4	brown
6	id.	141 milligram aspa- ragine = ± 1,06 milligrammolecule	5	+ 9,8	+ 5,0	brown yellow
7	id.	157 milligram glu- tamic acid = ± 1,06 milligrammol.	5	+ 10,3	+ 6,3 2)	yellow
8	id.	193 milligram tyro- sine = ± 1,06 milligrammolecule	5	+ 9,8	+ 5,9	yellow
9	id.		5	+ 9,7	+ 4,4	brown

TABLE IIIb.

Influence of tyrosine on the destruction of glucose by alkali.

No.	Added	Number of cm ³ 1,06 Norm NaOH- sol. added	Diluted to 50 cm ³ and placed in thermostat(temp. 34°)	Polarisation in grades VENTZKE (2 dm tube)		Colour after ± 24 hours
				At begin- ning	After ± 5 hours	
1	40 cm ³ of a sol. containing 50 Gr. gluc. p. L. 1)	3		+ 10,7	+ 5,4	yellow
2	id.	5		+ 10,3	+ 3,0	brown- yellow
3	id.	192 milligram tyrosine (= 1,06 milligrammolecule)	5	not deter- mined	+ 5,0	yellow, somewhat deeper than No. 1

1) This solution was boiled for a moment and afterwards cooled till the temperature of the room was reached.

2) All the glutamic acid is dissolved.

From Table II^b it follows in an analogous way that 2 milligram-molecules of leucin (α -aminoiso-caproic acid) neutralizes the action of $\pm 1\frac{1}{2}$ cm³ of normal hydrochloric acid. In acidic solution leucine behaves as $\pm \frac{3}{4}$ acidic alkali.

Then I set myself to the examination of three more complicated compounds viz.

COOH . CH . (NH₂) . CH₂ . CO(NH₂) Asparagine
Molecular weight = 132 (mono-amide of amino-succinic acid)

COOH . CH(NH₂) . CH₂ . CH₂ . COOH Glutamic acid
Molecular weight = 147 (α -aminoglutaric acid)

HO . C₆H₄ . CH₂ . CH(NH₂) . COOH Tyrosine
Molecular weight = 181 (p. hydroxyphenylalanine)

I observed that with my experiments acetamide CH₃ . CO (NH₂) and urea CO (NH₂)₂ behaved in alkalic and in acidic solution as practically neutral.

From this appears again a contrast between the acid amides and the amino acids; I observed before this contrast in another direction.¹⁾

Furthermore it has been proved in a previous communication²⁾ that in alkalic solution phenol acts about as a one-basic acid, whilst this compound practically has no influence on the inversion of sucrose by hydrochloric acid.

In agreement with these results it could be expected that in alkalic solution asparagine possessing the carboxyl group should behave as a one basic acid. For the presence of the amino group asparagine should behave as monacidic alkali in acidic solutions.

Glutamic acid, which compound possesses two carboxyl-groups in presence of sodium hydroxide should act as a two-basic acid; in acidic solution it should behave as monacidic alkali (NH₂-group). Finally tyrosine for the presence of the phenolic hydroxyl-group and the carboxyl-group in alkalic solution should be two basic acid; in acidic solution the (NH₂) group should render it monacidic alkali. These predictions were confirmed by the experiments (Table III^a, III^b and IV).

From the experiments mentioned in Table III^a it follows that under the circumstances described asparagine acts as monobasic acid.

1,06 milligrammolecule of asparagine neutralizes the action of about 1 cm³ 1,06 normal NaOH-solution, as results from the polarisation after 3 $\frac{1}{2}$ hours.

¹⁾ H. I. WATERMAN, Die Stickstoffnahrung der Presshefe, Folia microbiologica. (Holländische Beiträge zur gesamten Mikrobiologie) 2, 173 (1913).

²⁾ These Proceedings, Vol. XX, 88 (April 27, 1917).

TABLE IV. Influence of asparagine, tyrosine and glutamic acid on the inversion of sucrose by hydrochloric acid.

No.	Added	Number of cm ³ 1.01 Normal HCl-solution	Polarisation in grades VENTZKE (2 d.M. tube)										
			At beginning	After ± 16½ hours		After ± 24 hours		After 40-41 hours		After ± 72 hours		After ± 89 hours	
					Temp. of the polarisation liquid		Temp. of the polarisation liquid		Temp. of the polarisation liquid		Temp. of the polarisation liquid		Temp. of the polarisation liquid
1	50 cm ³ of a solution which contains 130 G. sucrose p. 500 cm ³	0	+ 49,6										
2	id.	3	+ 49,3	+ 13,7	(23°)	+ 6,0	(25°,5)	- 5,9	(24°,5)	- 13,4	(23°,5)	- 14,5	(23°,5)
3	id.	4	+ 48,9	+ 6,7	(23°)	- 0,5	(25°,5)	- 10,3	(25°)	- 14,7	(23°,5)	- 14,8	(24°)
4	id.	5	+ 48,4	+ 1,2	(23°)	- 5,0	(25°,0)	- 12,6	(25°)	- 15,1	(23°,5)	- 15,1	(24°)
5	id.	264 mgr. asparagine = 2 milligrammol.	+ 49,2	+ 10,5	(23°)	+ 2,7	(25°,5)	- 8,4	(24°,5)	- 13,9	(23°,5)	- 14,5	(24°)
6	id.	181 mgr. tyrosine = 1 milligrammol.	+ 48,2	+ 6,0		- 1,3		- 10,6		- 14,9			
7	id.		+ 48,6	+ 2,5		- 4,9		- 12,5		- 15,2		- 15,4	(23°)
8	id.		+ 49,0	+ 14,6	(22°,5)	+ 7,0	(24°)	- 5,5	(24°)	- 13,5	(23°)	- 14,4	
			At beginning	After ± 3½ hours		After ± 20 hours		After ± 137 hours					
					Temp. of the polarisation liquid		Temp. of the polarisation liquid		Temp. of the polarisation liquid				
9	id.	0	+ 49,6										
10	id.	3	+ 49,2	+ 43,4	(24°,5)	+ 10,6	(23°,5)	- 14,9	(24°)				
11	id.	4	+ 49,4	+ 41,7	(24°,5)	+ 4,0	(24°,5)	- 14,9	(24°,5)				
12	id.	5	+ 49,0	+ 39,4	(25°)	- 1,0	(24°)	- 15,2	(24°)				
13	id.	147 mgr. glutamic acid = 1 milligr.mol.	not yet dissolved			+ 3,0 ¹⁾		- 14,8					
14	id.		+ 49,1	+ 39,4		- 0,9		- 15,1					
15	id.		+ 49,2	+ 42,7		+ 10,6	(23°,5)	- 15,1	(24°)				

¹⁾ All the glutamic acid is dissolved.

Much stronger is the defending influence of 1,06 milligrammole glutamic acid and of 1,06 milligrammole tyrosine, which compensate the action of about 2 cm³ 1,06 normal NaOH-solution (polarisation after 3¹/₂ hours).

Glutamic acid acts just like tyrosine as almost two basic acid, which was once more confirmed for the latter compound by the experiment described in table IIIb.

It must be remarked that the glutamic acid (N^o. 7) did not quite dissolve even after being shaken repeatedly.

Nevertheless ± 14 cm³ of the clear solution were used at the beginning for the determination of polarisation.

In the remaining alkaline liquid all the glutamic acid was dissolved after some time (within 3¹/₂ hours). The tyrosine (N^o. 8, table IIIa and N^o. 3, table IIIb) was dissolved but little. At the addition of the NaOH-solution after being shaken it was quite dissolved.¹⁾

The addition of hydrochloric acid too causes the rapid solution of tyrosine.

This compound in this regard resembles substances such as zinc-hydroxide and aluminiumhydroxide.

In acidic solution the glutamic acid dissolved but gradually. I did not determine polarisation before all had dissolved. Although the glutamic acid therefore could not be active to a certain extent at the beginning of the experiments, from the results obtained it can be concluded with rather great certainty that glutamic acid in acidic solution behaves as monacidic alkali.

Tyrosine too (table IV, N^o. 6) behaves in acidic solution as monacidic alkali; 1 milligrammole compensates the action of about 1 cm³ of normal hydrochloric acid.

Asparagine acts as ³/₄-acidic alkali; 2 milligrammole compensates the invertive action of about 1,5 cm³ of normal hydrochloric acid (Table IV, N^o. 5).

Afterwards aniline and pyridine were subjected to research, in how far these compounds influence the destruction of glucose by alkali and the inversion of sucrose by hydrochloric acid.

C₆H₅.NH₂ Aniline.

Molecular weight = 93

C₅H₅N. Pyridine.

Molecular weight = 79

¹⁾ In heating the solution to the boiling point but without the addition of NaOH the tyrosine dissolved almost quite, but in cooling till the ordinary temperature was reached an important quantity crystallised, which was dissolved rapidly at the addition of NaOH.

The aniline present in the laboratory was distilled with steam and after drying distilled in the ordinary way. The boiling point was 180°.

The pyridine of the laboratory was distilled in fractions. The fraction which boiled between 115° and 117° was used for the research.

It could be expected that in alkalic solution both compounds should behave neutral, in acidic solution they should act as monacidic base.

The referential experiments which are mentioned in table V and VI have confirmed this expectation.

TABLE V.

Influence of aniline and pyridine on the destruction of glucose by alkali.

a. Aniline.

No.	Added	Number of cm ³ 1,06 Norm NaOH- sol. added	Polarisation in grades VENTZKE (2 dm tube)	Polarisation in grades VENTZKE (2 dm tube)		Colour after ± 24 hours
				At begin- ning	After ± 3 hours	
1	80cm ³ of a solution, which contains 50 Gr. gluc. p. Liter ¹⁾	0	Diluted to 100 cm ³ and placed in thermostat (temp. 34°)	+ 11,0	+ 11,1	colourless
2	id.	10		+ 9,8	+ 7,4	brownyellow
3	id.	1,55 Gram aniline		+ 9,7	+ 7,3	brownyellow (something deeper)
4	id.	10		+ 9,6	+ 7,2	brownyellow
b. Pyridine.						
1	id.	10	Diluted to 100 cm ³ and placed in thermostat (temp. 34°)	At begin- ning	After ± 5½ hours	
2	id.	1,66 Gram pyridine		+ 10,2	+ 3,4	brownyellow
3	id.	10		+ 10,4	+ 3,5	brownyellow

From table VIa it follows that the retarding power of aniline on the inversion is very great.

The polarisation proves that practically no sucrose has been inverted.

¹⁾ The solution was boiled for a short time and afterwards cooled down to the ordinary temperature.

a.

TABLE VI. Influence of aniline and pyridine on the inversion of sucrose by hydrochloric acid.

N ^o .	Added	Number of c.M. 1,01 Normal HCl-solut. added	Polarisation in grades VENTZKE (2 d.M. tube)										
			At beginning	After 5 $\frac{3}{4}$ hours	temp. of the polarisation liquid	After 8 $\frac{1}{2}$ hours	temp. of the polarisation liquid	After 24 hours	temp. of the polarisation liquid	After 4 \times 24 hours	temp. of the polarisation liquid		
1	50 c.M. of a solution containing 260 Gr. sucrose p.L.	0	+ 49,5	+ 49,4		+ 49,5							
2	id.	2	+ 49,6	+ 44,9		+ 41,2		+ 21,7		- 12,2	(16 $^{\circ}$,5)		
3	id.	4	+ 49,5	+ 40,7		+ 34,3	(18 $^{\circ}$,5)	+ 5,8	(18 $^{\circ}$,5)	- 16,3	(17 $^{\circ}$,5)		
4	id.	6	+ 49,5	+ 36,3	(19 $^{\circ}$,5)	+ 27,7	(18 $^{\circ}$,5)	- 4,2	(18 $^{\circ}$,5)	- 16,8	(17 $^{\circ}$,5)		
5	id.	10	+ 49,5	+ 27,2		+ 15,5		- 13,2		- 16,7	(17 $^{\circ}$,5)		
6	id.	1,72 Gram aniline	+ 49,5	+ 49,5	(19 $^{\circ}$,5)	+ 49,5	(18 $^{\circ}$)	+ 49,3					
7	id.	10	+ 49,2	+ 25,5	(19 $^{\circ}$,5)	+ 14,7	(18 $^{\circ}$)	- 12,7	(18 $^{\circ}$,5)				
b.			At beginning	After 18 hours		After 24 hours		After 48 hours					
1	id.	0	+ 49,7	+ 49,4	temp. of the polarisation liquid		temp. of the polarisation liquid		temp. of the polarisation liquid				
2	id.	2	+ 49,8	+ 27,1		+ 21,5							
3	id.	4	+ 49,4	+ 12,6	(16 $^{\circ}$)	+ 4,9		- 8,7	(19 $^{\circ}$)				
4	id.	6	+ 49,2	+ 1,4	(17 $^{\circ}$)	- 5,2	(16 $^{\circ}$)	- 13,6	(19 $^{\circ}$,5)				
5	id.	10	+ 48,9	- 9,8	(17 $^{\circ}$,5)	- 13,6	(16 $^{\circ}$)	- 15,8	(18 $^{\circ}$,5)				
6	id.	0,50 Gram aniline	+ 49,4	+ 8,1	(17 $^{\circ}$)	+ 1,2	(16 $^{\circ}$)	- 11,5	(18 $^{\circ}$,5)				
7	id.	0,64 Gram aniline	+ 49,2	+ 17,8	(16 $^{\circ}$,5)	+ 11,2	(16 $^{\circ}$)	- 4,8	(19 $^{\circ}$)				
8	id.	10	+ 48,8	- 8,4	(16 $^{\circ}$,5)	- 12,7	(16 $^{\circ}$)	- 15,9	(19 $^{\circ}$)				
c.			At beginning	After 6 hours		After 21 $\frac{1}{2}$ hours		After a long time					
1	id.	0	+ 49,8	+ 49,7	temp. of the polarisation liquid	+ 49,6	temp. of the polarisation liquid	+ 49,9	temp. of the polarisation liquid				
2	id.	2,1	+ 49,5	+ 42,0	± 20 $^{\circ}$	+ 14,6	(20 $^{\circ}$,5)	- 8,2	(21 $^{\circ}$)				
3	id.	4	+ 49,4	+ 35,3		- 1,7	(20 $^{\circ}$,5)	- 14,6	(20 $^{\circ}$,5)				
4	id.	6	+ 49,4	+ 28,0		- 9,5	(21 $^{\circ}$)	- 14,7	(20 $^{\circ}$,5)				
5	id.	10	+ 49,5	+ 18,0		- 14,2	(20 $^{\circ}$,5)	- 15,2	(20 $^{\circ}$)				
6	id.	0,494 Gr. pyridine	+ 49,5	+ 35,3		- 0,8	(21 $^{\circ}$)	- 14,5	(19 $^{\circ}$,5)				
7	id.	10	+ 49,2	+ 16,8		- 14,9	(20 $^{\circ}$,5)	- 15,7	(19 $^{\circ}$)				

Filled up to 100 c.M³. and placed in thermostat (temp. 34 $^{\circ}$).

Herewith the fact was in agreement that after 24 hours the liquid of N^o. 6 (VI α) did not possess any reducing power on FEHLING'S *solution*.

A iodometrical determination of invert-sugar proved that less than 60 milligrams of invert-sugar was present per 100 cm³.

If the liquid of N^o. 6 (VI α) after 24 hours is boiled for some time the reducing power on FEHLING'S *solution* becomes greater. Boiling with an extra quantity of strong hydrochloric acid gives a liquid that after being neutralized with alkali possesses a strong reducing action on FEHLING'S *solution*.

From table VI β it follows that 500 milligrams and 640 milligrams of aniline compensate the action of respectively ± 5 cm³. and 7 cm³. of normal hydrochloric acid, which proves that in acidic solution aniline behaves as monoacidic alkali.

From table VI γ it can further be concluded that 0.494 gr. of pyridine, compensates about 6 cm³. of normal hydrochloric acid, pyridine acts therefore about as monacidic alkali in acidic solution.

The basic and acidic character of the compounds described in the above is in accordance with the constitution-formula, which nowadays are assumed for these compounds.

The method of research described can help to find a better constitution-formula in cases where the said accordance does not exist ¹⁾.

For the rest one may be astonished a little by the strong neutralizing action against hydrochloric acid on the one hand, sodium-hydroxide on the other hand of compounds being generally known as feeble acids or basic substances.

Frequently we can make good use of this neutralizing action of substances with a but feebly acidic or basic character in watery solution in order to compensate the influence of strong alkali or strong acid.

In many experiments in the laboratory as well as in technical processes we have often to struggle with the formation of strong basic substances or strong acids. In such cases we can compensate the action of the strong alkali or acid by the addition of efficient amphoter or weak electrolytes.

Dordrecht, June 1917.

¹⁾ A first example of this was given in the preceding communication with the betain.

Chemistry. — "*On Black Phosphorus*". II. By Prof. A. SMITS, G. MEYER, and R. PH BECK. (Communicated by Prof. S. HOOGEWERFF).

(Communicated in the meeting of June 30, 1917).

As was already communicated before, our researches carried out with BRIDGMAN's black phosphorus have corroborated the supposition that this new form of phosphorus is always metastable under the vapour pressure.

That this is the case at the triple point temperature of the black phosphorus, is beyond doubt, for it appeared that the black phosphorus melts $\pm 2^\circ$ lower than the violet phosphorus, hence at $\pm 587.5^\circ$. The vapour tension determinations, however, gave results which, though this did not seem probable, pointed to the possibility that below $\pm 560^\circ$ the black phosphorus, and above that temperature the violet phosphorus would possess the smallest vapour tension, or in other words that there exists a transition point between black and violet P at 560° . This conclusion seemed, however, by no means necessary, as the results could also be explained by a too slow establishment of the internal equilibrium at temperatures under $\pm 560^\circ$.

To ascertain whether the black phosphorus under 568° is really stable, the following experiments were made. Equal quantities of violet and black P were heated with 1% Iodine in a tube of glass that melts with difficulty in vacuum 13 days in succession in a bath of KNO_3 — NaNO_3 at $\pm 480^\circ$.

Then the tube was quickly taken out of the bath, the contents extracted with CS_2 , etc. and then the specific weight is determined according to the suspension method. It then appeared that almost everything had been changed into a substance with a specific weight **2.3**, some particles still possessing the spec. weight **2.7**. Accordingly it already follows from this that 560° is no transition temperature, for at 480° the black P was still converted into the violet phosphorus and was therefore metastable¹⁾.

In the following experiment the proportion between black and

¹⁾ Without contact with violet P we have not been able to convert the black P into violet P. Even after 4 hours' heating of black P with 1% I at 580° not the slightest change had occurred.

violet phosphorus was chosen differently, viz. 0.9 black P and 0.1 violet P, and 1 % I was again added to this mixture. The result was that after 16 *days*' heating at 450° practically everything had obtained a specific weight of 2.4, from which therefore in agreement with the result of the preceding experiment, it follows that the violet P is metastable at 450° under the vapour pressure.

It was now the question whether this could also still be demonstrated at lower temperature.

Two tubes were taken of glass that does not melt easily; one filled with $\frac{4}{5}$ violet P + $\frac{1}{5}$ black P, and the other with $\frac{1}{5}$ violet + $\frac{4}{5}$ black P. Again 1 % I was added to both mixtures. After being pumped empty and fused off, the tubes were heated for 3 $\frac{1}{2}$ *months* at 380°. When then the contents of the two tubes was examined, it appeared that the mass, which at first consisted for $\frac{4}{5}$ of violet P and for $\frac{1}{5}$ of black P, had been *quite* converted to the violet modification, whereas the mixture that at first consisted for $\frac{1}{5}$ of violet, and for $\frac{4}{5}$ of black P, had not appreciably changed.

To what it is owing that when the black phosphorus was greatly in the minority, it was entirely converted to violet phosphorus, whereas in the other case nothing could be perceived of a conversion, cannot yet be stated with certainty; the one positive result, however proves already that also at 380° the black modification is the metastable one under the vapour pressure, and this makes the view, set forth in the preceding communication¹⁾, greatly gain in probability.

Amsterdam, April 10, 1917.

Anorg. Chem. Laboratory
of the University.

¹⁾ Proc. **18**, 992 (1915).

Chemistry. — “*On the Electro-Chemical Behaviour of Nickel.*” By Prof. A. SMITS and C. A. LOBRY DE BRUYN. (Communicated by Prof. S. HOOGWERFF).

(Communicated in the meeting of June 30, 1917).

1. Nickel is a metal that assumes internal equilibrium exceedingly slowly, and can therefore very easily be disturbed. When nickel, immersed in a solution of NiSO_4 or $\text{Ni}(\text{NO}_3)_2$ is made anode, resp. cathode, a very strong polarisation is found already at very small current densities. Also when attacked by chemical reagents as HNO_3 , H_2SO_4 etc. nickel is very easily disturbed in noble direction.

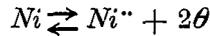
In a solution of NiSO_4 , which is in contact with the atmosphere, nickel does not assume the equilibrium potential, simply because the attack to which Nickel is subjected under these circumstances by the air oxygen dissolved in the electrolyte, is sufficient to give rise to a pretty great disturbance of the internal equilibrium in the metal surface. That these small quantities of oxygen exert so great an influence is owing to this that the oxygen is at the same time a negative catalyst for the setting in of the internal equilibrium. What is remarkable is this that not only oxygen but also hydrogen has appeared to be a negative catalyst for this process, so that nickel does not assume the equilibrium potential in a solution under a hydrogen atmosphere either.

2. These circumstances being unknown, the nickel potential has always been measured in a hydrogen atmosphere or in air and it was thought that in this way the equilibrium potential of this metal was measured. Only SCHUCH has measured the nickel potential also in vacuum, and found that it differs from that which is found in a hydrogen-atmosphere.

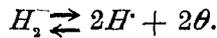
Led by the new considerations about the internal state and the chemical and electromotive behaviour of metals, we have made some experiments with the result that the behaviour of nickel, which is still much more remarkable than we thought, can be explained in an exceedingly simple way.

To show this it is necessary to discuss the condition for the hydrogen generation from a solvent containing hydrogen ions by means of a metal (here nickel).

As was already stated before, in this case we have to do with the two following equilibria (in the liquid)



and



When the electron concentration of the nickel equilibrium is greater than that of the hydrogen equilibrium corresponding to a hydrogen pressure of an atmosphere, hydrogen generation will have to be found.

We have:

$$L_{Ni} = (Ni^{..}) (\theta)^2 \quad \text{and} \quad L_{H_2} = (H \cdot)^2 (\theta)^2$$

from which follows:

$$(\theta)^2 L_{Ni} = \frac{L_{Ni}}{(Ni^{..})} \quad \text{and} \quad (\theta)^2 L_{H_2} = \frac{L_{H_2}}{(H \cdot)^2}$$

so that the condition for the H_2 -generation is:

$$\frac{L_{Ni}}{(Ni^{..})} > \frac{L_{H_2}}{(H \cdot)^2}$$

or

$$L_{Ni} > L_{H_2} \frac{(Ni^{..})}{(H \cdot)^2}$$

Put $(Ni^{..}) = 1$, then:

$$L_{Ni} > \frac{L_{H_2}}{(H \cdot)^2}$$

or

$$(H \cdot)^2 > \frac{L_{H_2}}{L_{Ni}}$$

Now

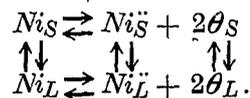
$$L_{H_2} = 10^2 \times 10^{-48} \quad \text{and} \quad L_{Ni} = 10^2 \times 10^{-45}$$

hence $(H \cdot)$ must be $> 10^{-3}$.

When therefore the hydrogen-ion concentration is more than 10^4 times the concentration in pure water, the metal nickel must give hydrogen generation, which, however, is not the case.

How to account for this will appear from what follows.

For this purpose we consider here the equilibrium that we have to do with in the system Ni — electrolyte, viz.:



Now we know that hydrogen generation occurs when the electrons combine with the hydrogen-ions to hydrogen molecules. These

electrons would, therefore, have to be withdrawn from the metal equilibrium, here therefore from the nickel equilibrium, which would cause this equilibrium to be disturbed. If nickel behaved normally, this disturbance would be immediately negated, and it is easy to see in what way this disturbance would be annulled.

This cannot take place through the reaction:



for, the concentration (Ni_L) being very small, this is a reaction that can produce but exceedingly few Ni -ions and electrons per second. What would have to happen is this: the electrons and nickel ions would have to go into solution from the metal and in the metal the reaction



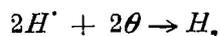
would have to take place.

In this case the potential difference during the hydrogen generation would be exclusively determined by the Ni -ion concentration prevailing at the moment.

The metal nickel however, behaves quite differently.

As was already observed, nickel is exceedingly inert, i.e. its internal equilibrium is very slowly established, and to this comes that the hydrogen, which dissolves in the nickel to a small degree, greatly retards the setting in of internal equilibrium.

Now we may imagine the phenomenon to be like this: when electrons have been withdrawn from the solution by the reaction:



and in consequence of this ions and electrons have gone into solution from the metal, the disturbance of the internal equilibrium is not abolished any longer, and the potential difference Ni -electrolyte has consequently become less negative.

For nickel, which is so exceedingly inert under the influence of the dissolved negative catalyst, hydrogen, the supposition suggests itself that this process can continue till the electron concentration of the nickel equilibrium in the electrolyte has become equal to that of the hydrogen equilibrium.

It is self-evident that it is supposed here that the electrolyte is perfectly free from oxygen and that the result in question is to be expected when we work e.g. in vacuum or in a hydrogen atmosphere. We shall now examine what the potential difference nickel-electrolyte has become in this case.

For this purpose we return to the derivation of the equation of electrons for the potential difference. The condition of equilibrium

for the equilibrium between the electrons in the metal and in the coexisting electrolyte is:

$$(\mu_{\theta_S})_{\Delta=0} - FV_S = (\mu_{\theta_S})_{\Delta=0} - FV_L \dots (1)$$

in which $(\mu_{\theta_S})_{\Delta=0}$ and $(\mu_{\theta_L})_{\Delta=0}$ indicate the molecular thermodynamic potentials of the electrons in the metal and in the coexisting electrolyte for the case that the potential difference = 0, V_S and V_L being the electric potentials of the metal and of the electrolyte, so that FV_S and FV_L denote the molecular electrical potentials of the electrons in these two phases.

It now follows from this equation that when we omit the index $\Delta = 0$:

$$V_S - V_L = \Delta = \frac{\mu_{\theta_S} - \mu_{\theta_L}}{F} \dots (2)$$

As it was our purpose to derive an equation for the potential difference in which not only the concentration of the electrons in the electrolyte occurs, but also that in the metal, the splitting up of the molecular thermodynamic potential into a concentration-free term and into a concentration member, viz.:

$$\mu = \mu' + RT \ln C \dots (3)$$

has been applied both to the electron in the electrolyte and to the electron in the metal. We then get:

$$\Delta = \frac{\mu'_{\theta_S} - \mu'_{\theta_L} + RT \ln(\theta_S) - RT \ln(\theta_L)}{F} \dots (4)$$

If we now put:

$$\mu'_{\theta_S} - \mu'_{\theta_L} = RT \ln K'_{\theta} \dots (5)$$

we get:

$$\Delta = \frac{RT}{F} \ln \frac{K'_{\theta}(\theta_S)}{(\theta_L)} \dots (6)$$

the electron equation, derived by SMITS and ATEN, for the potential difference.

When we now again return to equation (5), and add $RT \ln \theta_S$ to the two members, we get:

$$\mu'_{\theta_S} + RT \ln(\theta_S) = RT \ln K'_{\theta}(\theta_S) + \mu'_{\theta_L} \dots (7)$$

or

$$RT \ln K'_{\theta}(\theta_S) = \mu_{\theta_S} - \mu'_{\theta_L} \dots (8)$$

We get for the potential difference of 2 different metals:

$$\Delta_1 = \frac{RT}{F} \ln \frac{K'_{\theta_{S_1}}(\theta_{S_1})}{(\theta_{L_1})} \dots \dots \dots (9)$$

and

$$\Delta_2 = \frac{RT}{F} \ln \frac{K'_{\theta_{S_2}}(\theta_{S_2})}{(\theta_{L_2})} \dots \dots \dots (10)$$

From which follows that the electromotive force of a circuit consisting of these two metals, immersed in the corresponding salt solutions is:

$$\Delta_1 - \Delta_2 = \frac{RT}{F} \ln \frac{K'_{\theta_{S_1}}(\theta_{S_1})}{K'_{\theta_{S_2}}(\theta_{S_2})} - \frac{RT}{F} \ln \frac{(\theta_{L_1})}{(\theta_{L_2})} \dots \dots (11)$$

Let us now apply the just found relation (8), then we get:

$$\Delta_1 - \Delta_2 = \frac{\mu^{\theta_{S_1}} - \mu^{\theta_{L_1}}}{F} - \frac{\mu^{\theta_{S_2}} - \mu^{\theta_{L_2}}}{F} - \frac{RT}{F} \ln \frac{(\theta_{L_1})}{(\theta_{L_2})} \dots \dots (12)$$

Now $\mu^{\theta_{L}}$ is the same for different solutions with the same solvent, so that we get:

$$\Delta_1 - \Delta_2 = \frac{\mu^{\theta_{S_1}} - \mu^{\theta_{S_2}}}{F} - \frac{RT}{F} \ln \frac{(\theta_{L_1})}{(\theta_{L_2})} \dots \dots (13)$$

The term:

$$\frac{\mu^{\theta_{S_1}} - \mu^{\theta_{S_2}}}{F}$$

represents the volta-effect, viz. the potential difference that appears when the two metals are brought in contact in dry condition. Now we know that this potential difference is very small, so that this equation (13) tells us that when the electron concentrations (θ_{L_1}) and (θ_{L_2}) have become equal, $\Delta_1 - \Delta_2$ will be very small or zero, so that then

$$\Delta_1 = \Delta_2$$

will hold in first approximation.

This result tells us, therefore, that finally the potential difference nickel-electrolyte will have become equal to the potential difference hydrogen-electrolyte. The experiment was, in fact, entirely in accordance with this.

3. An NiSO₄-solution, in which a slight cloudiness had been brought about by the addition of a little NaOH, to make the solution as little acid as possible, was brought in a vessel with 5 tubes. These were closed by means of rubber stoppers, through which were led two nickel electrodes [very pure KAHLBAUM Ni-wire 3 mm. thick,

fastened in a glass tube by means of sealing-wax], a platinized Platinum electrode, which could be immersed in the liquid just before the measurement, a bevel, which was in connection with the calomel electrode, and a supply and exit tube for the hydrogen. In the middle tube there was placed a stirrer with mercury closure to make stirring possible if necessary. Very pure hydrogen which was obtained by leading the hydrogen from a cylinder or from an electrolytic hydrogen apparatus (with nickel electrodes) through a glass tube with Pt-asbestos, which was heated up to $\pm 500^\circ$ in a furnace, and then through two blown washing bottles with a suspension of $\text{Fe}(\text{OH})_2$, was first led through and later over the NiSO_4 solution, while from time to time the potential differences of the different electrodes were measured.

The result was:

$$\begin{array}{l} \text{Ni} - 0.640 \text{ V} \\ \text{Pt} - 0.640 \text{ V} \end{array} \left\{ \begin{array}{l} \text{electrolyte } 2,5 \text{ n } \text{NiSO}_4; \text{ potential} \\ \text{with respect to } 1 \text{ n } \text{calomel-electrode.} \end{array} \right.$$

As follows from WILSMORE's¹⁾ calculation and SCHUCH's determinations²⁾, as also from determinations made by us, the equilibrium potential of Ni lies at $\pm -0,48 \text{ V}$ with respect to 1 n calomel electrode. Hence the above found nickel potential is not the equilibrium potential, but the potential of a state disturbed superficially in the base direction. We see here that the nickel has assumed the same potential as the H_2 -electrode, which is in agreement with the above given theoretical derivation.

When we consider the solutions of NiSO_4 with increasing H-ion concentration by continually adding more H_2SO_4 , we see that the equality continues to exist also for other values of the H-ion concentration:

Ni	Pt
— 0,640 V	— 0,640 V
— 0,517 „	— 0,517 „
— 0,350 „	— 0,348 „

On measurement in hydrogen atmosphere the found Ni-potential is accordingly quite dependent on the H-ion concentration, and always equal to the H_2 potential.

Before going on we will anticipate and mention already here that according to the here given theoretical considerations the potential of the unary nickel, or the nickel in internal equilibrium, can only be measured in a solution in which the electron concen-

¹⁾ Z. phys. Chem **35** [1900] 291.

²⁾ Amer. Chem. J. **41** [1909] 208.

tration of the hydrogen equilibrium is smaller than that of the nickel equilibrium. We shall, therefore, have to make the H-ion concentration as small as possible by the addition of a base. In this case a few nickel ions and electrons will go into solution, and, no hydrogen separating on the metal, the internal equilibrium can set in. In the determination of the equilibrium potential, however, we may have no hydrogen atmosphere, for hydrogen of a pressure of 1 atmosphere would render the electron concentration of the hydrogen equilibrium too large. Nor may we have an oxygen atmosphere, because when there is oxygen present in the solution, the equilibrium



exists, in which case the electron concentration is much smaller than would correspond with the unary nickel equilibrium. The consequence is then that electrons are withdrawn from the nickel equilibrium, and the nickel sends ions and electrons into solution. The nickel is therefore attacked, and it results from the inertia of the nickel, together with the negative catalytical action of the dissolved oxygen that this disturbance is not negated, and the nickel is superficially in such an ennobled condition that the corresponding electron concentration is in agreement with the electron concentration of the oxygen equilibrium. Accordingly the potential of Ni with respect to a nickel salt solution measured in contact with the air, lies at a much less negative value than would correspond with the equilibrium potential.

It is therefore clear that to find the unary equilibrium potential of nickel, we shall have to work in a solution, in which for $(Ni^{2+}) = 1$ the H-ion concentration is $< 10^{-3}$, and in an atmosphere free from H_2 and O_2 , or in vacuum.

Thus we really easily find the unary equilibrium potential.

SCHOCH¹⁾ and in imitation of him later on SCHILDBACH²⁾ are the only investigators who as far as we know, have also worked in vacuum. They have, however, not succeeded in finding the true explanation of the disturbing influence of H_2 and O_2 .

In a determination of the equilibrium potential in a 1 N. $NiSO_4$ -solution boiled out in vacuum, the following values were found:

Potential	— 0.453 V	— 0.477 V	— 0.480 V	— 0.480 V
of the nickel:	after 4 hours	after 47 h.	after 52 h.	after 70 h.

Then hydrogen was led through the same solution, and the H_2 -potential was measured. After 48 hours we found:

¹⁾ loc. cit.

²⁾ Z. f. Electr. Chem. 22 [1910] 977.

$$\text{Ni} \quad - 0.630 \text{ V}$$

$$\text{Pt}(\text{H}_2) - 0.640 \text{ V}$$

and the nickel electrode had therefore again assumed the H_2 -potential.

That in this measurement the H-ion concentration must be smaller than 10^{-3} follows from an analogous determination with an NiSO_4 -solution boiled out in vacuum and acidified with H_2SO_4 as electrolyte.

The Ni-potential was now constant at -0.317 V immediately after the boiling.

On conduction of H_2 through the same solution -0.315 V was found later for the H_2 -potential.

4. When we consider the different determinations of the equilibrium potential of Ni, the following facts are worth noticing:

NEUMANN ¹⁾ finds -0.538 V for electrolytic Ni, hence Ni charged with H_2 and disturbed towards the base side. He does not speak about the atmosphere in which the determination has been made.

PFANHAUSER ²⁾ and SIEMENS ³⁾, who worked in the same way as NEUMANN, found values deviating comparatively little from the real value.

MUTHMAN and FRAUENBERGER ⁴⁾ find -0.880 V as most negative value for nickel charged with H_2 , which value they took for the equilibrium potential. The values found by PFANHAUSER and SIEMENS can probably be explained by this, that two counteracting influences, the H_2 charge and the air atmosphere, compensated each other. PFANHAUSER could only obtain the most negative value -0.466 V found by him when the electrode was measured in the vessel in which it was formed by electrolysis. Transmission through the air always yielded less negative values.

KÜSTER ⁵⁾ found -0.800 V as minimum value for the tension of separation of nickel.

SCHWEITZER ⁶⁾ carries out the measurement in the H_2 -atmosphere, because he wanted to exclude the influence of O_2 . He finds -0.616 V , a value, which as was set forth above, is not the equilibrium potential, but a value which is determined by the H-ion concentration in the electrolyte used.

¹⁾ Z. phys. Chem. **14** [1894] 215.

²⁾ Z. f. El. Chem. **7** [1901] 698.

³⁾ Z. f. Anorg. Chem. **41** [1904] 249.

⁴⁾ Sitz.ber. Bayr. Akad. Wiss. **34** [1904] 201.

⁵⁾ Z. f. El. Chem. **7** [1900] 257.

⁶⁾ Z. f. El. Chem. **15** [1909] 602.

SCHOCH¹⁾ found $-0,48 V$ by the method described above, and also when measuring in an N_2 -atmosphere.

SCHILDBACH²⁾, working according to the method SCHOCH, likewise finds a value which is in very good agreement with that of SCHOCH.

It was of importance to examine whether in a solution of $NiCl_2$ the same influences of H_2 and O_2 would be found. The Cl -ions exerting so strong a catalytic influence on the setting in of the internal equilibrium of iron, it was possible that here too the influence was noticeable, and would prove to be stronger than the disturbing influence of O_2 and H_2 . This has not appeared to be the case.

In 2.5 n. $NiCl_2$ in H_2 -atmosphere we found:

$$Ni I - 0.604 V, \quad Ni II - 0.600 V, \quad H_2 - 0.607 V$$

after addition of HCl :

$$Ni I - 0.379 V, \quad Ni II - 0.372 V, \quad H_2 - 0.376 V.$$

The behaviour of nickel in $NiCl_2$ is therefore quite analogous to that in $NiSO_4$.

S U M M A R Y.

The researches on the electromotive behaviour of some metals, made in the Amsterdam laboratory of late years show that one of the most characteristic properties of a metal is the velocity with which it assumes equilibrium at a definite temperature and pressure. At the ordinary temperature and pressure this velocity is on the whole exceedingly small for a metal in dry condition. In contact with an electrolyte this is, however, quite different, but at the same time we meet then with complications through the appearance of catalytic actions, both positive and negative ones, which render a comparison of the behaviour of different metals difficult. It occurs namely that in the same metal the equilibrium sets in quickly in one electrolyte and slowly in another; thus iron assumes internal equilibrium e.g. with great velocity, when it is immersed in a solution of $FeCl_2$, and this takes place much more slowly in a solution of $FeSO_4$.

There are, however, metals that also in contact with an electrolyte assume internal equilibrium slowly, and nickel, which has been discussed in this communication, is one of these metals.

Now it has appeared of late, that not only oxygen, but also hydrogen can be negative catalyst for the establishment of the internal

¹⁾ l.c.

²⁾ Z.f. Electr. Chem. 22 [1910] 977.

equilibrium, and the remarkable feature in the behaviour of nickel is this that the influence of these negative catalysts is exceedingly great.

This is accompanied with something very remarkable, viz. this that when hydrogen of e. g. 1 atm. is conducted through an NiSO_4 -solution, in which Ni-electrodes stand, the metal through the deposition of electrons + nickel-ions resp. through the going into solution of these components, is disturbed so far in base resp. noble direction till the electron-concentration of the metal equilibrium in the liquid has become equal to that of the hydrogen equilibrium in the electrolyte.

It can be demonstrated that in this case the potential difference of the nickel with respect to the electrolyte, with exception of the Volta-effect, must become equal to the potential difference of the hydrogen electrode.

Experimentally it was found that under the circumstances given here, practically equality of the two potential differences is found.

The theoretical considerations led us further to expect that the unary equilibrium potential for nickel was only to be expected in the experiment in an atmosphere free from O_2 - and H_2 , or in vacuum, and when an Ni-salt solution was used in which the H-ion concentration is smaller than 10^{-3} for an Ni-ion concentration of 1.

Experiments made in this direction gave as result $-0,480$ V. with respect to the 1n. calomel-electrode, a value that agrees entirely with the value calculated by WILSMORE and also with that found by SCHOCF in an experiment in vacuum.

In the many potential measurements of the metal nickel which were carried out in the air or in a hydrogen atmosphere, the equilibrium potential of the unary nickel has not been measured, but the potential of a state of this metal that was disturbed in base or in noble direction.

Amsterdam, June 29 1917.

*Laboratory for Anorg. and General
Chemistry of the University.*

Physiology. — “On the transmission of *stimula* through the ventricle of frogs' hearts”. By Dr. S. DE BOER. (Communicated by Prof. VAN RIJNBERK).

(Communicated in the meeting of June 30, 1917).

The following facts were among others stated by me in the pharmacophysiological investigations I made into frogs' hearts, after I had poisoned them with veratrine or digitalis.

1. The duration of the refractory stage of the ventricle-muscle increases after the administration of each of the two poisons, and so does likewise the *a-v*-interval, at last the contractility of the ventricle-muscle decreases.

2. As soon as the relative duration of the refractory-stage $\left(\frac{\text{duration of the total refract. stage}}{\text{duration of a sinusperiod}} \right)$ surpasses the value 1, suddenly or gradually the normal ventricle-rhythm changes into the halved one.

a. The sudden halving of the ventricle-rhythm comes about in the following manner:

The duration of the refractory-stage of the ventricle has increased during the normal rhythm of the ventricle for this reason that the ventricle-muscle was not yet entirely restored at the beginning of every ventricle-systole. What was still wanting to this restoration, was called by me the *residue refractory stage*.

The *periodical refractory-stage* was added to it by every systole, so that the total refractory-stage consists of two components. If now the relative duration of the refractory-stage has become longer than 1, the next following ventricle-systole falls away, and a protracted ventricle-pause is the consequence. This protracted pause influences the two components in an opposite sense.

The ventricle-muscle restores itself better, so that the residue-refractory-stage decreases. But after a protracted pause the next following systole of the ventricle is considerably enlarged, consequently the duration of the periodical refractory-stage of the ventricle increases. If now this increase of the duration of the periodical refractory-stage surpasses the decrease of the residue-refractory stage, then suddenly halving of the ventricle-rhythm sets in.

b. The gradual transition to the halved ventricle-rhythm however

takes place, when the decrease of the residue-refractory-stage surpasses the increase of the periodical refractory-stage. For, if this takes place, the normal ventricle-rhythm continues after a protracted pause, till by accumulation the duration of the residue refractory-stage causes again the falling away of a ventricle-systole, and the normal ventricle-rhythm is resumed again. So groups of ventricle-systoles come into existence, which become gradually smaller and smaller, till in the end the halved ventricle-rhythm is reached in this way.

3. Spontaneous alternations between the halved ventricle-rhythm and the normal one occur frequently. The cause of these alternations lies in the fact that during the halved ventricle-rhythm the katabolic index of the ventricle $\left(\frac{\text{duration of the refract. stage of the ventricle}}{\text{duration of a ventricle-period}} \right)$ decreases again by restoration, till it has become less than $\frac{1}{2}$. Then the normal ventricle-rhythm sets in again. In this twice as rapid ventricle-rhythm¹⁾ the katabolic index of the ventricle increases again, and consequently the halved rhythm of the ventricle sets in again. So these alternations can repeat themselves again several times.

4. By extra stimulation of the ventricle the halved ventricle-rhythm can artificially be converted into the normal twice as rapid rhythm by the addition of one little ventricle-systole. This proves, that during the halved rhythm of the ventricle the sinus-impulses that are not answered by the ventricle, did really reach this part of the heart, but rebounded on the not yet irritable ventricle-muscle.

The normal ventricle-rhythm can likewise be converted into the halved one by extra-stimulation. The enlarged post-compensatory-systole fixed then the ventricle in the halved rhythm.

I attributed these and many other results, not mentioned here, to the fact, that an important factor of the action of the heart, viz the refractory stage had been modified under the influence of the employed poisons. Its duration increased by veratrine and by digitalis. These poisons had no further possible mysterious actions for the results, mentioned above.

The following observations made with regard to not poisoned frogs' hearts afforded an unmistakable affirmation of this fact. *The before mentioned sudden and gradual transition into the halved ventricle-rhythm occurs likewise in the not poisoned frog's heart, the spontaneous alternations between the halved rhythm of the ventricle and the normal one can also be stated.*

¹⁾ During the normal ventricle-rhythm the katabolic index of the ventricle is equal to the relative duration of the refractory stage.

In fig. 1¹⁾ we give a reproduction of the suspension-curves and the electrograms of a frog's heart (*rana esculenta*). More than an hour after the suspension this heart shows constantly repeated

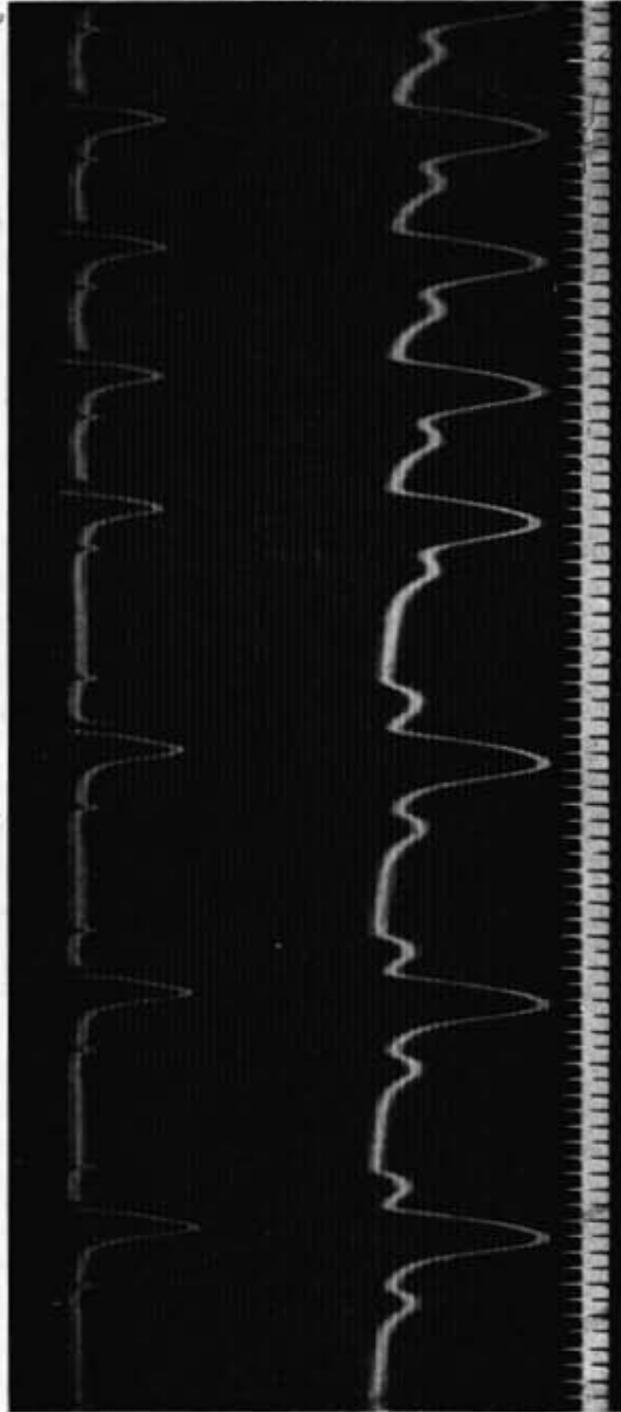


Fig. 1.

¹⁾ Constantly 1 electrode was placed on the auricle — and 1 on the ventricle-point in the following reproductions.

alternations between the normal ventricle-rhythm and the halved one. I succeeded in photographing such a spontaneous alternation under simultaneous registration of the action-currents.

This reproduction shows a great number of important details, and affords a formal confirmation, likewise for not-poisoned frogs' hearts, of the theoretical explanations communicated by me in former essays. In the figure we see suddenly appear the halved ventricle-rhythm after 4 normal ventricle-systoles. Three of these are still registered.

I intend more explicitly to explain here the following details, which, in my opinion, are of interest for my subject.

1. As I indicated in my former investigations the a-v-interval increases during the normal ventricle-rhythm till the halving of the ventricle-rhythm sets in. Afterwards the duration of the a-v-interval decreases. The suspension-curves of this figure show a much shorter a-v-interval after the halving than before it. But the electrograms indicate these differences much sharper. The P-R-interval increases still during the last 4 systoles. The first curve of the halved ventricle-rhythm shows a much shorter P-R-interval of the normal ventricle-rhythm. The restoration of the ventricle-muscle in the halved rhythm is even distinctly to be seen in these 3 first curves of the halved ventricle-rhythm. The P-R-interval of the 2nd systole is shorter than that of the first, and that of the 3rd still shorter than that of the 2nd.

We must attribute the shortening of the P-R-interval after the halving to a shortening of the electric latent stage, as all sinus-impulses reach the ventricle along the connection-systems (BUNDLE of HIS), and consequently the time of conducting along these has not in the least changed. It appears that this shortening still proceeds from the moment of the first ventricle-systole of the halved rhythm.

2. The duration of the R-oscillation is after the halving shorter than before it. This duration is now also again shorter during the 2nd systole than during the first, and at the 3rd systole shorter than at the 2nd.

In the halved ventricle-rhythm the conductivity through the ventricle is consequently better than in the normal twice as rapid rhythm of the ventricle. From the first systole of the halved ventricle-rhythm the conductivity still improves from systole to systole.

The P-R-interval and the duration of the R-oscillation consequently sustain alterations in exactly the same sense. We must attribute both these alterations to the changed metabolic condition of the ventricle-muscle (katabolic index). This metabolic condition deteriorates in the normal ventricle-rhythm. If now the rhythm of the

ventricle suddenly halves, the metabolic condition of the ventricle-muscle suddenly improves much, but also in the halved ventricle-rhythm this improvement increases from systole to systole.

This reproduction which for the present moment will remain most likely exceptional among my material, afforded me an irrefutable confirmation of the theories I explained before. For the present I

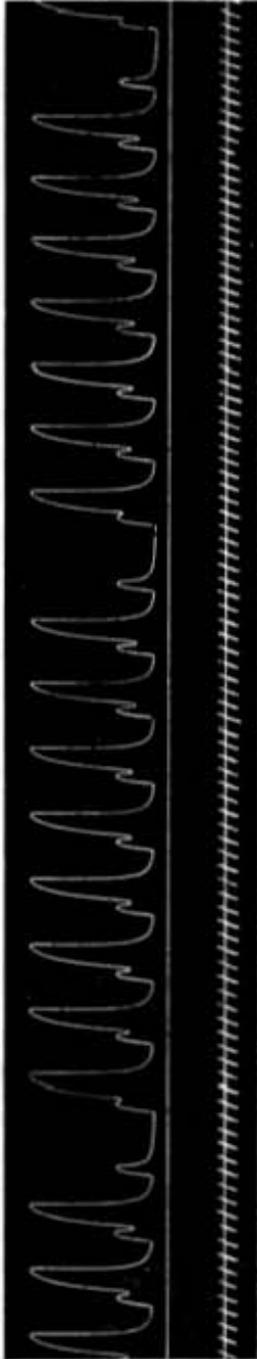


Fig. 2.

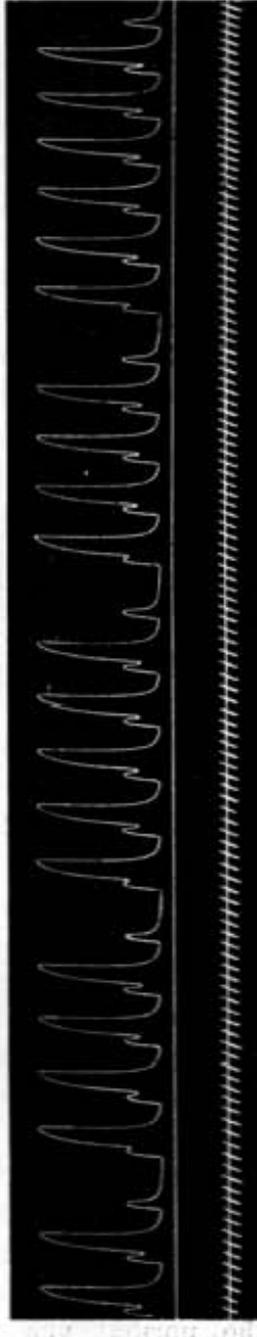


Fig. 3.

shall most likely be compelled in my further investigations to restrict myself to artificial transitions of poisoned frogs' hearts, and, when doing so, I shall at the same time register the action-currents.

I am likewise in possession of beautiful examples of the slow transition to the halved rhythm of unpoisoned frogs' hearts. One example of these is reproduced in the figures 2, 3, 4, and 5.

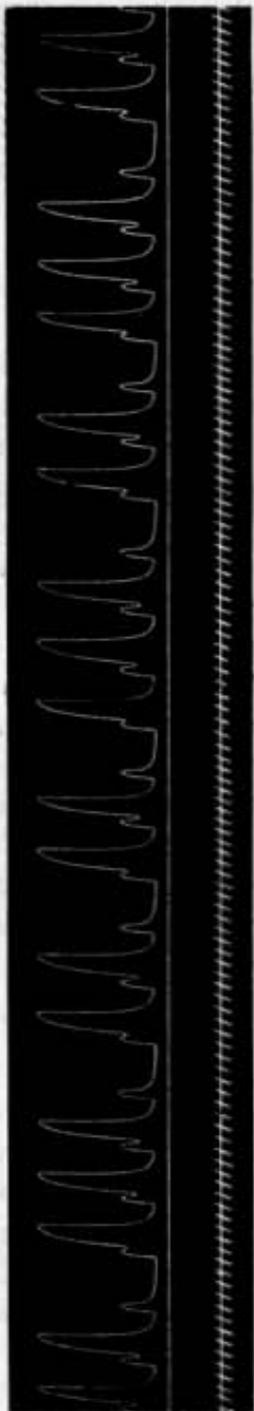


Fig. 4.

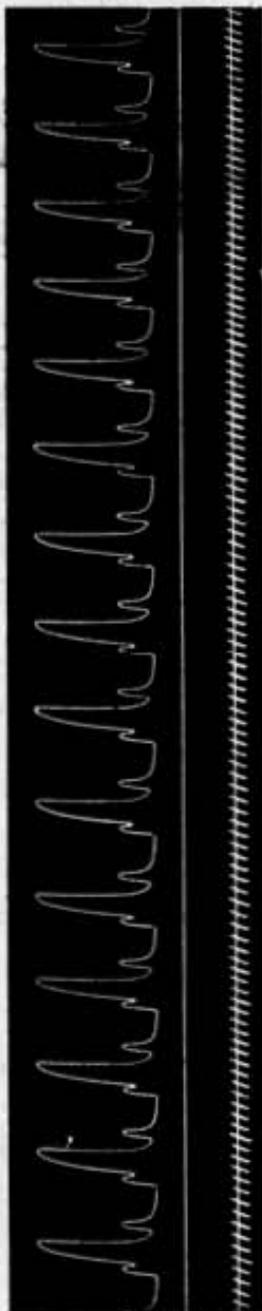


Fig. 5.

The heart of a *rana temporaria* was suspended and soon showed group-formation, because constantly 1 systole of the ventricle fell away. The groups grow gradually smaller, till groups of 2 and 3 systoles (fig. 4) form the last transition to the halved ventricle-rhythm. (fig. 5). We see during the groups the duration of the $a-v$ interval increasing splendidly; again and again the ventricle-systole sets in later in the auricle-diastole, till one ventricle-systole falls away. After this the interval is shortened again, to be protracted again in the same way during the following group. The ventricle-systole of each first curve of the group commences in the figures 2, 3 and 4 close to the top of the auricle-curve. The ventricle systole of each last curve begins at about the middle of the diastolic line of the auricle-curves. This is the case with the large groups, but also with the little ones (bigeminus groups). Consequently in the beginning more systoles of the ventricle are required than later to protract the $a-v$ -interval as much. The deterioration of the metabolic condition of the ventricle-muscle is announced here by the formation of smaller groups. It is likewise clear, that during the groups the metabolic condition of the ventricle-muscle deteriorates, and improves again after a protracted pause. In my opinion we must here also attribute the protraction of the $a-v$ -interval again to a protraction of the latent stage of the ventricle-muscle.

It is the active contracting terminal organ, the ventricle-muscle, the refractory stage of which increases during the groups and so does at the same time likewise the latent stage. The increase of the refractory-stage is here likewise caused by the increase of the duration of the residue-refractory-stage by accumulation. During the protracted pause after a group the decrease of the residue-refractory-stage surpasses the increase of the periodical refractory-stage. In this way the constantly decreasing groups come into existence, which ends in the halved ventricle-rhythm.

The conductivity through the ventricle was examined by me still in another way. In a former communication it was already stated, that the T-oscillation had altered in a negative sense after extra-stimulation of the ventricle-basis or of the auricle. A positive T of the normal ventricle-systole decreased during the extra-systole which was excited in this way, a negative T increased. In some cases a positive T became negative. The T oscillation had changed in a positive sense after extra-stimulation of the ventricle-point. A negative T decreased, a positive one increased¹⁾.

¹⁾ Zeitschrift für Biologie. Bd 65, Seite 428.

These modifications of the T-oscillations were now examined by me more carefully, and it appeared to me, that the conductivity of the ventricle plays here an important part. *I stated in this examination that the T-oscillation varies the more in a negative sense, after*

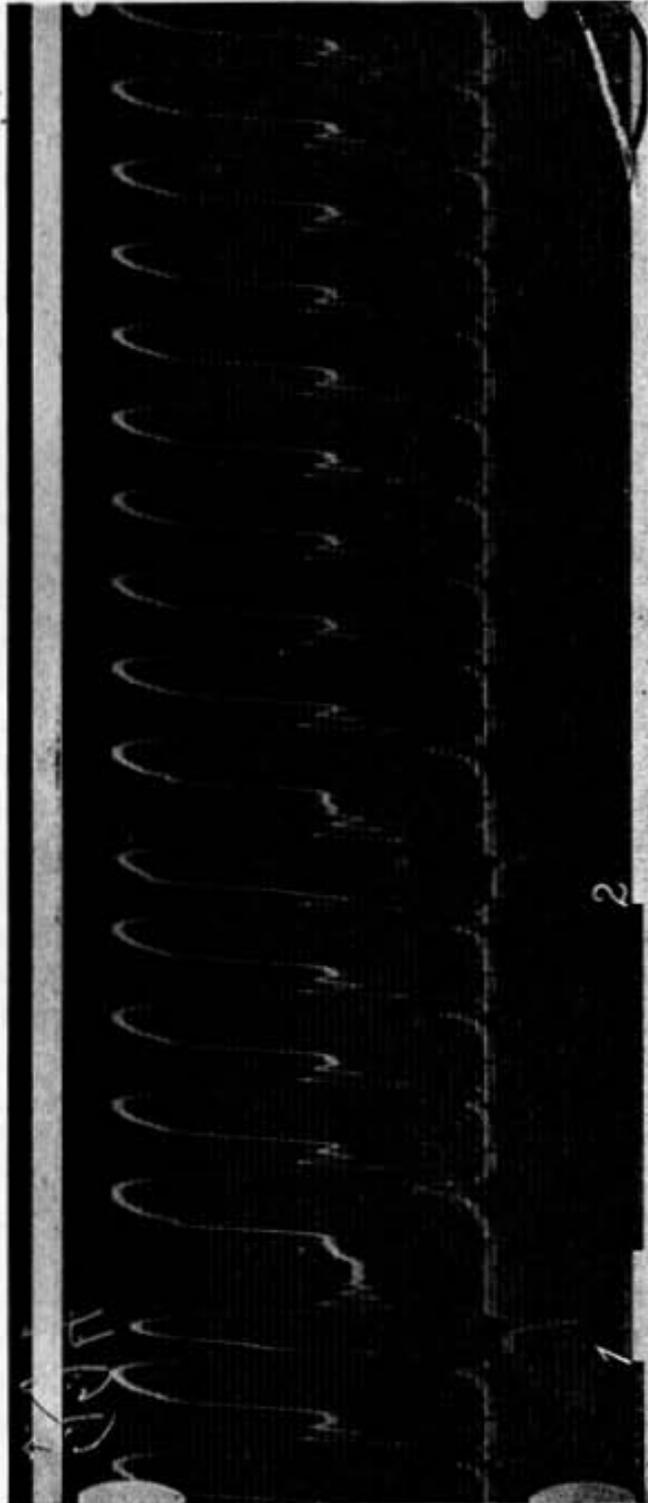


Fig. 6.

extra-stimulation of the ventricle-muscle or of the auricle, in proportion as the conductivity of the ventricle is worse at the moment, when the extra stimulation or the "Erregung" conducted after the provoked auricle-extra-systole reaches the ventricle at an earlier epoch of the ventricle-period.

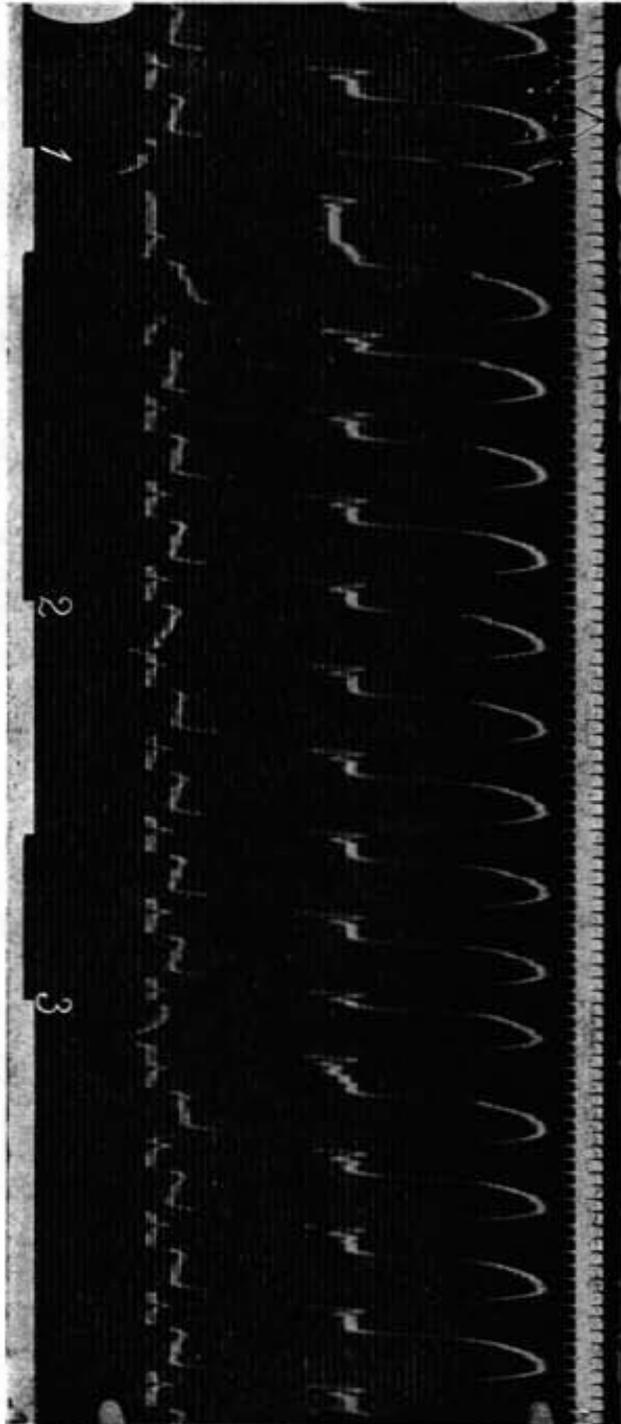


Fig. 7.

The positive T-oscillation of the normal systoles during an extra-systole can even produce a negative T, if at an early epoch of the ventricle-period the ventricle is excited to an extra-contraction, and a decreased positive T, if at a later epoch of the ventricle period the ventricle is excited to an extra-contraction.

A few examples may explain the above more accurately.¹⁾ In the figures 6 and 7 extra-stimula were applied to the ventricle-basis at the upward oscillations of the signal. In Fig. 6 at 1 an extra-stimulus is applied to the ventricle-basis immediately after the completion of the preceding T-oscillation. The T-oscillation of the extra-systole which is positive at the normal ventricle-systole, becomes now decidedly negative. At 2 a following extra-stimulus hits the ventricle-basis at a much later epoch; consequently the negative T-oscillation is now much smaller. Here I already fix the attention to the fact that the enlargement of the positive T-oscillation is so much the more important during the postcompensatory-systole, in proportion as the preceding extra-systole has been brought about at an earlier epoch of the ventricle-period.

In fig. 7 an extra-stimulus hits the ventricle-basis at 1 soon after the completion of the preceding T-oscillation. This causes a great negative T in the electrogram of the ventricle-extra-systole. At 3 the extra-stimulus hits the ventricle at a later epoch, this makes the T-oscillation smaller, at 2 the extra-stimulus comes still later, an extremely little negative T-oscillation is the consequence.

It is beautifully brought out here, that the enlargement of the positive T-oscillations of the postcompensatory systoles is so much the more important, in proportion as the extra-stimulus has hit the ventricle-basis at an earlier epoch of the ventricle-period.

The extra-stimulus was applied to the auricle in the figures 8 and 9, which proceed from the same frog's heart. At about the same epoch of the ventricle-period the ventricle-systoles set in that are brought about after auricle-extra-systoles by the conducted "Erregung" after the extra-stimula applied at 1 and 4. The T is negative and of the same dimension at both the ventricle-systoles brought about in this way. The ventricle-systole sets in at a much later epoch of the ventricle-periods after the extra-stimulus applied to the auricle at 2. The T-oscillation remains now positive, though distinctly reduced.

At 3 an extra-systole of the ventricle is brought about through current-loops directly by the stimulus.

¹⁾ In the following figures extra-stimula were only applied at the upward oscillation of the signal.

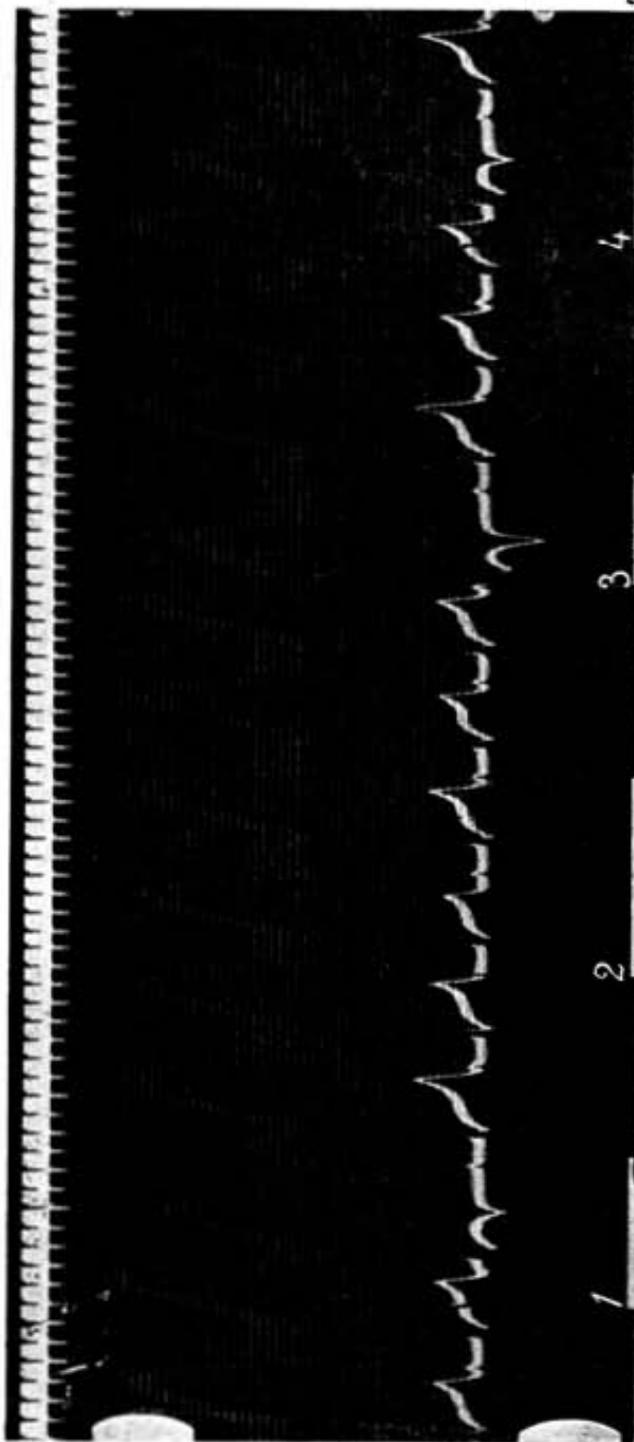


Fig. 8.

At 5 and 7 the ventricle-systoles caused in the same way set in at a much earlier epoch of the ventricle-period than at 1 and 4. In conformity herewith both the negative T-oscillations are now also much greater. The ventricle-systoles that are brought about

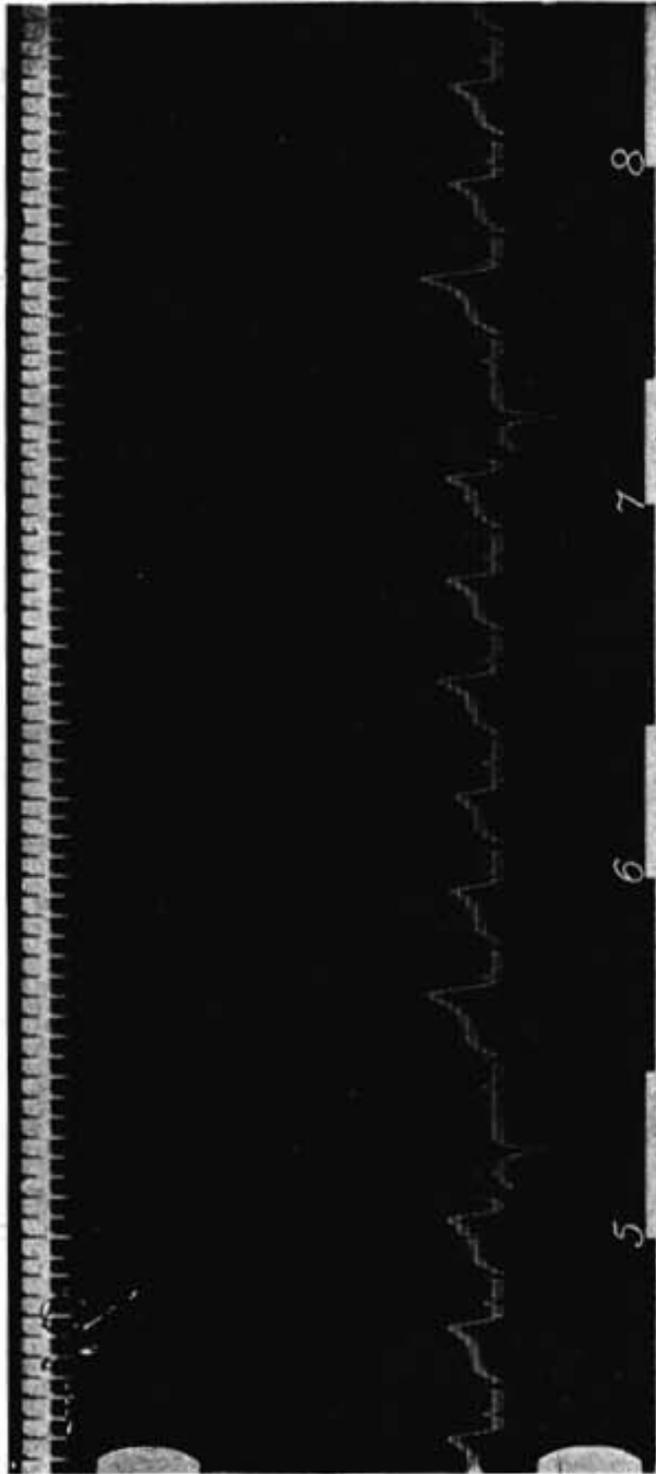


Fig. 9.

after 5 and 7 teach us how exactly the dimension of the negative T-oscillations is determined by the epoch of the ventricle-period at which the ventricle systoles are brought about. After the extra-stimulation of the auricle at 5 the string is a little longer in the

position of rest, after the completion of the T-oscillation of the ventricle, before the R-oscillation of the anticipated ventricle-systole begins, than after the extra-stimulation at 7. The difference is little but it can distinctly be observed. Entirely in conformity herewith the negative T is after the extra-stimulation at 5 smaller than after the extra-stimulation at 7. At 6 the anticipated ventricle-systole begins, after the extra-stimulation of the auricle at a much later moment of the ventricle-period. The T-oscillation remains now positive, but is somewhat reduced. The extra-stimulation at 8 has evidently hit the auricle at the same moment, as it was reached by the sinus-impulsion.

In these representations the enlargement of the positive T-oscillation of the post-compensatory systoles is also the greater, in proportion as the extra-systole of the ventricle sets in more anticipated.

If now we try to answer the question, why the T-oscillations of the ventricle-electrograms change the more in a negative sense after extra-stimulation of the ventricle-basis and the auricle, in proportion as the extra-ventricle-systole begins earlier in the ventricle-period, then we must look for the cause of this phenomenon in the conductivity of the ventricle. At an earlier epoch of the ventricle-period this conduction is slower than at a later period.

This is the cause that the negativity of the point at an extra-systole, which has been brought about at an earlier epoch of the ventricle-period, begins later than at an extra-systole that has been brought about at a later epoch. Consequently the point-negativity domineers the more in the latter part of the ventricle-electrograms, in proportion as the extra-systole has been brought about at an earlier epoch of the ventricle-period. The earlier the extra-systole is brought about in the ventricle-period, the more the T-oscillation changes in a negative sense. It is likewise moreover of importance in this respect that the contractility of the basis at an early epoch of the ventricle-period is still trifling; when from there the contraction-wave reaches the point in a slow tempo, its contractility has become more intensive. But this factor can be reduced again to a slackened conductivity at an early epoch of the ventricle-period. This theoretical explanation corresponds so perfectly with the experimental results, that I can discretionally produce extra-systoles with reduced positive T-oscillations and with negative T-oscillations.

I wish to fix here the attention to one point that is distinctly demonstrated in the figures 8 and 9, I pointed out in my former communication already, that after extra-stimulation of the auricle and of the basis ventriculi the T-oscillations of the ventricle-

systoles were modified in an equal sense. This appears most distinctly from the figures 8 and 9, in which at about the same epoch of the ventricle-period, at 3 by extra-stimulation of the basis ventriculi (by current-loops), and at 5 and 7 after extra-

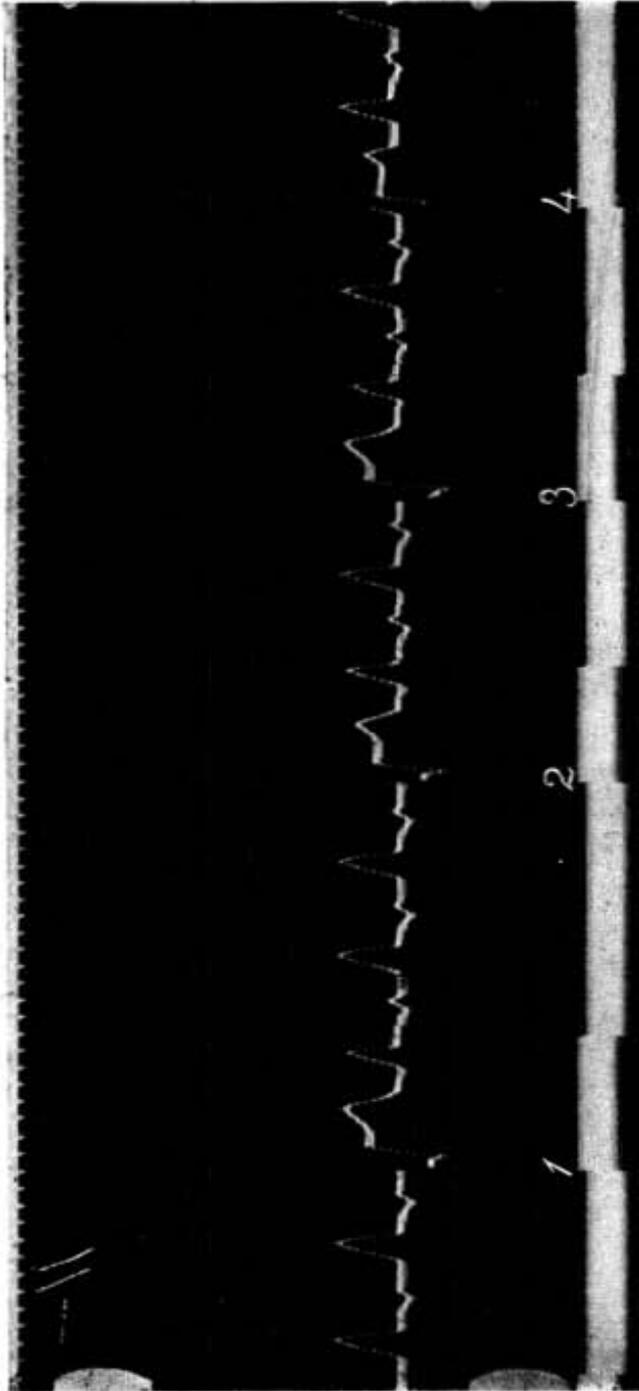


Fig. 10.

stimulation of the auricle, an extra-ventricle-systole is brought about. We see now the T-oscillation after extra-stimulation of the basis ventriculi about as large as after extra-stimulation of the auricle. The anticipated ventricle-systole is brought about in the latter case by the "Erregung" that reaches the ventricle along the usual connection-systems. The epoch of the ventricle at which the anticipated ventricle-systole begins, and not the place where the stimulus attacks, determines the extent of the T-oscillations. It is obvious that this does not hold, when an extra-stimulation hits the point. But here the T-oscillation of the ventricle-systole varies the more intensively in a positive sense, in proportion as the extra-stimulus reaches the ventricle at an earlier epoch of the ventricle-period. This is distinctly to be seen in Fig. 10. At 1 and 3 the extra-stimulation reaches the ventricle-point at an early epoch of the ventricle-period. Now very large positive T-oscillations set in. At 2 the extra-stimulation hits the ventricle-point at a later epoch. Consequently the positive T is now smaller. If at 4 the ventricle-point is hit by the extra-stimulation at a still later epoch, the positive T is again still considerably smaller. At 4 the basis-negativity had already begun, when the extra-stimulation set in, and brought the string back to and beyond the O-position. It appears consequently that the ventricle-point is irritable in the ascending line of the R-oscillation.

The basis-negativity is consequently so much the more intensive in the ventricle-electrograms of the extra-systoles after extra-stimulation at the end of these electrograms, in proportion as the extra-stimulation hits the ventricle-point at an earlier epoch of the ventricle-period.

Mathematics. — “Surfaces that may be represented in a plane by a linear congruence of rays”. By Prof. JAN DE VRIES.

(Communicated in the meeting of April 27, 1917).

1. In order to obtain a representation (1,1) of a cubic surface in a plane we may make use of the bilinear congruence which has two straight lines lying on that surface as directrices. To this purpose the linear congruence (1,3) may also be used, which is formed by the bisecants of a twisted cubic lying on the surface¹). It would also be possible to make use of the congruence (1,3) of the rays that intersect a twisted cubic and one of its bisecants, provided that those two directrices are lying on the surface.

We shall now consider, more in general, the surfaces that can be represented by means of a *linear congruence of rays* (1, n).

The representation of a surface Φ^{n+p+1} with an n -fold and a p -fold straight line by means of a *bilinear congruence* has been amply treated by GUCCIA and MINEO²).

2. Let now be given a surface Φ^{2n+1} with an n -fold twisted cubic α^3 . Through a point P of Φ passes a bisecant of α , which intersects the plane of representation τ in P' ; in general a point P has *one* image P' , and, inversely, a point P' of τ is the image of *one* point P .

Let us now consider the ruled surface \mathcal{G} formed by the bisecants t projecting the points of a plane section γ^{2n+1} . In the plane of that curve lie three straight lines t , \mathcal{G} is consequently of order $(2n+4)$.

That cone, which projects α^3 out of one of its points, determines on γ^{2n+1} evidently $(n+2)$ points P , consequently α is an $(n+2)$ -fold curve on \mathcal{G}^{2n+4} .

The image of γ^{2n+1} is therefore a curve of order $(2n+4)$ with three $(n+2)$ -fold points A ; this curve will be indicated by the symbol $c^{2n+4}(3A^{n+2})$.

The images of two plane sections have the $(2n+1)$ points P' in common, which are the images of the points P lying on the intersection of the two planes.

¹) See e.g. R STURM, *Geometrische Verwandtschaften*, IV, 288

²) GUCCIA, *Sur une classe de surfaces, représentables point par point sur un plan* (Ass. française pour l'avancement des sciences, 1880). MINEO, *Sopra una classe di superficie unicursali* (Le matematiche pure ed applicate, volume I, p. 220).

Besides the $3(n+2)^2$ intersections lying in the principal points A they have consequently moreover $m = (n^2 + 2n + 3)$ points G in common; they are evidently the intersections of as many bisecants g of α^3 lying on Φ^{2n+1} .

On the surface lie therefore at least $(n^2 + 2n + 3)$ straight lines.

From this it ensues in particular that any twisted cubic lying on a cubic surface has six straight lines of Φ^3 as bisecants.¹⁾

The complex of plane intersections of Φ^{2n+1} is consequently represented by a complex (∞^3) of curves c^{2n+4} , which has three $(n+2)$ -fold and $(n^2 + 2n + 3)$ simple base-points.

3. The curve α^3 is represented by the ruled surface \mathfrak{A} of the bisecants t , which touch at Φ^{2n+1} in one of its two points of support: The straight lines g are double generatrices of \mathfrak{A} ; for they may be considered to touch in two points of α^3 .

Let now x be the order of \mathfrak{A} , y the multiplicity of α^3 on that ruled surface. The intersection on τ is then a curve $\alpha^x(3A^y, mG^2)$. As α^3 has evidently $3n$ points in common with a plane section γ^{2n+1} , the consideration of their images produces the relation

$$(2n+4)x = 3(n+2)y + 2(n^2 + 2n + 3) + 3n.$$

As two bisecants of α^3 can only intersect on that curve \mathfrak{A} has $2y$ points in common with an arbitrary bisecant; so we have $x=2y$.

We now find $y = 2n + 3$, $x = 4n + 6$.

The image of the curve α^3 is therefore a curve $\alpha^{4n+6}(3A^{2n+3}, mG^2)$.

4. Each of the n planes that touch Φ^{2n+1} in a point R of α^3 , contains a generator t of the ruled surface \mathfrak{A} , which moreover intersects α^3 in a point S . The remaining $(n+3)$ straight lines t meeting in R touch in Φ^{2n+1} in another point of α^3 . The pairs of points R, S belong to a correspondence with characteristic numbers $(n+3)$ and n . The points S belonging to the same point R form pairs of an involutory correspondence with characteristic number $(n+3)(n-1)$; the coincidences originate from points R , where two of the tangent planes coincide: On α^3 lie therefore $2(n+3)(n-1)$ *cuspidal points*

To each point R correspond n points of the image α , so the points of α are arranged in an involution I_n .

5. Let in the plane τ a curve f be given of order p , which passes a_k times through the principal point A_k , and g_k times through the principal point G_k . With the image $c^{2n+4}(A_k^{a_k+2}, G_k)$ it has apart from the principal points a number of points in common, indicated by

$$p^+ = (n+2)(2p - \sum a_k) - \sum g_k.$$

¹⁾ For $n=2$ we find the surface Φ^5 with nodal curve α^3 amply discussed by R. STURM, (*Geom. Verw.* IV, 311).

This number is evidently the order of the twisted curve Φ , which has f as image.

As f has apart from the principal points, a number of points in common with $a^{4n+6}(A_k^{2n+3}, G_k^2)$, represented by

$$n^* = (2n + 3)(2p - \sum a_k) - 2\sum g_k,$$

the curve Φ rests in n^* points on the curve a^3 . A straight line l is therefore the image of a λ^{2n+4} , which intersects a^3 in $(4n+6)$ points.

6. For the simplification of the representation we submit the figures in τ to a quadratic transformation, which has A_k as principal points. By this the curve c^{2n+4} is transformed into a curve c^{n+2} , which does not pass through A_k , but does pass through the (n^2+2n+3) points \mathfrak{G} , in which the principal points G are transformed.

To the curves γ^{2n+1} , in which the surface Φ^{2n+1} is intersected by the planes γ of a pencil, correspond now the curves of a pencil (c^{n+2}). Among them there are $3(n+1)^2$, which possess a nodal point, which is then at the same time the case with the corresponding curves γ^{2n+1} .

The surface Φ^{2n+1} is consequently of class $3(n+1)^2$.

The straight line $\mathfrak{G}_1 \mathfrak{G}_2$ is transformed by the quadratic transformation into the conic $f^2(A_k G_1 G_2)$ and the latter is the image of a twisted curve Φ^n , which rests on a^3 in $(2n-1)$ points. For through f^2 and a^3 passes a hyperboloid, which has the curve f^2 and n times the curve a^3 in common with Φ^{2n+1} ; the residual section is the Φ^n in question.

7. *We shall now consider a surface Φ^{n+p+1} that passes n times through a twisted curve a^q of order q , and p times through a straight line β , which is $(q-1)$ times intersected by a^q .*

The straight lines t , which intersect a and β , form a linear congruence $(1, q)$, by which Φ is represented in a plane τ , for t intersects Φ , except on a and β , only in one point P more.

The ruled surface \mathfrak{E} , which represents the plane section γ^{n+p+1} is of order $(n+p+q+1)$; for in the plane γ lie q generators.

Out of a point of β the curve a^q is projected by a cone of order q with $(q+1)$ fold edge β , which intersects γ^{n+p+1} in $(p+q)$ points P . Consequently \mathfrak{E} passes $(p+q)$ times through β .

Out of a point of a the line β is projected by a plane that determines $(n+1)$ points P on γ . Consequently a^q is an $(n+1)$ fold directrix.

The image of γ^{n+p+1} is consequently a curve $c^{n+p+q+1}(qA^{n+1}, B^{p+q})$.

Two curves c have apart from the points A and B and the images of the $(n+p+1)$ points in the section of their planes a number of points G in common represented by

$$\begin{aligned}
 m &= (n+p+q+1)^2 - (n+1)^2q - (p+q)^2 - (n+p+1) = \\
 &= n(n+1) + (2n+1)p - (n^2-1)q.
 \end{aligned}$$

From this it ensues that the surface Φ^{n+p+1} contains at least m straight lines.

If we take here $q=1$, it appears that a surface Φ^{n+p+1} with an n -fold and a p -fold straight line contains $2np + n + p + 1$ straight lines resting on the multiple straight lines¹⁾. For $n=1$, the number m appears to be independent of q ; we find that a surface Φ^{p+2} with p -fold straight line contains $m=3p+2$ straight lines g , resting on α and β . A plane passing through β and one of those straight lines contains one more straight line h , which does not rest on α ; on Φ^{p+2} lie therefore at least $6p+4$ straight lines.

8. Let us now determine the image of the straight line β . A plane γ passing through β contains one more curve γ^{n+1} , which has on α but not on β , an n -fold point Q . As it intersects β in $(n+1)$ points, the plane contains $(n+1)$ straight lines t , which touch the surface in points of β , consequently are generators of the ruled surface \mathfrak{B} by which β is represented; α is therefore an $(n+1)$ fold directrix. As Q comes to lie on β for $(q-1)$ different positions of the plane γ , t will as many times coincide with β , consequently β is a $(q-1)$ fold torsal line. But each of the p planes that touch at Φ in a point of β , contains one straight line t ; consequently the multiplicity of β on \mathfrak{B} is equal to $(p+q-1)$ and the order of \mathfrak{B} equal to $(n+p+q)$.

The image of the straight line β is therefore a curve $b^{n+p+q} (qA^{n+1} B^{n+q-1}, mG)$.

This result may be controlled by determining the number of points that b has in common with a curve c apart from the principal points A, B, G ; we promptly find then the number p , being the number of common points of β^p and γ^{n+p+1} .

9. Let us now determine the image of $\alpha\gamma$. Each of the n planes that touch at Φ in a point Q of α , contains one straight t of the ruled surface \mathfrak{U} that represents α , consequently α is an n -fold directrix.

If β is a y -fold directrix a plane passing through β contains a section of order $(n+y)$, and the image of α has as symbol $a^{n+y} (qA^n, B^y, mG)$.

By combining with $c^{n+p+q+1} (qA^{n+1}, B^{p+q}, mG)$ we find for the determination of y , the relation $(n+p+q+1)(n+y) = n(n+1)q + (p+q)y + m + nq$, in which it has been taken into account that a plane section has nq points in common with $\alpha\gamma$.

¹⁾ See MINEO *ibid.* page 221 or J. DE VRIES, *Surfaces algébriques renfermant un nombre fini de droites* (Archives Teyler, serie II, tome VIII, p. 262).

From this relation it ensues that $y = p + q$.

Consequently the image of α^q is a curve $a^{n+p+q} (qA^1, B^{p+q}, mG)$.

The combination with the image of β produces a control; from which it appears that the curves a and b have promptly $n(q-1)$ points in common, apart from the principal points.

10. If we write in the results arrived at, $n = 1$, $q = 3$, $p = 1$, we obtain the representation of the cubic surface to which we referred in § 1. The directrices of the linear congruence (1,3) are then a twisted curve α^3 of Φ^3 and one of the bisecants of α^3 lying on Φ^3 .

The image of a plane γ^3 is then a $c^6 (3A^2, B^4)$. If the six bisecants mentioned above are indicated by b_k , and if b_1 is the directrix of the (1,3), the five straight lines c_{1k} are represented by points.

The image of α^3 is a curve $a^3 (3A, B^4, 5C)$ the image of b_1 a curve $b^5 (3A^2, B^3, 5C)$; these curves have, as they ought to have, two more points in common, which are the images of the points of support of the bisecant b_1 .

It is easy to determine from these data the images of the remaining 21 straight lines of Φ^3 .

Chemistry. — "*Observations about hydration under the influence of Colloidal Catalysers and how to account for this process*".

By Prof. J. BÖESEKEN and Mr. H. W. HOFSTEDE.

(Communicated in the meeting of June 30, 1917).

Some time ago ¹⁾ we performed and described a number of hydrations with the aid of colloidal catalysers. At the same time we gave an outline of what might be expected during the development of this process, and what we shall therefore observe in measuring the absorption of the hydrogen, viz:

The hydrogen and the matter to be reduced will pass from the gas-space into the liquid medium, then they will pass one or more layers covering the atoms of the catalyser and finally they will coalesce. Hence we first observe a succession of diffusion-processes, before the catalytic-chemical reaction enters. It was assumed that the rapidity of the latter process is always considerably greater than that of the former, so that the observed rapidity of absorption, would seem to refer to a diffusion-process.

The assumption of the all-surpassing velocity of the catalytic-chemical process is arbitrary; the rapidity will of course depend on the nature of the catalyser. But we have been guided in the first place by the consideration that the action of platina-metals on some of the processes brought about by them is exceedingly great indeed, so that few thousandths millimol are sufficient to bring molecular quantities to a fairly rapid chemical change.

It appears then that we want far greater quantities of catalyser, say from 50—100 millimol, to reach the result, obtained in the observations made. So it is obvious that we must rather look for the cause of that very moderate velocity in the possibility, that of these 50—100 millimol only a very small part can be reached at the same time by the reacting substances, than to suppose that the process of *these particular* reactions is such an extraordinarily slow one.

In my opinion the very potent catalytic action of the metal-atoms results from the nature of these atoms themselves. Owing to their

¹⁾ Recueil **35** 260 (1916).

capacity of rapidly transmitting electricity from atom to atom they must be pre-eminently adapted to decrease chemical resistances, the latter being probably occasioned by electrical tension.

Secondly we have been guided by the consideration, that the "activation" of a colloidal catalyser is frequently due to a finer division i.e. to an increase of the number of atoms, coming into contact with the reacting substances at one time so that inversely the paralysis must be caused by a decrease of this number. We have assumed that this is the result of the presence of the above-mentioned layers about the atoms of the catalyser, which may include both the layer of the protecting colloid (gum-arabic, sodium-salt of *protalbinic* acid, etc.) and the layer of all other molecules existing in the medium — also that of the catalyser itself ¹⁾. (l. c. p. 262—263).

We shall call these layers the "paralysis-layers" ²⁾.

Following up this assumption we have argued that with a not very active catalyser the process is bound to proceed almost till the very end with constant velocity, if only care is taken to bring the H_2 with sufficient velocity into the liquid space. If the concentration of the substance to be reduced is not too slight, then the outer side of the paralysis-layer will remain saturated with the mixture of this substance + hydrogen, whereas on the side of the catalyser the concentration of this mixture (or rather of one of the components) is kept at zero as a result of the great velocity of reaction. Thus we measure a diffusion-process with a constant difference of level.

Seeing that the concentration of the substance to be reduced decreases towards the end, so that the paralysis-layers on the outer side no longer remain saturated, the velocity of absorption is bound to decrease towards the end.

The saturation of the paralysis-layers with gaseous hydrogen was brought about by me by forcibly shaking the colloidal solution with H_2 and by raising the number of shocks in one minute, until the velocity of absorption when using a very active catalyser no longer increased. In this way we could make ourselves independent of the first phase of diffusion (l.c. p. 262): the dissolving-velocity of the gaseous hydrogen.

But it is especially by the following observations we believe we have

¹⁾ This may be observed as agglutination, flocking out or even crystallization.

²⁾ We have imagined these layers to be close and more or less permeable; it may be, though, that with very slight concentrations of the interacting molecules they must be represented as impermeable and as having smaller or larger interstices. It stands to reason that in this case a quite different explanation than the provisional one we have given, would be required.

demonstrated that the analytic-chemical reactions proper have certainly not been measured by us.

1. The velocity of reduction of α -crotonic acid, isocrotonic acid and tetrolic acid under the influence of a very active palladium-catalyser (P_{AAL}¹⁾) was perfectly equal under otherwise equal conditions.

2. The reduction and substitution of trichloroacrylic acid to propionic acid and the substitution of pentachloropropionic acid took place without any sudden changes of velocity and even for these two acids with almost equal velocity.

3. The two double bonds of the sorbinic acid were hydrated without any sudden change of velocity, and the velocity was equal to the substitution-velocity of the two chlorated acids mentioned under 2.

4. It was ascertained (with a less active catalyser) that cinnamic acid, muconic acid, malonic acid and vinylglycolic acid were hydrated almost quite as rapidly, if only the decreasing activity of this catalyser was taken into account.

5. The result obtained with a relatively large quantity of palladiumsol (SKITA²⁾) that under otherwise equal conditions, equimolecular quantities of cinnamic acid, glutaconic acid, muconic acid and vinylglycolic acid were hydrated with approximately equal velocities whereas itaconic acid, mesaconic acid and citraconic acid were hydrated, with somewhat lesser velocities, though mutually equal ones, than the former acids.

6. It is true that during the reduction of the cinnamic acid under the influence of finely divided platinum, a decrease of velocity was noticed after the absorption of about one molecule of hydrogen; it could be determined however, that this divergence decreased in proportion as a greater quantity of the catalyser was taken. This cannot be accounted for if we assume a chemical cause of the decrease in velocity, which is besides very slight and not very perceptible.

7. It was found that the velocity of the hydration was largely dependent on the condition of the catalyser p. 275—279 and p. 286.

8. The temperature-coefficient was but a small one (We do not set great store by this argument, because an increase of temperature may cause a diminution of the surface of the catalyser, the result of which will be a decrease of velocity).

¹⁾ B. 38, 1401 (1905).

²⁾ B. 37, 24 (1904), 40. 2209 (1907), 41. 805 (1908).

§ 2. Now the very rapid hydration of undecylenic acid-sodium, with palladium-sol, during which process the contents of the reaction-vessel were changed into a froth (p. 270), had revealed to us that the method of investigating pursued up till now, did not sufficiently guarantee the demand that we should keep the paralysis-layers about the catalyser saturated with H_2 .

Hence it was necessary :

1. to improve the hydration-vessel ;
2. to take a quite definite catalyser, if possible the activity of the same must be constant, and at any rate easy to control ;
3. to work in a constant temperature.

As regards the first requisite we selected the apparatus employed by Mr. COHEN and one of us in our experiments on light, with which the H_2 is spouted in small particles with great velocity through the liquid ¹⁾, the contact-surface of the gas with the colloidal catalyser being thus very considerably enlarged. This is brought about by rotating a hollow stirrer with great rapidity through the liquid ; in the gas-space above the surface of the liquid is an opening. During the rotation the gas is sucked through the stirrer and dashed into small bubbles against a wave-breaker. This wave-breaker keeps the fluid-level constant.

A revolution-counter indicated that the number of revolutions was at least 2200 a minute. It is probable that we succeeded in keeping the paralysis-layers saturated with hydrogen, as with a much slighter velocity of rotation the same velocity of hydration was obtained in otherwise similar conditions and when applying but moderate quantities of the catalyser.

As catalyser we used the palladiumsol prepared according to SKITA and MEYER ²⁾, which proved to be very active, so that we needed but few milligrams of metal to obtain a velocity of hydration that could be measured. The hydration-apparatus was placed in a thermostat, in which was also an electric lamp, so that the vessel could be observed without taking it out of the thermostat. We were enabled to do so, because the hydration-apparatus had been fixed in an iron frame-work that could be moved up and down with the apparatus.

The hydrogen was purified by conducting it through alkaline and acid permanganate of potassium, through silver nitrate, through alkaline pyrogallol solution and finally through concentrated sulphuric acid.

¹⁾ Proc. Kon. Ak. Wet. 25 March 1916.

²⁾ B. 45, 3579 (1912); one c.c.m. contained one m.g. of palladium.

Before use the palladiumsol had been saturated with hydrogen, the gas was also conducted for some time through the hydration-vessel, while the spray-stirrer had been brought into action, and the substance to be reduced was already in the vessel.

By means of a three-way tap the hydration-vessel was connected with a graduated Lunge-burette, which the H_2 filled. By means of a simple lever-apparatus gas-volumes could always be read during a constant mercury-level. The accompanying figures show the complete installation in elevation and in plan. By way of elucidation it may be remarked that in the drawing we find between the purification-flasks of the hydrogen and the dryingflasks a copper tube with iron mantle, filled with copper-shavings. This tube is heated in a chamotte-oven and serves to free the hydrogen from oxygen. The ends of this metal tube are provided with refrigeration-jackets. (See below).

The first experiments were made with cinnamic acid in aqueous solution at high temperature and without thermostat; afterwards in 96 % alcohol at the usual temperature. Herein the catalyser frequently proved to flock out, so that we finally worked in 80 % alcohol, always about 25°. Besides cinnamic acid, we also examined other substances.

With the readings of the hydrogen that had been absorbed we noticed the barometer and the temperature in the neighbourhood of the gas-burette; as a rule we took 3 m.g. palladiumsol against 0.5 to 1.5 gr. of the hydrated substances.

We subjoin a tabulated summary of a series of experiments.

The summary gives two series of experiments; in the first series of 15 the H_2 had not been conducted along a red-hot copper-spiral.

Though the character of the results obtained is in accordance with what was found before, yet it appears even in a superficial investigation that great irregularities occurred.

The velocities of hydration diverged in a rather considerable degree under comparable conditions; this is especially striking in the reduction of the cinnamic acid-aethylesters where the initial-velocity of absorption was found to be within the limits 5.5 and 80 c.m. per 10' (N°. 8—11).

The cinnamic acid-methylester too revealed strange leaps, the commencing velocity being between 10 and 40 ccm. per 10'.

Then we were struck with another phenomenon, viz. that not unfrequently the number of absorbed cc.m. H_2 surpassed the number calculated to a considerable extent; we had observed this before and this fact has been repeatedly observed by other investigators

No.	Substance	Quant. in gr.	Solvent	Quant. in ccm.	Pd-sol. in ccm.	ccm H ₂ calculated	ccm H ₂ absorbed	Velocity in ccm. per 10'	T.	Observations
1	Cinnamic acid	0.7265	H ₂ O	75	3	117	118	25	94°	Irregular
2	"	0.4792	"	"	"	62	78	"	"	Idem.
3	"	"	96% alc.	"	"	146	144	13	18	Very regular
4	Undecylenic acid-aethylester	1.3010	"	100	"	147	149	80	18	After the first 10' a considerable retardation; flocking-out.
5	"	1.6514	"	"	"	189	192	110	16	Idem.
6	"	1.1263	80% alc.	"	"	132	130	92	17.7	Retardation; no flocking-out.
7	"	1.2387	"	"	5	144	143	105	18.2	Idem
8	Cinnamic acid-aethylester	0.8909	"	75	3	"	113	5.5	26	The course of the hydration was a very slow one, cause: very pure H ₂ (c.f. text).
9	"	1.0971	"	"	"	175	153	75	"	Hydrogen contained O ₂ ; course very regular.
10	"	0.9533	"	"	"	155	133	80	"	Idem.
11	"	1.3059	"	"	"	"	"	28	"	Course auto-catalytic, was not continued up to the end.
12	Cinnamic acid-methylester	0.6840	"	100	"	158	103	40	"	Hydrogen contained O ₂ .
13	"	0.8447	"	"	"	"	"	± 10	"	Great retardation, cause unknown.
14	"	3.0390	"	"	"	493	447	35	25	Hydrogen contained O ₂ .
15	"	2.1397	"	"	"	351	313	40	"	Idem.
16	"	8.0519	"	"	"	1276	1161	± 50	"	Idem; course auto-catalytic.
17	"	2.0832	"	"	"	"	"	1	"	H ₂ very carefully purified, from oxygen.
18	"	not meas	"	"	"	"	"	58	"	H ₂ not conducted over Cu-spirals.
19	"	"	"	"	"	"	"	56	"	Cu-spiral was used, but H ₂ still contained O ₂ ; very regular reduction.
20	"	2.1102	"	100	"	314	308	52	"	Strongly inclined curve
21	"	2.0403	"	"	"	303	299	45	"	Idem.
22	"	2.0176	"	"	"	295	294	"	"	Idem; towards the end almost completely paralysed.
23	Cinnamic acid-aethylester	1.4190	"	"	2 after 30' still 3	193	189	8 after 30' 100	"	Partially flocked-out, after the addition of 3 ccm Pd. sol unexpectedly strong acceleration, then paralysis again.
24	"	2.0210	"	"	1 after 30' still 1 etc. (c.f. text)	283	270	(c.f. text)	"	
25	"	2.3121	"	"	1 after 30' still 1 etc. dito	"	"	"	"	No flocking-out; but decrease of velocity.
26	"	2.2081	"	"	"	313	288	"	"	Idem.

as well. In our first experiments we had used the hydrogen out of a KIPP apparatus and had conducted it through a flask with alkaline pyrogallol-solution; the quantities of hydrogen that had been calculated and measured did not diverge greatly.

Afterwards we employed a hydrogen-bomb and obtained far too great absorption-numbers (nos. 9, 10, 12, 14 and 15). At first not being prepared for the presence of oxygen in the purified gas we excluded as well as we could all other sources of the coming in of oxygen in the apparatus by repeated washing, preliminary treatment of the palladium, and the avoiding of rubber-junctions.

When however the surplus continued, the presence of oxygen was thought probable and determined in the following way.

1). By hydration of larger quantities of substance in the same quantity of solvent and with the same amount of catalyser.

And indeed it was found that on applying:

± 1 gram cinnamic acid-methylester	the surplus =	55 cc.m. N ^o . 12.
3 " " " " "	=	46 " " 14.
8 " " " " "	=	115 " " 16.

In case of the presence of oxygen in the hydrogen the surplus used must be approximately proportional to the quantity of methylester reduced, if at least the amount of the oxygen in the H₂ is constant. Whereas we conducted the gas through an alkaline pyrogallol solution, this will surely not have been the case, but an increase of the surplus when applying more substance is indubitable.

2). By some blank experiments.

For this we took 100 ccm. 80 % alcohol and 3 ccm. palladiumsol saturated with H₂, they were put into the hydration-vessel, after it had been filled with hydrogen in the usual manner.

We actually observed an absorption of gas in four control-experiments, it amounted to between 20 to 30 ccm.; it is curious that though far more gas was in the burette, the action came to an end with this.

The cause of it may be, that on account of diffusion all oxygen had come from the burette into the hydration-vessel, or that the catalyser is paralysed; the former cause seems the more probable. Now the hydrogen was freed from oxygen by means of a tube with red-hot copper shavings; hereupon a decrease of only one ccm. took place in 60'.

But when we were now going to hydrate the cinnamic acid-methylester with this very purified hydrogen, which had also been carefully freed from oxygen, the process was an extremely slow one. (N^o. 17).

Of course this might be due to an accidental paralysis of the

catalyser; in order to investigate this the Cu-spiral was switched off without substituting a pyrogallol-solution, the reduction was once more very regular and even took place with greater velocity than when the pyrogallol-solution was used. (N^o. 19).

The Cu-spiral was switched on again, but this time it had evidently not completely freed the hydrogen from oxygen, as the course of the reaction was fairly rapid and regular. (N^o. 19).

Therefore some quantitative experiments were started with the Cu-spiral as above; the reaction took place; but no paralysis set in, it appeared finally that 6 ccm. too much had been absorbed. As the contents of the hydration-vessel are ± 600 ccm., and 300 ccm. have been received from the burette, the total amount of gas that has been in contact with the catalyser amounts to ± 900 ccm. The surplus 6 ccm. corresponds to 2 ccm. O₂, hence its amount is ± 0.2 %. So this quantity proves to be amply sufficient, to keep up the reaction. (N^o. 20).

With a subsequent experiment (N^o. 21) we had reduced the O₂-quantity (calculated from the surplus gas that had been used) to 0,1 %; otherwise everything being similar; the velocity of reduction was appreciably less and a stronger retardation set in.

This was still more obvious, when we had decreased the O₂-quantity to 0,003 %; towards the end the velocity had decreased to zero, so that a small amount of catalyser had to be added to bring the reduction to an end.

To demonstrate the activating effect of the oxygen still more clearly, the hydrogen was mixed with a still far greater quantity, viz. with 4,8 % and compared with hydrogen that had been carefully purified (but evidently still containing oxygen).

2,0336 Gr. cinnamic acid-methylester hydrated with 4 ccm. sol, absorbed 391 ccm., calculated 306 ccm.

The blank experiment also with 4 ccm. Pd sol showed volume-contraction of 65 ccm. It is remarkable that this reaction i. e. the water-formation, proceeded rather slowly, the sol being completely paralysed, even after the addition of another cmm. Pd-sol.

The control-experiment with purified H₂ with a very slight oxygen-quantity was performed with 1,9958 substance, 4 ccm. Pd-sol and like the two preceding ones at 25° C. and with 2250 rotations of the spray-stirrer.

Absorbed 291 ccm., calculated 294. (This deficiency is probably to be attributed to a not inconsiderable change of temperature in the neighbourhood of the gas-burette; during the experiment, on account of which the volume-calculation has been less accurate).

The reduction took place altogether regularly without any considerable paralysis, as a sign that the H_2 contained some O_2 after all.

Yet the difference in velocity with the H_2 containing $\pm 5\%$ O_2 is very striking as may be seen from the subjoined table.

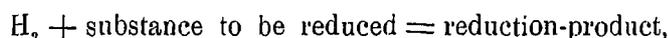
No.	Gas-absorption of the cinnamic acid methylester	5 min.	10 min.	15 min.	20 min.	Duration of reduction	No. of the graphic representation
I	In H_2 with 4.8% O_2	66	120	175	230	60'	27
II	" H_2 " a trace O_2	25	40	52	64	180'	28
III	Combination of H_2 and O_2	20	35	44	49		29
	Difference I—III	46	85	131	181		

When we also observe, that the oxydation of the H_2 proceeds rather slowly (II) we draw the conclusion, that the two reactions: the oxydation of the H_2 and the reduction of the ester, influence each other very favourably.

This might lead us to suppose that owing to the presence of the oxygen the palladium is continually freed from a paralysis-layer, so that the number of atoms becoming available for the reduction-reaction is greater than when no O_2 is present. But if this were so, the paralysing of the catalyser, when no reducible substance is present would be unintelligible. It may be, that the solvent, the 80% alcohol, which no doubt will be acted upon by the oxygen and converted into aldehyde, plays an important part.

A closer investigation will have to elucidate this question, but it appears at any rate that this catalytic reduction is far more complicated, than would appear at first sight.

It is certain that the velocity of the hydration proper:



can be considerably modified by a by-reaction, so that we feel still more positive in concluding, that we have not measured the velocity of this *reaction*.

The question, whether we shall ever be able to measure this velocity of reaction when using colloidal catalysers cannot be solved yet.

It would be indispensable for us to be able to introduce these catalysers into the reaction-mixture in such a state and to bring about the course of the reaction in such a manner, that the forma-

tion of paralysis-layers is altogether excluded; but the part the oxygen has played in our experiments, gives but little hope that we shall be enabled to fulfil this condition in the near future.

§ 3. On examining the graphic representations we notice especially in those hydrations with gas-mixtures deficient in oxygen, a strong curved-line, pointing to paralysis. This paralysis evidently enters sooner with the cinnamic acid aethylester than with the methylester, moreover part of the catalyser repeatedly flocked out.

To make the phenomenon stand out the more, we at first added somewhat less Pd-sol.

With N^o. 23 we first used 2 ccm.; after 30' another 3 ccm. were added. Though the velocity after the second addition was very considerable, yet a strong retardation soon set in.

When starting from 1 cc.m. sol, the velocity had soon decreased to zero, but when a second cc.m. sol was added, the initial velocity was of a similar order of magnitude and occasionally even somewhat greater than if we had immediately started from 2 ccm. sol.

With a view to the ever varying quantity of oxygen we must be very cautious in drawing a conclusion. But it may be indubitably concluded that the paralysis of the first quantity of sol does not happen to the same extent, as otherwise hardly any hydration would have set in. The first quantity of sol will probably fix an impurity of unknown nature; perhaps the second quantity can partially take on the paralyzing substance from the first quantity. A closer investigation is desirable.

§ 4. With the undecylenic aethylester too, a great retardation in the second part of the hydration had been observed, during the first experiments. (N^o. 4—7, without thermostat).

The same took place with the undecylenic acid when using H₂ freed from oxygen, 2.0237 gr. dissolved in 100 ccm. 80 % alcohol + 4 ccm. Pd-sol, employed 252,5 ccm. calculated 253 ccm. (N^o. 30).

The first 130 ccm. were absorbed in 5 minutes, then a very pronounced retardation set in, in the following 5 min. 24 ccm. were absorbed and in the then succeeding 5 min. 16 etc.

Simultaneously a flocking-out had set in, which proved to be complete when the reduction was over.

As a solution of undecylenic acid + 4 ccm. Pd-sol remained unchanged for days, it may consequently be ascribed either to the undecylenic acid formed, to the reduction itself, or to both.

From an experiment with undecanic acid it appeared that this substance indeed, flocked out the sol in 80% alcohol.

Now a flocking-out need not necessarily cause a paralysis; but as the first phenomenon is a visible indication of the diminution of the surface of the catalyser it is most probable that in this instance the decrease of the velocity of reaction is related to the flocking-out. It stands to reason that in determining the velocities of hydration, the possibility of the paralysis must always be reckoned with, and that any cases in which flocking-out sets in are of but little value for the comparison of these velocities.

We consequently give a short summary of the substances, which at a normal temperature immediately or after a short time completely flock-out the Pd-sol:

in aqueous solution: diluted HCl, diluted KOH; in 80% alcohol undecanic acid, cinnamic acid, phenol, acrylic acid methylester, isocrotonic acid, oleic acid, glacial acetic acid, propionic acid, butyric acid, valeric acid, capric acid, caproic acid, lauric acid, palmitic acid.

On the other hand the sol remained unchanged for a considerable time: in aqueous solution on the addition of diluted sulphuric acid, acetic acid to 80%, diluted soda, undecylenic acid, undecylenic acid aethylester, cinnamic acid methyl- and aethylester. Diluted nitric acid dissolved the metal.

On summarising the phenomena described in these pages, we undoubtedly get an idea, that even in this apparently so simple catalytic reduction, viz. an irreversible reaction with an elementary catalyser, the events are far more complicated and far more sensitive to by-circumstances than could be expected.

Not until these events have been sufficiently studied, so that they can be entirely brought under the control of the experiment, can a mathematical treatment produce good results.

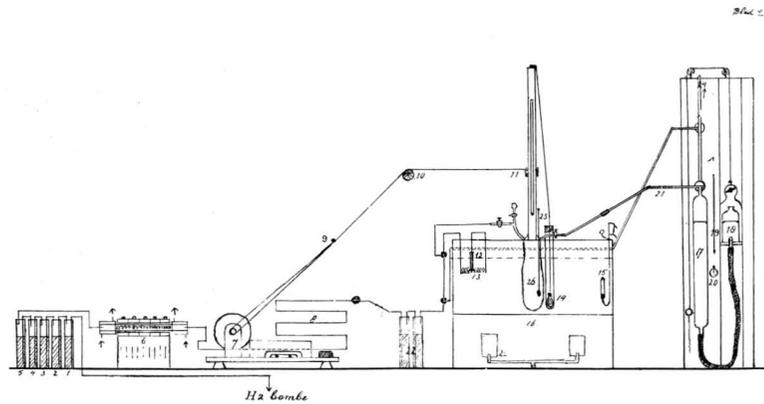
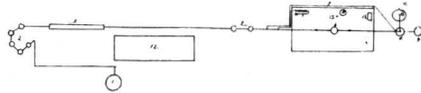
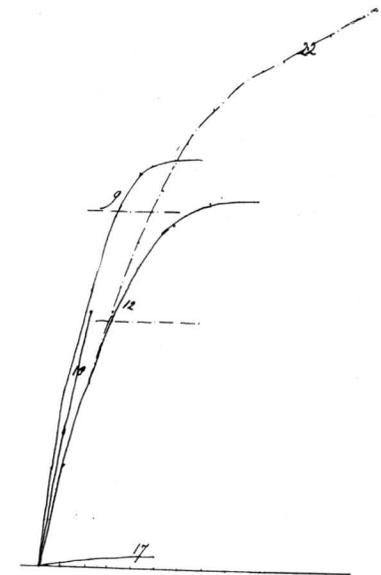
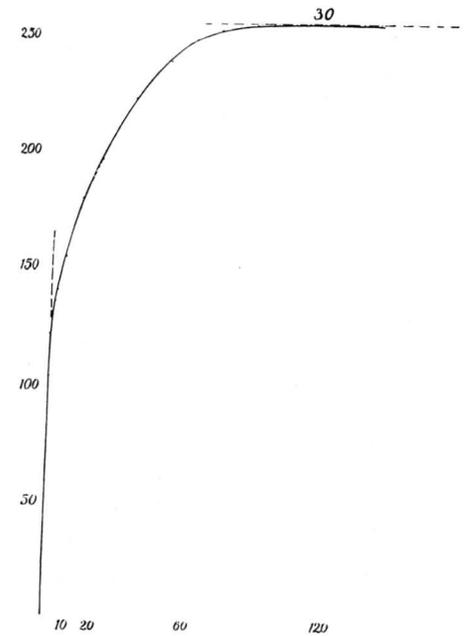
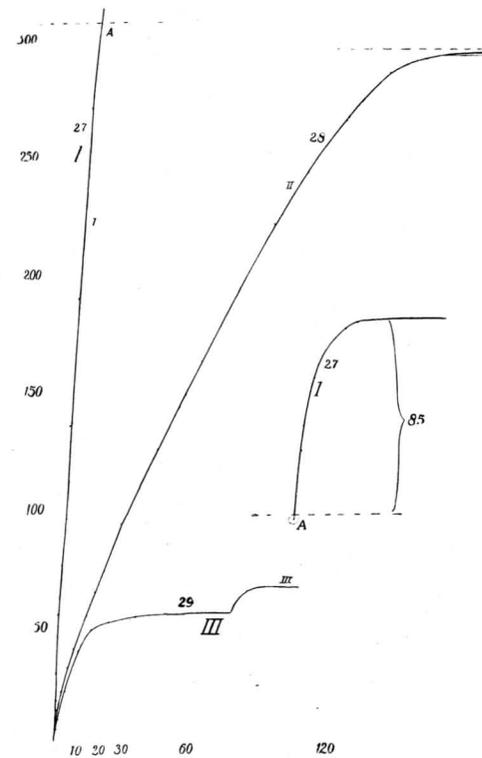
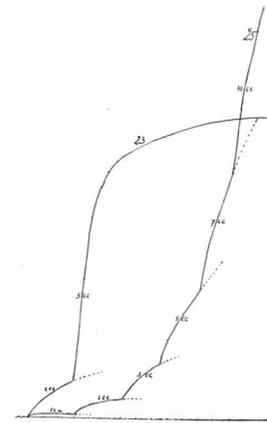
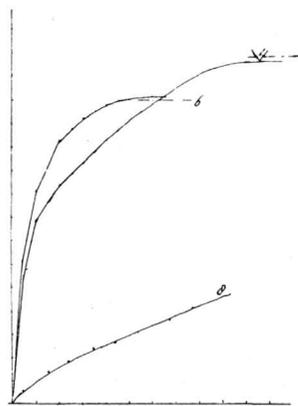


Fig. 1.



- | | |
|---|---|
| 1. H_2 bomb. | 9. Mercury-flask. |
| 2. Rinsing-flasks. | 10. Escape-tube for the H_2 . |
| 3. Cu-tube. | 11. Cup-shaped glass with water in which the escape-tube empties. |
| 4. H_2SO_4 rinsing-flasks. | 12. Motor. |
| 5. Glass spiral to saturate Pd sol with H_2 . | 13. Thermometer in the thermostat. |
| 6. Hydrogenation-apparatus. | 14. Electric lamp " " " |
| 7. Circulation-tube for the H_2 . | 15. Thermo-regulator. |

Fig. 2.



Anatomy. — “*On Mendelian Segregation with the Heredity of Headform in Man*”. By G. P. FRETZ. (Communicated by Prof. C. WINKLER.)

(Communicated in the meeting of June 30, 1917).

The significance of the shape of the head as an anthropological characteristic was brought to light by the investigations of ANDERS RETZIUS (1842—1860)¹⁾. RETZIUS introduced craniometry and based the classification of races on the dimensions of the cranium. He discriminates the brachycephalic or short and round, occasionally square, and the dolichocephalic or long and oval skull type.

With this method of investigation began a new period in anthropology. The task was, to examine with various peoples and races the index of the cranium i. e. the shape of the skull, expressed in the proportion $\frac{100 \times \text{width}}{\text{the length}}$. It was further inquired into — fixed values having been accepted for the dolichocephalic and the brachycephalic skull — how dolichocephaly and brachycephaly are spread over the various countries.

For the experimental doctrine of heredity the significance of the shape of the head is a different one, viz. its behaviour in heredity. This question is not entirely strange in anthropology, but was eliminated there. A. RETZIUS e. g. points out that — in order to be sure of having to do with the pure type, — one has to choose material from the country, and when he disposes of a considerable collection of skulls, e. g. Swedish ones, he selects by a first comparative examination, a few of those that do not show accidental or strange properties.

The experimental doctrine of heredity examines the heredity with regard to its significance in connection with the problem of the origin of species. Besides with regard to its practical significance for man, as to the breeding of animals and the cultivation of plants, and also with regard to diseases of man and the improvement of race. This latter part of the science of heredity is distinguished as eugenics.

Only few investigations into the heredity of race-characteristics

¹⁾ A. RETZIUS. *Ethnologische Schriften*. Stockholm 1864.

have been made as yet. The inheritance of the headform has not yet been investigated methodically. HURST¹⁾ mentions in a list of properties, which segregate according to MENDEL's rules, that round-headedness is dominant over longheadedness and E. FISCHER²⁾ concludes, from his bastard-material, that the headform is most probably hereditary according to the rules of MENDEL. FISCHER gives moreover quotations from the literature of non-mendelistic investigations, which are in favour of the theory that brachycephaly is dominant over dolichocephaly.

The above-mentioned twofold signification of analytic investigations into heredity in man has induced me to investigate the heredity of the headform. The present first communication regards the results of a thousand measurements. My material consists of the visitors calling on the patients of the lunatic asylum Maasoord of Rotterdam. By numerous journeys to Rotterdam and other places, consequently somewhat in the manner of the fieldworkers, I have measured as completely as possible all the members of those families for whom this was of importance. Also a few other families have been inserted into the tables. The extensive tables, on which the communication rests, will be published later. All the measurements and calculations have been executed by myself.

The anthropological knowledge of the headform may likewise serve as a guide for the choice of the shape of the head for a Mendelian investigation. A. RETZIUS has not given any fixed values for the dolichocephalic and the brachycephalic skull. In a letter to DUVERNOY (1852) he says³⁾ that with the dolichocephalic skull the length as a rule surpasses the width by $\frac{1}{4}$, whereas with the brachycephalic skull this difference varies between $\frac{1}{5}$ and $\frac{1}{6}$. These figures mean for the dolichocephalic skull an index value < 75 and for the brachycephalic one an oscillation of the index between 83 and 88. G. RETZIUS adds to this information the interpretation that his father left a space between the typical measures, fixed for the two groups; he fixed centres, round which the various sizes of the skull can be arranged.

If this should be so, one might expect that, in case a population contained besides dolichocephalic also brachycephalic race-elements, the indices calculated from many observations, being united in a

¹⁾ C. C. HURST. Mendelian Characters in Plants, Animals and Man. S. 192. Mendel Festschrift in Verh. d. nat.forsch. Ver. in Brünn. 49. Bd. 1910.

²⁾ E. FISCHER, Die Rehobother Bastarde und das Bastardierungsproblem beim Menschen. Jena 1913.

³⁾ l. c. p. S. 18.

curve, this difference would appear in the shape of the curve, viz. a twotoppedness. One top would be found at about 75 and another at 85. As far as in literature such curves have been communicated, no distinct twotoppedness is to be seen (RETZIUS and FÜRST¹), BOLK²), E. FISCHER³); comp. also WELCKER⁴) S. 42.) Also in the curves of my material they are failing (Fig. 1—5). This is possible, when the dolichocephalic type, whilst crossing with the brachycephalic, originates equally all possible intermediate shapes, but still the more so, if there are not two types, but several. The solution of these problems is being searched for by the experimental science of heredity. Generally biological the question is: are the dolichocephalic and the brachycephalic headforms characteristic marks of distinction between two races, consequently of elementary species, and expressed mendelianly: is the headform determined by units of heredity and by how many? Thus the investigation of the headform is a hereditary-analytical problem, to be studied by family investigations.

The material, of which the composition is represented by the curves (Fig. 1—5), consists of families from one generation (brothers and sisters), from two generations (parents and children), and from three generations (one to four grandparents, parents and children).

At a first glance at the material the impression is made that of a family of brothers and sisters the brothers often have lower indices than the sisters. In the curves 6^a and 6^b 169 brothers and 169 sisters have been brought together, who are chosen in such a way that constantly from each family as many brothers as sisters have been taken. If consequently two brothers and two sisters of one family have been measured, then two brothers and two sisters (i.e. the two elder) have been inserted into the curves. From these curves it appears still more distinctly than from the curves of the total number of men and women (Fig. 2 and 3) that as a rule the men have a somewhat lower index than the women. Of the men (Fig. 2 and 3) one top lies at 77,5, and another at 82, of the women the top lies at 80; of the brothers (Fig. 6^a) the top lies at 79, of the sisters at 81,5. 33 brothers and 12 sisters have indices under 77. The variability of width of the sisters (74—89) is likewise somewhat smaller than that of the brothers (72—90).

¹) RETZIUS und FÜRST. *Anthropologia Suedica*. 1902.

²) L. BOLK *De bevolking van Nederland in haar anthropologische samenstelling*. (Uit Gallee. Het Boerenhuis. Utrecht 1908).

³) E. FISCHER l. c.

⁴) H. WELCKER. *Untersuchungen über Wachstum und Bau des menschlichen Schädels*. 1. Theil. Leipzig. 1862.

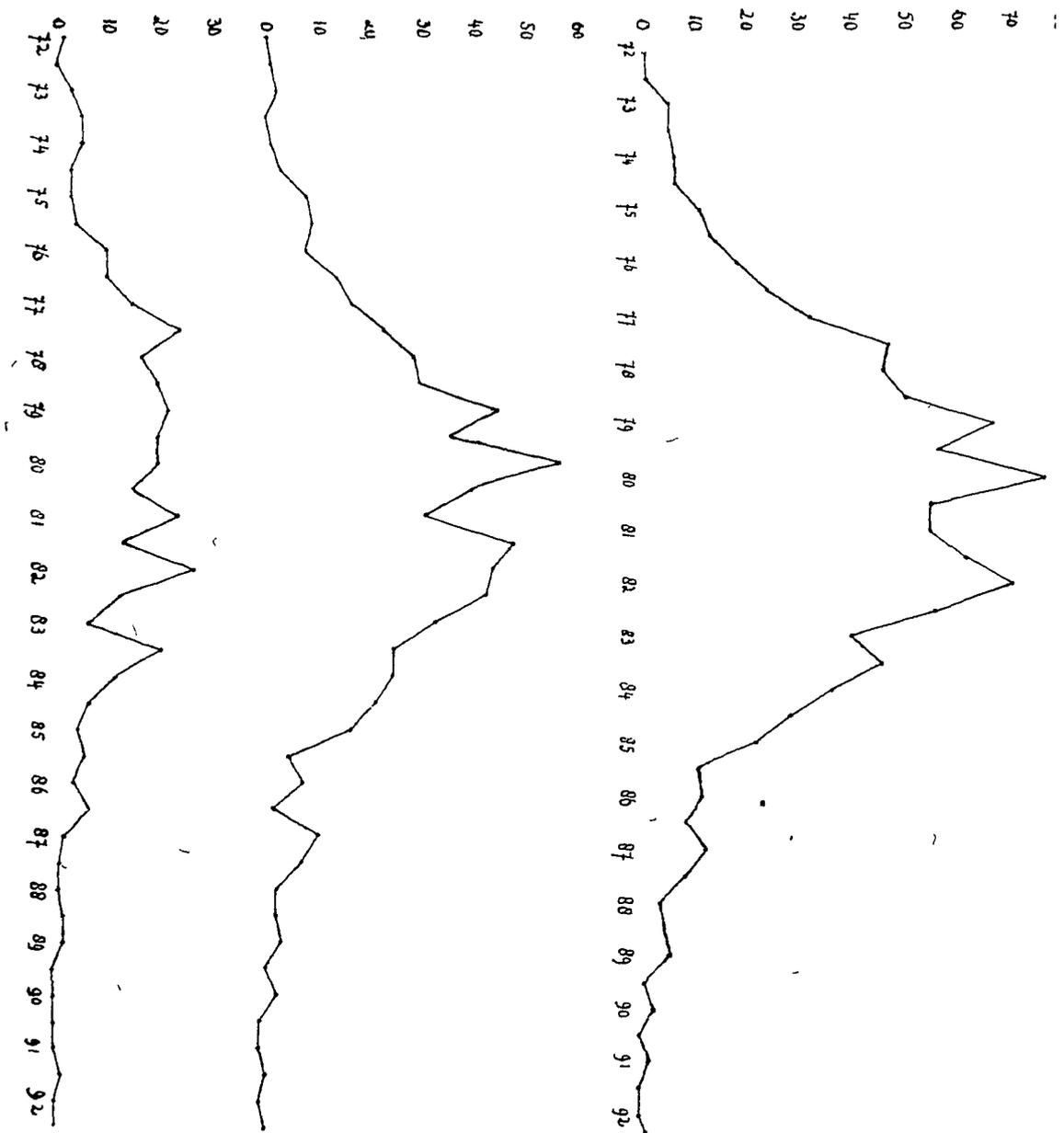


Fig. 3. Fig. 2. Fig. 1.

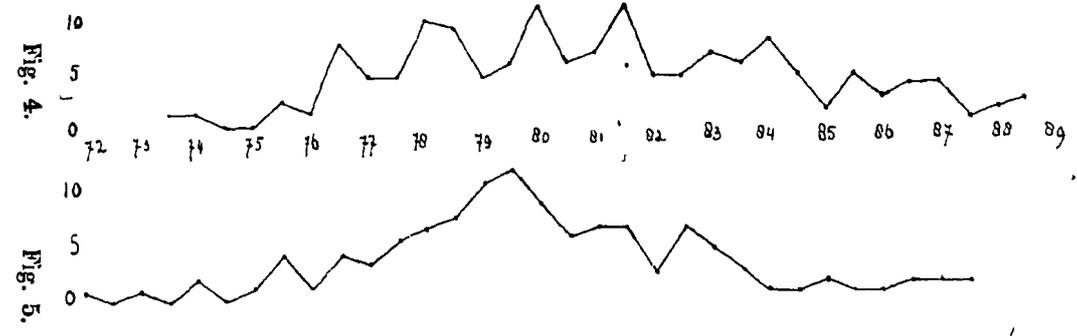


Fig. 1—5. Curves giving a general survey of the material. Fig. 1. The material containing 10 measurements. Fig. 2 The measurements of women 661. Fig 3. The measurements of men 353. Fig 120 natives of the islands of South Holland; of the parents and likewise usually of the grand-pare it is known that they were born there. Fig. 5 100 persons, natives of Rotterdam, as likewise pare and grand-parents.

If now we pass to the examination of the behaviour of heredity of the headform of the material at our disposal, then we follow, when doing so, the way taken by other investigators (RUDIN, DAVENPORT, LUNDBORG): we examine if the data admit of a Mendelian explanation. We assume in this respect that the index of length-

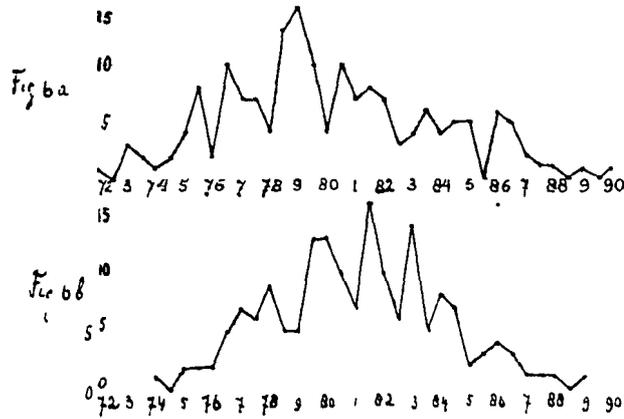


Fig. 6.

169 brothers and 169 sisters. Of each family as many brothers as sisters have been inserted.

width types the headform. A. RETZIUS has answered to the objection ¹⁾ that the index represents only two dimensions, that experience teaches the index may in reality be taken as the expression of the headform. Another question is, whether the Mendelian analysis of the factors of heredity of the shape of the head can restrict itself to trace the heredity of the index. In this case we should have to do here with one pair of units of heredity (for the large and small index, or for several different large indices). If the length and the width mendel separately, we have to do either with two pairs of units of heredity or with two progressions of it (respectively for the large and the small length and idem width or for several different large lengths and different large widths). Both possibilities will be examined. If the length and the width of the head mendel separately phenomena of segregation will come to expression in the index. We begin by tracing these. This gives us the advantage, that the complete material, likewise that of not fullgrown persons, can be considered. In the first place we examine if there is segregation. In favour of segregation plead these cases where, with little differences in the indices of the parents, the children show a great divergence of values, or if a single child has a strongly deviating index. In the tables I and II some of these cases are collected.

¹⁾ A. RETZIUS, l.c. S 57.

T A B L E I.

Little difference of the indices of the parents, great difference of those of the children.

Family-number	Father	Mother	Children										Number of table ¹⁾			
			Sons						Daughters							
			1	2	3	4	5	6	1	2	3	4		5		
XLVIII	79.7	78.7	79.9	83.6							86	83.1	79.1	80.6	82.4	I
LVI	80.1	79.9	76.3								84.8					I
LXIV ^b	77.6	76.2	73.2								80.9					I
CXXIV ^a	80.1	79.8	78.9	82.1	86.5	85.1					85.9	79.8	83.1	79.7		I
CXXXVII	80	82.1	76.9								82.9	81.4	82.5			I
CLXXIII	80.1	81.3	87	81.8							83.8	83.2	82.8			I
CLXXVII	81.4	81.4	81.4	84.5							81.3	79.4	83.6	79.7		I
XL		81.8	83.6	80.5							77.8	83.6	81.7	82.1		II
CXIV			82.5	81.8	76.7						78					II
XXXIV ^a	79.7	79.1	78.7	81.9	83.6	80.3	84.8				80.1	81.7				III
LXXXVII ^c	82.2	81.8	81.8								84.7	79.1	80.3			III
LXXXVII ^d	82.7	82.2	75.9	80.9	84.3						77.8					III
LXL	80	80.4	81.3	79.7	73.7	80.8	81.7	79.2			80.1	88.8				III
XCIII ^a	81.8	82.6	83.7	78.4	81.7	86.1										III
CLXXIX ^a	80.8	80.9	80.9	84.7							88.9	86.7	86.6	82	81.6	III
XXII ^d	81.4	81.7	80.4	82.9							83.5	79.6				III
XXII ^c	80.2	80									83.8	78.6				III
LXXXIV	84.7	85	85.4	80.8												V
CLXXVII ^d	81	81.5	75.2								77.9					V
CLXXXII ^b	83.7	81.3	82.6	81.7	79.4						77.5	84.7	85.3	80.8		V

The examples of table I and II may be regarded as the expression of the formula $DR \times DR = DD + 2 DR + RR$, those of table II of a more complicated segregation (vide page. 441). When perusing the lists made from the material, we are struck both by the great variability and also by the irregularity of the indices. The great variability renders it unlikely that heredity should simply be determined by a pair of units of heredity brachycephaly-dolichocephaly.

¹⁾ Number of the large tables which will be published later.

If this were the case we should more frequently meet with homozygotic pairs of parents, to whom would consequently belong a group of children with very slight differences of the indices. These however do not occur in the lists. The Table which contains the families with four grandparents of which consequently three complete generations are known furnishes moreover the indubitable proof that the headform is not inheritable on account of a single pair of allomorphic factors.

Consequently we reject the indication of the motion of heredity according to the monohybridic scheme.

It is very well possible that inheritance of the headform is determined by a progression of units. Heredity goes then according to a type that NILSSON-EHLE¹⁾ (1909—1911) has systematically worked out for cereals and that according to different investigators (LANG, T. TAMMES a.o.) may be applied to their results. If the head form in the conception of NILSSON-EHLE is determined by a few pairs of units, consequently $A_1 A_2 A_3 \dots$ and $a_1 a_2 a_3 \dots$ then of a pair of parents, the father can possess a factor of heredity that the mother misses, and the reverse, or in heterozygotic form. Among the children may then, by combination of factors, occur headforms with indices larger, resp. smaller, than those of the parents. Generally a great variability is to be observed with mutually slight differences, which in a restricted number of individuals may give the impression of intermediary heredity. By special combinations which, as can easily be calculated, are very rare, greater deviations may occur. By a separate breeding of the third bastard-generation (F_3) it can be proved that a cross-breeding follows this scheme. Then different proportions of number must occur, according to the number of Mendelian factors which has been adopted for the explanation of the second bastard-generation. This took indeed place in NILSSON-EHLE's experiments.

The data of different families plead for the fact, that, if the heredity of the headform follows the rules of segregation of MENDEL, factors working in the same direction in the sense of NILSSON-EHLE must be admitted. So e. g. those, that have been gathered in table VI, where one index deviates considerably from the others. Likewise those of table VII, where the indices of the children surpass those of the parents on both sides or on one side.

We find consequently in the collected material indications for the

¹⁾ H. NILSSON-EHLE. Kreuzungsuntersuchungen an Hafer und Weizen. I und II. 1909 u. 1911. Acta Universitatis Lundensis Lund.

TABLE II.

Series of indices a single one of which strongly deviates

Number of the Family	Father	Mother	Children					Number of the table				
			Sons			Daughters						
			1	2	3	1	2		3	4	5	
I	76.3	80.3	80.3	80.2	81.1	80.6	84.3					I
III	76.5	81.5	77.3	79.2	84.1	82.7	80.9	78.6	81.3			I
XVII	77.8	81.7	78.7	79.2	79.5	77.7	88.4	84.8				I
CLXIV	79.2	77.8	76.3			79.7	76.8	75.8	77.8	83.5		I
CXCVI	74.7	79.5	74.1	82		78.3						I
CLIV						77.8	75.1	79.6	82.5	79.2		II
XXXVII	77.3	76.8	77.9	82.3		79.6						III
CCXV	78.1	81	77.5			85.6						III
XVI		80.5	83.8	73.5		84	85.6	82.3	82			II
CXVb		76.3	76.8	77.7		83	75.4	79.6	79			IV

view, that segregation occurs with the heredity of the shape of the head, and that some pairs of factors of heredity are concerned in it.

A second question is, if, with this alternative heredity, the first bastard-generation (F_1) is intermediary or that there exists dominance. If, as HURST indicates from literature, brachycephaly is dominant over dolichocephaly, only dolichocephalic children will be born from the marriage of two dolichocephalic persons. For the brachycephalic headform is then defined by the factor D (dominant) the dolichocephalic one by the factor R (recessive), the former can be represented by the formula DD or DR , the latter only by RR and the pairing of two RR 's gives only RR descendants. The great variability, the non-occurrence of families in whom a definite headform is nearly constantly inherited, the complication in the cases, in which three generations are completely known brought us to the conclusion, that not one single pair of factors determines the inheritance of the headform, but we think it possible that some more factors working in the same direction are active in this respect. Moreover dominance may occur, and the occurrence of families (table III) among whom only comparatively low head-numbers are found, seems to speak in favour of it. Families (table IV) of whom one of the parents is brachycephalic, and all or most of the children are brachycephalic,

occur likewise. There are however also families (table V) for whom this is not the case, likewise families are met with (table VI), for whom the indices differ very little, but are somewhat higher than those that hold for dolichocephaly. Consequently we cannot admit beside segregation simple dominance of brachycephaly.

The cases mentioned already (table VII), where the indices of children surpass those of the parents, either on one or on both sides are especially in favour of the possibility, that the inheritancy is determined by a series of factors working in the same sense, which each individually give an intermediary first bastard-generation (F_1). This method of explanation can moreover very well be applied to other phenomena of our material. The great variability of the indices of the children and the slight differences of those of the parents (table I) can e.g. be occasioned by the fact that the parents contain the factors in a heterozygotic form, so that exteriorly they are intermediary. Consequently different homozygotic, thus greatly divergent values of indices, will occur among the children. The separate occurrence of a strongly deviating index-value is caused, according to this view, by the rare combination of two or more factors working in the same direction in a homozygotic form (one of the 16 cases in the dihybridic scheme, one of the 64 cases in the trihybridic one). The slight mutual differences of the tables III and VI can be explained by admitting, that the forms of issue contain nearly the same factors, so that consequently no new divergent combinations occur in the children. The cases of table VIII containing examples of extreme values of indices of one of the parents may be explained in the same way. A very low index-value is caused by the deficiency of, a very high one by the existence in homozygotic form of some factors working in the same direction. It is consequently clear that among the children, as a rule, the extreme value will not occur.

What gives likewise significance to this manner of explanation, is the possibility of explaining the limitedness of the selection: by selection no more can be reached than the form that contains all the factors of heredity working in the same direction in a homozygotic form. Examples in our material of "selection-working" (according to NISSON-EHLE's explanation, consequently of combination of factors) are the fam. III and XXXIV (vide the genealogical trees, p. 448). The parents and eleven children of fam. XXXIV have rather low indices viz. the parents 79 and the children 72—79. If now we admit that the parents possess each a different factor for brachycephaly, with which consequently absence of a similar

T A B L E III.
Low indices of the parents and the children.

Number of the family	Father	Mother	Children										Number of the table				
			Sons				Daughters										
			1	2	3	4	1	2	3	4	5	6		7			
XXI	75.8	77.9	79.7	77.1					76.9	74.2	81.2						I
XXXVII	76.8	78.9	76.3						79.8	79.4	78.8						I
XXXIV	79.1	79.7	73.6	75.3	73.1	72			79.1	75.6	75.8	77.9	77.8	77.4	78.6		I
LXXXVI	79.2	78.7	78.7	79.5	75.5				75	77.8	78.5						I
CXXXVI	78.5	80	78.3						77.6								I
CCV	78.1	78.9	78.2						77.5								I
IX									77.4	78.2	78.2						II
XXXIIa			76.5	74.6	73.7				75.9								II
XXXVIIa	76.7		79.2	76.5	75.7				77.2	78.2	76.8	77.1	76.8	79.8			II
LXI		79.5							74.2	76.9	77.6						II
LXXXIII		79.2							76.5	74.9	76.6						II
CLI			78.3						78.8	78.5							II
CXV		73	77.8	74.3					74.9	76.3							II
CLII	78.8								79.9	77.1							III
CLXL		79.3	77.3	78.8					77.2	78.1	78.1	79.2					II
CLXXXII	77.6	79.8	78.3	78.3	78	74.5			80.7	77.4	79.5						V

T A B L E IV.
Families of which one of the parents and most of the children have a high index.

Number of the family	Father	Mother	Children								Number of the table			
			Sons			Daughters								
			1	2	3	1	2	3	4	5		6		
IIIb	82.4	78.3					83	87.2	83.9	84.7	83	86.1		I
LXXXIII	77.3	85.3					84.7	84.1	87.3					I
LXXXV	75	84.7	83.6	78.9	79.4		81.3	79.2	79	80				I
LXXXVIII	78.3	83.2	83.3				76.4	84						III
CLXVII	76.4	89.2	85.8	86.1			83	79.3						I
CCXXXIV	82.2	87.3	86.3				84.5	86.7	87.9					I
CLXXVIII		75.5					80.4	81.6	83.5					II
CLXXIX		74.3	84.2				82.5	80.7						II
XVIc	77.8	85.6	85.9	84.3			81.6	84.2	82.2	80.2	87			III
LXXXVIIe	75.4	87.8	78.7	86.2	81.9		84.6	83.1						III
CLXXIXb	77.2	85.2	80.6				85.8	83.2	80.8	83				III
CCXII							82.5	83.7	83.4	84.9				II
IIIa			84.5	82.4			83.6	82.9	81.5					II
CXCVII			86.5	85.3			85.7							II

TABLE V.
Family of which one of the parents has a higher index, whilst only *one* of the children has a high index.

Number of the Family	Father	Mother	Children														Nr. of the table
			Sons						Daughters								
			1	2	3	4	5	6	1	2	3	4	5	6	7		
IIIe	83	86	79.1	81	86.1	78.5	85.2	78.2	80*)	81.8	80.8	84.5	86.5	84.2		III	
CXLVII	85	79	79.3	80.2	84.4	80.8	85.2	78.5	78*)	86.8*)	81.2*)	80.2	81.8			I	
CLXXIXc	79.7	82.2	80.8	80.7					80.7	81.8	77.5					I	
CXCV	79.2	83.3	78.8						81.5	82.6	81.8					I	
VII		84.2	74.5	79.7					76.7							II	
XCVI		84.6	79						77.7							II	
XVIb	78.7	84	77.9	80.7	79.7	83.4	80.7		80	79.7	79.5	79.7	81.8	81.6	83.2	III	
XI	83.4	75	76						81.8	80	80.6	79.4				I	
XIX	78.5	84.2	77.6	79.4					79.8	80.5	77.5	78.5				I	
XVIIa	76.7	84.7	76.6	76	76.2				75.5	78.8						I	
XXXII f	79.2	84.1	78.7						81.7	80.8	85					I	
LXVIII	79.8	83.6	78.7	77.8	79.8				77							I	
LXXVI	78.7	85.9	77.4						81.3**)	77.1**)						I	
CXXX	84.9	78.4	75.5													I	
XXXIVc	75.3	83	75.5	85.2					76.8	76.3						III	
XXIIe	75.6	83.8	81.1	81.1					79.7	80.2						V	
XII	79.6	82.1	80.8						81.4	79.2	78.1	78.4				I	

*) Sons, consequently 7 sons and 5 daughters and 9 sons and 2 daughters.

**) 2 daughters of the first marriage of the mother.

TABLE VI.
Somewhat higher values of the indices of the parents and of the children.

Number of the Family	Father	Mother	Children									Nr. of the table				
			Sons			Daughters										
			1	2	3	1	2	3	4	5	6					
XII	79.6	82.1	80.8				81.4	79.2	78.1	78.4						I
XV	81.2	84.4	83	82.2			81.3	78	78.5	83.5	82.2	82.4				I
CXXXIa	81.8	80.4	78.7	78.8	81		79.7									I
CLX	81.8	77.8					77	77.5	77.6	79	78.1	78.7				I
LI		80.2	80	80.4			81.5									II
LX		81.6					81.6	81.1								II
LXXXVIIb		80.3	80.7	81.3			79.9	80	79.8	82.1						IV
CLXXIa			79				80.5	79.8	81.6							II
CLXXVIIb	82.1	82.3	78.8				82.6	81.3	82							III

TABLE VII.

Transgression of the variation-width to both sides towards the dolichocephalic and the brachycephalic side.

Number of the Family	Father	Mother	Children												Nr. of the table		
			Sons						Daughters								
			1	2	3	4	5	6	1	2	3	4	5	6			
XXII	77.9	81	76.3	75.6	79.7	76.5					81.7	79.4	82	82.2			I
XXXVIa	79.8	81.5	85.8								84.1	76.4	78.1				I
CLXXI	78.3	79.8	77.4	81.7	82.7	81.5	81.2	81.8			77.3	82.8	82.6	79.8	80.3		I
CXCIII	81.8		76.7								85.9	85.2					II
XVa	83	80.2	77.7	87.7	88												III
XXXIVa	73.1	76	74.1	70													V
XXXIVe	81.3	78.3	73.2								76.7	76	80.3				I
XXXIV	79.1	79.7	73.6	75.3	73.1	72			78.6*)		79.1	75.6	75.8	77.9	77.8	77.4	I
IIIc	84.5	80.2	83.3	80	83.7						86	83.5	86.7				I
IIIf	82.2	83.5									87.5	91					I
XXIIb	82.4	78	81.5	84	84.6						79.7						I
XXXVIb	78.8	84	86.7	88.2	79.7						83.1	83.5	81.2	87.4	80.2	86.7	I
LXXXIVa	80.4	75.5	84.7	79	81.3	81.5	83.3	82.2			81.1						I
LXXXIX	81.3	78.9	83.7	85.1							81.4						I
CIX	75.8	80	83.2								83.8	80.3					I
CXIII	83.1	83.7									89.5	84.1					I
CXXIV	82.2	86.9	80.8	84.9	86.3						87.4	88.1	86.6				I
CXLVIII	73.8	77.4	81.5								83						I
CXVe	77.8	76.3	80.7	81	83.7	80.5					80						III
XXII	76.3	76.2	78.2	76.7							82.2						III
CXVa	74.3	78.2	79.8	76.8							79.6	81.5	80				III
CLXV	85.1	83.8	88.2	89													I
CXVIII		81.1	87.1								83.7	85.7					II
LXXXVII		81.2	85.6	82.2							82.2	87.8					II
CXXII		80.9	89	83.2							86.8	84.1	80.5	82.6			II
XXXIIe	76.7	81.7	85								84.7	87.5					V

*) Seventh daughter.

factor (by which dolichocephaly comes into existence) corresponds, and that they possess e. g. still a third factor in heterozygotic form, so that the formulas of the parents are $A_1A_1a_2a_2A_3a_3$ and $a_1a_1A_2A_2A_3a_3$, then the low values 72 and 73 of the children are explained e. g. by the absence of the two factors for brachycephaly ($a_1a_1a_2a_2A_3a_3$). The daughter and the two sons who marry into families where several higher indices occur, will consequently among their seven, five and four children see higher values show themselves, the son 73.1 however who marries a daughter 76 of a family whose members have also rather low indices, has a great chance, that there are among his children some who represent a combination of factors, that answers to the absence of e. g. three factors of heredity ($a_1a_1b_1b_1c_1c_1$); suchlike children surpass then the low indices of the parents towards the dolichocephalic side. This is indeed the case in this family: The two sons have an index of 74 and of 70. The same reasoning, but now for the combination of the factors whose

TABLE VIII.
Extreme value of one of the parents.

Number of the Family	Father	Mother	Children					Nr. of the table				
			Sons			Daughters						
			1	2	3	1	2		3	4	5	
LVII	72.6*)	78.9	81.6			81.3						I
LVIIa	72.6*)		75.3	80.5		79.8						II
XLIII		72	79	75		81	79	78	81.3			II
LXXXVIIe	75.4	87.8	78.7	86.2	81.9	84.6	83.1					III
CVIII		87.6				82.2	83.1					II
CXII		85.9	81.8	82								II
CXV		73	77.8	74.3		74.9	76.3					II
XVIa	73.5	82.3	80.4	82.2	75.5	82.5	79.7	80	80.5			III
XXXIVb	73.6	80.2	75.5	79.2	79.7	82	80.6					III
LXVI	88.5	81.1	91.4	89.5		90	86.9	86	92	85.8		III
CLXXIIIa	87	78.5	75.6									III
LVIIa	72.6		75.3	80.5		79.8						IV
CLXXVIIa		85.7	80	79.8	81.3							IV

*) The same person; first and second marriage.

existence cause brachycephaly, gives for Fam. III the explanation of the occurrence of very high indices 90—95 in the third generation. Difficulties, which our results still contain for the mendelian explanation, will be dealt with in a following communication.

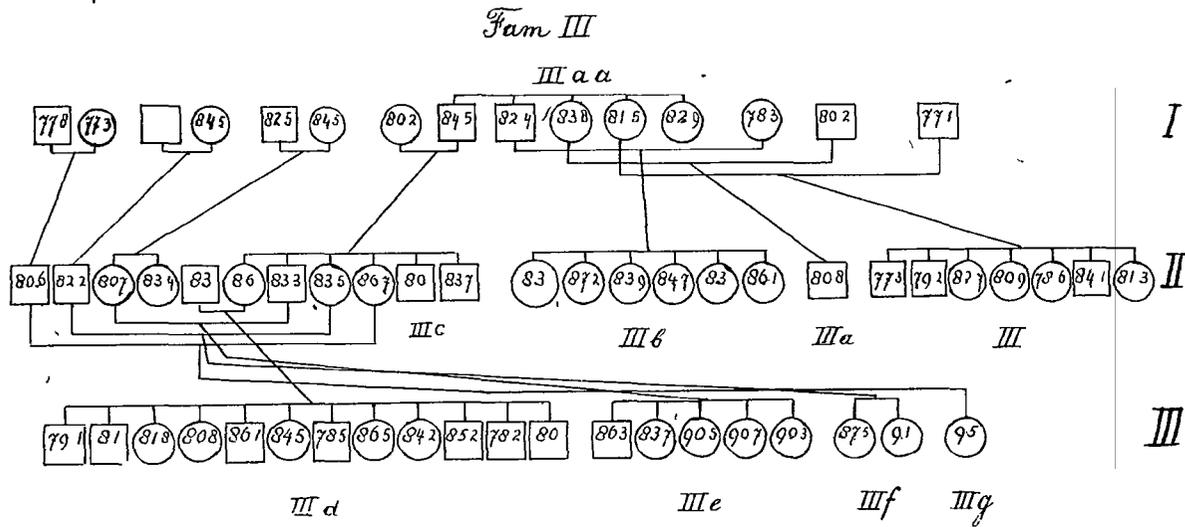


Fig. 7a.

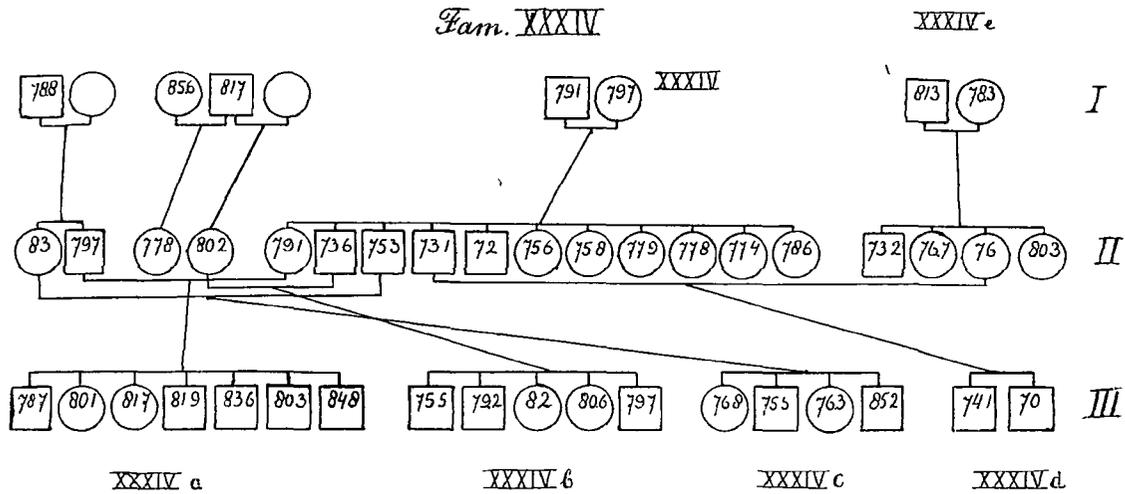


Fig. 7b.

Mathematics. — “*Some Considerations on Complete Transmutation.*”
 (Third Communication). By Dr. H. B. A. BOCKWINKEL. (Com-
 municated by Prof. L. E. J. BROUWÉR.)

(Communicated in the meeting of November 25, 1916.)

14. In connection with the preceding considerations the continuity of a transmutation we shall refer to an inaccuracy that occurs in the proof of theorem X of BOURLET, which will give us an opportunity to observe that the theorem itself stands in need of a clearer statement.

Theorem X is as follows *Toute transmutation additive, uniforme, continue et régulière est donnée par la formule*

$$Tu = a_0 u + \frac{a_1}{1!} u' + \frac{a_2}{2!} u'' + \dots, \dots \dots \dots (1)$$

où a_0, a_1, \dots désignent des fonctions régulières et u', u'', \dots les dérivées successives de la fonction régulière u .

If this theorem, and the proof BOURLET gives of it, is considered more accurately, its meaning appears to be not over-clear, and this is to be attributed to the fact that BOURLET has omitted to fix a functional and a numerical field in which the transmutation is to be thought as defined. Are we to suppose that the transmutation, for *any* function that is *regular* in the neighbourhood of a certain point, produces a transmuted that is regular in the neighbourhood of the same point? Are there *points* that form an exception to this? Or *functions* for which this is the case? Are only *analytical* functions to be thought of as objects of the transmutation? Or also such as coincide in a certain N.F. with the analytical function $f_1(x)$, and in another N.F., lying outside it, with the analytical function $f_2(x)$? Is the *transmuted* an analytical function?

The matter does not become quite clear, for the definitions given by BOURLET, are all highly incomplete. By a *regular* transmutation he understands, according to his own words, a transmutation that makes a *regular* function pass into an equally *regular* function. But what is a regular function? BOURLET answers this in a footnote: “Je prends pour définition de la fonction *régulière* celle de M. M. MÉRAY, WEIERSTRASS, FUCHS, etc.: “Une fonction de la variable x est dite *régulière*, dans le domaine de rayon ρ , autour du point

$x = x_0$, si elle est développable en une série ordonnée suivant les puissances croissantes de $x - x_0$, pour toute valeur de x telle que l'on ait $|x - x_0| < \rho$." All right, it is clear now, what has to be understood, when is said: a function is regular *in a domain with radius ρ* . But we do not know yet when a function is to be called regular, if the emphasized words are omitted. It is not to be supposed that by this should be meant a function that is regular in the neighbourhood of *any* point, for in that case, a simple function as $u = \frac{1}{1-x}$ could never be object of the transmutation. *Exceptional points* must therefore be admitted. But how many, and how situated? A function which within a certain circle is equal to 1, outside it equal to 2, and on its circumference indefinite, is that a regular function? Etc.

All these and similar questions BOURLET has avoided by adding at once, in the definition he is going to give of *a regular function*, the words *dans un domaine de rayon ρ* . It may be assumed however, that BOURLET, when he spoke of a regular function, always had in view, consciously or unconsciously, a *definite domain*, in which the function in question is to be regular, no matter how it behaves in a domain outside it. Indeed, if matters are put in that way, everything tallies. Moreover, the short parenthetic clause, thrown in at random, as it were, speaks for the correctness of this view.

We consequently assume as BOURLET's intention that the functions to which the transmutation is to be applied, are *regular* in a certain circular domain round a point x_0 , no matter how such a function has been defined elsewhere; further that the same holds for the transmuted of these functions, and that this marks the transmutation to a *regular* one, independent of the question whether or not it produces functions with the same property for *all* functions that are regular in a neighbourhood of x_0 . When, therefore, BOURLET speaks of a regular transmutation, we shall assume that is meant: *regular with respect to a certain functional field*.

With regard to this F. F., BOURLET tacitly makes two important hypotheses. He begins his proof with the construction of the series of functions

$$a_0, a_1, \dots, a_m, \dots \quad (20)$$

with which the series (1) is going to be built up, and he deduces it from the functions into which the series of integral powers of x

$$x^0, x^1, \dots, x^m, \dots \quad (21)$$

is transformed by T. Consequently it has been *tacitly* supposed that

the functions (21) form part of the F. F., of T , in other words, that any function of the series

$$\xi_0, \xi_1, \dots, \xi_m, \dots \quad (22)$$

into which (21) is transformed by T , is regular in a neighbourhood of x_0 .

This tacit supposition, however, is essential. To see this we observe that, if we start from the supposition that a series of the form (1) represents the given transmutation, the existence of the ξ 's follows from this. For, that series is finite for any function of the series (21), consequently its convergence is beyond doubt; we find, if m_1, m_2, \dots are the binomial coefficients of m ,

$$\xi_m = x^m a_0 + m_1 x^{m-1} a_1 + \dots + a_m = (x+a)^m \quad (23)$$

in which the last member is a symbolic form, indicating that in the expansion of the binomium a^k must be replaced by a_k , and in the term without a , that is the one with x^m , the factor a^0 must be added.

Thus, if we should suppose that x^m has not a transmuted for every integer m , the existence of the series (1) would at once be excluded.

On the other hand, however, the a 's are completely determined by the ξ 's; for from (23), by respectively writing $m = 0, 1, 2 \dots$, we can solve the functions a_0, a_1, a_2, \dots , giving

$$a_m = (\xi - x)^m \quad (24)$$

where the second member is again a symbolic binomium, in the expansion of which ξ^k must be replaced by ξ_k , whereas in the term without ξ , that is in $(-x)^m$, the factor ξ must be added.

The second supposition we have in view, not less essential for the theorem, is since follows: *There is a circle (σ) to which all ξ 's belong.* If this were not the case, the lower limit of the radii of convergence of the functions (22) would be equal to zero (without the limit being reached, since this would not agree with the supposition already made, that all ξ 's are regular in x_0). The existence of the series (1), in a neighbourhood of x_0 , for other than rational integral functions, is then apparently excluded as well, however small this neighbourhood may be taken. Only in the point x_0 itself a result would not necessarily be impossible, but in every case x_0 could not be considered as a *centre* of a domain.

We may therefore assume that it must have been BOURLET'S intention to make this second supposition as well.

That there is a circle (σ) to which all ξ 's belong, also agrees

with our conception of the nature of a functional field, as we set forth in N^o. 9: we stated there that the F. F. will of course be of such a nature that all its functions are regular in a *common* domain, which we have called the numerical field of the functions (N. F. F.); this is here the circle (σ). It further follows from (24) that all α 's belong to that same circle. On the other hand, it can be inferred from (23) that, if all α 's belong to a circle (σ), this is also the case with the ξ 's, but PINCHERLE proves that the domain of validity of the series (1) extends moreover over an infinite aggregate of other, transcendent functions, of which all transmuted belong to the circle in question.

The functions α_m having thus been constructed, BURLLET says: "Considérons alors la série (1)

$$P(u) \equiv a_0 u + \frac{a_1}{1!} u' + \frac{a_2}{2!} u'' + \dots;$$

pour toute fonction régulière u qui rend cette série convergente, cette égalité définit une transmutation additive, uniforme, *continue*¹⁾ et régulière". These statements are not further explained by him.

Here, in the first place, the *mode of expression* does not seem exact to me; we can say: "pour toute fonction régulière cette égalité définit une transmutation *uniforme et régulière*, but not: "pour toute fonction régulière cette égalité définit une transmutation additive" or "continue"; for an operation cannot be *additive* for one function, nor can it be *continuous* since for the idea "additive" at least *two*, for the idea continuous, in any case an *infinite number* of functions are wanted. The meaning, however, cannot be other than the one which would be expressed if the words "pour toute fonction régulière" were replaced by "pour l'ensemble des fonctions régulières considéré." But in that case it follows at once from the investigation in N^o. 13 (2nd communication) that the statement, at least so far as regards *continuity*, cannot be true in its generality; for, we found there that the series Pu is *convergent* for all functions belonging to a circle (β) in all the points of the corresponding domain (α), but that it does not represent an operation that is *continuous* in the functional field of these functions with regard to the N.F.O., the continuity being disturbed in the point $x = \alpha$.

Since, however, the further reasoning, from which it must appear that Pu is identical with Tu , is based on the pretended continuity of Pu , the proof must be considered as incorrect. It might be still

¹⁾ The italics are my own. The statement that the transmutation is *regular* cannot be objected to if the convergence of the series is *uniform* in the N.F.

meant that the continuity of Pu could be deduced from the *supposed* continuity of Tu , and that after this the identity of Pu and Tu might be proved. But this idea would not do either, and it may be convenient to set forth this somewhat more clearly, as it may contribute to enable us to understand the rather restricted tendency of the theorem X of BOURLET. This theorem is of great importance as it states, broadly speaking, that an arbitrary transmutation may be developed into a series of integral *positive powers* of the *special* transmutation D ; in this respect it is to be compared with the theorems of TAYLOR or MAC-LAURIN in the theory of functions.

15. Before starting with the statement in question we shall for the sake of brevity introduce a name for the transmutation we have gradually begun to realize; we shall call such a transmutation *normal*.

A *normal*, additive transmutation is therefore a transmutation for which the following holds:

1. There is a functional field $F(T)$, all the functions of which belong to a circle (σ) , for which functions the transmutation produces as result functions belonging all to a circle (α) .

2. All *rational integral* functions belong to the field.

3. The transmutation is *continuous* in the pair of associated fields $F(T)$ and (α) .

A *normal* transmutation therefore is always *regular*, without the reverse being necessary. It further follows from the definition in connection with the property of *continuity* of a *complete* transmutation that any such transmutation is also *normal*. On the other hand, however, so far I can see, it cannot be proved that the series, which answers to a *normal* transmutation, has also necessarily the property of *completeness*.

The circle (σ) may be equal to and smaller or greater than (α) ; the first is for example the case with the transmutation D^{-1} , the second and third with the operation of substitution S_ω , if ω is respectively equal to $\frac{1}{2}x$ and $2x$ ($x_0 = 0$).

We now develop an arbitrary function u of $F(T)$ into a series of powers

$$u = c_0 + c_1(x-x_0) + c_2(x-x_0)^2 + \dots$$

If we write

$$\varphi_m(x) = c_0 + c_1(x-x_0) + \dots + c_m(x-x_0)^m \dots \dots (25)$$

the fundamental series

$$\varphi_0(x), \varphi_1(x), \dots, \varphi_m(x), \dots \dots \dots (26)$$

converges in the domain (σ) *uniformly* towards the function u , because u *belongs* to (σ) .

The functions α_k have now been constructed in such a way that for all integral values of k

$$T(x^k) = P(x^k)$$

On account of the additive property of T and P , in connection with the fact that the quantities $\varphi_m(x)$ are rational integral functions of x , it follows from this that

$$T(\varphi_m(x)) = P(\varphi_m(x)) \dots \dots \dots (27)$$

Since, now, the series of functions (26) in the domain (σ) converges uniformly to u , it follows from the supposed *continuity* of T (cf. the second form of the definition of series continuity in N^o. 9, 2nd communication) that the series of functions

$$T(\varphi_0(x)), T(\varphi_1(x)), \dots, T(\varphi_m(x)), \dots$$

in the domain (α) converges *uniformly* towards Tu . The same therefore takes place according to (27) with the series

$$P(\varphi_0(x)), P(\varphi_1(x)), \dots, P(\varphi_m(x)), \dots,$$

which we express in the usual notation

$$T(u) = \lim_{m=\infty} P(\varphi_m(x)), \dots \dots \dots (28)$$

with the restriction that this equation is valid in the circle (α) .

It appears therefore that from the premises follows that $\lim (P\varphi_m(x))$ exists in the whole N. F. But the existence of $P \lim (\varphi_m(x)) = P(u)$ ¹⁾ does not follow from this. Neither had this been asserted by BOURLET, who had *expressly assumed* that Pu exists. But even if this is done it has not yet been proved that $Tu = Pu$, since we are not allowed to conclude without more that

$$\lim_{m=\infty} P(\varphi_m(x)) = P(\lim_{m=\infty} \varphi_m(x)) \dots \dots \dots (29)$$

This conclusion might be drawn if it were already known that the transmutation P is continuous in the F. F. and the N. F. considered, but from the example quoted already in N^o. 13, we may infer that the *existence* of P in a pair of associated fields does not imply its *continuity* in the same fields. Yet, some one might ask: Is it perhaps possible to prove that P is continuous for the *special* fundamental series (26), of which u is the limit, and which merely consists of *rational integral* functions? In that case too (29) would have been proved.

Let us suppose therefore that the series Pu exists in the domain (α) for a certain function u of $F(T)$, of which the circle of convergence (r) , on account of the form of the series P , is of course greater than (α) . We substitute, in the terms of P , for the function u and its derivatives their developments in series, which

¹⁾ Cf. the examples in Nos. 16 and 17.

now also hold in the domain (α) . For shortness we write $x - x_0 = y$, and indicate the coefficients in the various derivatives by means of accents. We then obtain the following schemes

$$\begin{aligned}
 P(\varphi_m(x)) &= a_0(c_0 + \dots + c_m y^m) + \\
 &\quad + a_1(c'_0 + \dots + c'_{m-1} y^{m-1}) + \\
 &\quad + \dots \\
 &\quad + a_n(c_0^{(n)} + \dots + c_{m-n}^{(n)} y^{m-n}) + \\
 &\quad + \dots \\
 &\quad + a_m c_0^{(m)}. \\
 P(u) &= a_0(c_0 + \dots + c_m y^m) + a_0(c_{m+1} y^{m+1} + \dots) + \\
 &\quad + a_1(c'_0 + \dots + c'_{m-1} y^{m-1}) + a_1(c'_m y^m + \dots) + \\
 &\quad + \dots \\
 &\quad + a_n(c_0^{(n)} + \dots + c_{m-n}^{(n)} y^{m-n}) + a_n(c_{m-n+1}^{(n)} y^{m-n+1} + \dots) + \\
 &\quad + \dots \\
 &\quad + a_m c_0^{(m)} + a_m c_1^{(m)} y + \dots \\
 &\quad + \dots
 \end{aligned}$$

Now, it is first possible to find, corresponding to a given arbitrary small number ε , an integer Q , such that we have in a point x of the domain (α) at the same time

$$\begin{cases} |P(u) - P_n(u)| < \varepsilon \\ |P(\varphi_m(x)) - \lim_{m \rightarrow \infty} P(\varphi_m(x))| < \varepsilon \end{cases} \text{ for } \frac{m}{n} \geq Q; \dots \quad (30)$$

in this $P_n(u)$ represents the sum of the first $n + 1$ terms of the series Pu . If this has been done the only thing left is to compare $P_n u$ and $P\varphi_m(x)$ for values of n and $m \geq Q$. It is sufficient to think $m \geq n$, for if we choose $n > m$, the contribution which the terms in $P_n u$, for which $n > m$, produce for the difference between P, u and $P\varphi_m(x)$ would be smaller than 2ε , because we have already $m \geq Q$.

If we therefore choose $m \geq n$, we have for the difference between $P_n(u)$ and $P\varphi_m(x)$ the following scheme

$$\begin{aligned}
 P_n(u) - P(\varphi_m(x)) &= a_0(c_{m+1} y^{m+1} + \dots) + \\
 &\quad + a_1(c'_m y^m + \dots) + \\
 &\quad + \dots \\
 &\quad + a_n(c_{m-n+1}^{(n)} y^{m-n+1} + \dots) + \dots
 \end{aligned} \quad (31)$$

We therefore suppose, more exactly, that the transmutation P is complete in the circular domain (α) , with centre x_0 , which forms the numerical field of operation of T ; further that there are among the functions belonging to the domain (β) corresponding to (α) , such as are contained in the F.F. $F(T)$ of T ; the aggregate of these functions we represent by $F_1(T)$. The equation (28) now holds in the N. F. O. (α) of T for *all* functions contained in the F. F. of T . A fortiori the equation holds in the domain (α) for a function u of $F_1(T)$. But we further have

$$\lim_{m=\infty} P(p_m(x)) = Pu \dots \dots \dots (29a)$$

For 1° there is, because u belongs to (β) , a circle $(\rho) > (\beta)$, in which the fundamental series (26) converges *uniformly* towards u , and 2° the series P , on account of its completeness in (α) with regard to (β) , is *continuous* in any associated pair of fields, of which (α) is the N.F. and the F.F. consists of the functions belonging to (ρ) , (cf. N° 12, 2nd communication).

From (28) and (29) it now follows that

$$T(u) = P(u)$$

this equation being valid in the domain (α) and for the functions of $F_1(T)$.

We now have proved a limited validity of MAC-LAURIN'S¹⁾ theorem for the functional calculus, which is expressed in the following proposition:

If the series P , answering to a normal additive transmutation T , is complete in the circular domain (α) , which forms the N.F.O. of T , we have in this domain

$$T(u) = P(u)$$

for such functions of the functional field $F(T)$ of T as belong to the circle (β) corresponding to (α) .

With this for the first time, in so far as I know, an exactly defined category of cases has been given, in which TAYLOR'S theorem for the functional calculus may be stated.

It follows from it that, before we can proceed to the treatment of this theorem, we have first to consider *those* series of the form (1), which represent a *complete* transmutation. The treatment of theorem XI of BOURLET must therefore precede the one of theorem X.

Observations 1st. We have not violated the generality by suppos-

¹⁾ We call the proposition especially *theorem of MAC-LAURIN* when we oppose it as a special case to the general *theorem of TAYLOR* which we are going to treat in N° 19.

ing that P is complete in the whole N.F. $O.(\alpha)$ of T . For if P were only complete in a certain part (α_1) of this N.F., we would simply, in order to be able to apply the theorem, have to replace the first pair of fields by another, of which the numerical field is the part (α_1) mentioned.

2nd. We have spoken of the part $F_1(T)$ that the functional field $F(T)$ of T has in common with that of P , formed by the functions belonging to (β) . In this room has been left for the possibility that *not all* functions belonging to (β) form part of $F(T)$. Should this case, however, be realised, then the series P produces of course at once the "analytic continuation" of T over the functional field formed by the functions in question. Any definition of T for these functions that should lead to another result, would make of T a transmutation, which would be no longer *continuous* for the *extended* F.F. The reason for it is that a function of the F.F. *added* to it, is the limit, in the domain (β) , of the fundamental series (26), all functions in which form already part of the uncompleted F.F. Consequently we have again for such a function in the domain (α) the equation (27)

$$T(\varphi_m(x)) = P(\varphi_m(x)), \dots \dots \dots (27)$$

from which we deduce here, by passing to limits

$$\lim_{m \rightarrow \infty} T(\varphi_m(x)) = P(u), \dots \dots \dots (28a)$$

the counterpart of (28). If, however, T should keep its property of continuity in the *extended* F.F., the left-hand member ought to be made equal to Tu . For, if we have $\beta > \sigma$, the function u , which in the domain (β) is the limit of the fundamental series (26), is this *a fortiori* in (σ) . And if we have $\beta < \sigma$, and we want to include *all* functions belonging to (β) in the new F.F. of T , the numerical field of the functions is no longer (σ) but (β) , so that now *in the latter* we have $u = \lim \varphi_m(x)$.

16. We now apply "MAC-LAURIN's theorem" to a few examples. We consider a neighbourhood of the origin O , and the operation $T = D^{-1}$, which transforms a function u into the integral of that function, the origin $x = 0$ being taken as the lower limit of the integration. This is a *normal* additive transmutation. For in the first place it produces for *all* functions belonging to a certain circle (σ) , functions belonging to *the very same* circle, with which the conditions under 1 and 2 for a normal additive transmutation are satisfied (with $\alpha = \sigma$). It is further *continuous* in the pair of fields connected with this; for, corresponding to any arbitrarily small number τ ,

there is a number σ , such that in the whole field (α)

$$|D^{-1}(u)| < \tau, \text{ if } M_u < \sigma,$$

where M_u is the maximum modulus of u in that same domain (α), which here represents both the N. F. F. and the N. F. O. of T . D^{-1} is a fortiori continuous with regard to the same N. F. (α) in any F. F. of functions belonging to a greater circle than (α).

For the construction of the series P we have

$$\xi_k = \int_0^x z^k dz = \frac{x^{k+1}}{k+1}.$$

If this result is substituted in the formula (24), we find, if m_k indicates the binomial coefficient of m for the ordinal number k ,

$$\begin{aligned} a_m &= \sum_0^m m_k \xi_k (-x)^{m-k} = \sum_0^m m_k \frac{x^{k+1}}{k+1} (-x)^{m-k} \\ &= \frac{(-x)^{m+1}}{m+1} \sum_0^m (m+1)_{k+1} (-1)^{k+1}. \end{aligned}$$

We now have

$$\sum_{-1}^m (m+1)_{k+1} (-1)^{k+1} = \sum_0^{m+1} (m+1)_i (-1)^i = (1-1)^{m+1} = 0$$

so that

$$\sum_0^m (m+1)_{k+1} (-1)^{k+1} = -1.$$

Consequently

$$a_m = \frac{(-1)^m x^{m+1}}{m+1}.$$

$D^{-1} u$ therefore answers to the "series of MAC-LAURIN"

$$P(u) = \sum_0^\infty \frac{(-1)^m x^{m+1}}{m+1} \cdot \frac{u^{(m)}}{m!}.$$

The upper limit

$$a_x = \overline{\lim}_{m=\infty} |a_m|^{\frac{1}{m}} \dots \dots \dots (6)$$

is here equal to $|x|$; the upper limit $a(\alpha)$ of a_x , for the domain (α), is therefore equal to α , and the transmutation is complete in the domain (α), with a corresponding domain (β), the radius of which, according to the formula (7) (1st communication), is determined by

$$\beta = \alpha + \alpha = 2\alpha.$$

If these equations are added according to columns, the sum of the coefficients for the k^{th} column is equal to $1 + (1-1)^k$, that is 1 for every column, and we see how in this way the binomial coefficients, though *increasing* towards the right, balance each other. By this it is explained how it comes that the series *arisen* after the summation in question

$$P(r_m(x)) = x + x^2 + \dots + x^{m+1} = \frac{x(1-x^{m+1})}{1-x},$$

has still a limit for *all* values of x in the domain (α) for $m = \infty$, whereas by summation according to horizontal *rows* when they are infinite, a limit does not exist for *all* such like values. We finitely arrive at

$$\lim_{m=\infty} P(r_m(x)) = \frac{x}{1-x},$$

agreeing with the right-hand member of (33). Thus the general formula (28), according to which $\lim P r^m(x)$ in the *whole* F. F. of T , therefore eventually also *outside* the F. F. of P , must exist and be equal to Tu , has been proved *directly* in this special case.

17. As a second example we consider the *substitution*. Let $\omega(x)$ or shortly ω be the function that is to be substituted for x , and let us take again as N. F. of $T = S_\omega$ a neighbourhood of O ; we have then to suppose that O is an *ordinary* point of $\omega(x)$ and that the N. F. of S_ω is a domain *within* the circle of convergence (A) of ω , say a circle with radius $a < A$. In order to see which group of functions have a transmutated in (α), we consider the corresponding domain Ω of (α), which is obtained by conformal representation of the relation $x' = \omega(x)$, and is a domain round the point $x = \omega(0)$. Let the maximum modulus of this domain be σ , then S_ω produces for all functions belonging to the circle (σ) a uniquely determined transmutated $v(x)$ in the domain (α). These transmutated *belong* to the circle (α); for it follows from the equation

$$v(x) = S_\omega(u(x)) = u[\omega(x)],$$

on account of the well-known theory about *functions of functions* that $v(x)$ is *regular* in the domain (α) including the circumference. The conditions under 1 and 2 for a normal additive transmutation are therefore satisfied. S_ω is further *continuous* in the pair of fields in view: if $u(x)$ tends towards zero in the N. F. F., that is the domain (σ), this is a fortiori the case in the domain Ω , which lies within (σ); thus $v(x) = u[\omega(x)]$ tends towards zero in the N.F.O. (α).

The transmutation S_ω therefore is normal. For the construction

of the corresponding series P we have $\xi_m = \omega^m$, which, substituted into (24) gives

$$a_m = (\omega - x)^m$$

$S_\omega(u)$ answers therefore to the "series of MAC-LAURIN"

$$P(u) = \sum_0^{\infty} \frac{(\omega - x)^m}{m!} u^{(m)}.$$

The functions $a_m(x)$ are regular in (α) , since it had been assumed that α is smaller than the radius of convergence A of $\omega(x)$; the number

$$a_x = \lim_{m \rightarrow \infty} |a_m|^{1/m} = |\omega - x|$$

is limited in (α) and its upper limit is

$$a(\alpha) = |\omega(x_m) - x_m|,$$

if x_m is the point on the circumference of (α) , where a_x attains its maximum value. The series Pu represents therefore a transmutation that is complete in (α) , with a corresponding domain (β) the radius of which is determined by

$$\beta = \alpha + |\omega(x_m) - x_m|.$$

The F. F. of P is in most cases a part of the one of S_ω , because as a rule $\beta > \sigma$. For we have in general, if x_σ is the point on the circumference of (α) where $\omega(x)$ assumes its maximum modulus σ ,

$$\begin{aligned} \beta &= |x_m| + |\omega(x_m) - x_m| > |x_\sigma| + |\omega(x_\sigma) - x_\sigma| \\ &> |x_\sigma + \omega(x_\sigma) - x_\sigma| = |\omega(x_\sigma)| = \sigma. \end{aligned}$$

If, however, $\omega(x_m)$ has the same argument as x_m , β is equal to $|\omega(x_m)|$; the result $\beta > \sigma$ or

$$|\omega(x_m)| > |\omega(x_\sigma)|$$

would then be inconsistent with the meaning of $\omega(x_\sigma)$; in this case the points x_m and x_σ must coincide, as well as the circles (σ) and (β) , so that now the F. F. of P is exactly equal to the one of S_ω .

In any case all functions belonging to (β) form part of the F. F. of S ; therefore according to the theorem proved we have for those functions, in the domain (α) ,

$$S_\omega(u) = P(u).$$

We already observed in the discussion of an example of this series P , in N^o. 7 (2nd communication) that it might be deduced at once from the ordinary theorem of TAYLOR of the theory of functions. Indeed, if we write

$$S_\omega(u) = u[\omega(x)] = u[x + (\omega(x) - x)],$$

it appears that $S_\omega u$ in the point x_1 of the domain (α) may be developed in the series of TAYLOR

$$S_{\omega}(u(x_1)) = \sum_0^{\infty} \frac{(\omega(x_1) - x_1)^m}{m!} u^{(m)}(x_1),$$

if the circle with x_1 as centre and

$$|\omega(x_1) - x_1|$$

as radius lies within the domain of convergence of $u(x)$. But this is evidently exactly the case when u belongs to the circle with O as centre, and

$$\beta = \alpha + |\omega(x_m) - x_m|$$

as radius, owing to the signification of x_m . We arrive thus at the same result as higher up, so that the theorem of TAYLOR for the *functional calculus*, in case the operation is a substitution, may at once be deduced from that same theorem of the *theory of functions*.

Now that this has become evident, the fact that the theorem of TAYLOR is exactly valid for the functional calculus, if the series P in question represents a *complete* transmutation, appears in a clearer light. For with regard to the *convergence* of a series, the behaviour of the terms *at infinity* only is decisive, and we can say now that any series of the nature in question behaves, as regards its terms at infinity, in a certain sense as a *substitution*. For, since

$$a_x = \lim_{m \rightarrow \infty} |a_m|^{\frac{1}{m}}$$

we have for large m *approximately* (at least for an infinite number of terms)

$$|a_m| = a_x^m$$

so that, in a definite point x , the modulus of a_m behaves for *great* values of m as the m^{th} power of a positive number a_x . This, now, is also the case for the *substitution*, where this number is $a_x = |\omega(x) - x|$; only the behaviour in question has already been present here *from the first values* of m .

The domain in which the series P corresponding to a transmutation converges for a certain function u is naturally *smaller* than the circle of convergence (r) of u , because the series P consists of powers of Du . If therefore the numerical field of operation (α) of T is *greater* than the numerical field of the functions (σ), Pu will not exist everywhere in (α) for *such* functions of $F(T)$ as do belong to (σ), but not to (α). But the limit-relation (28),

$$Tu = \lim P(\varphi_m(x)) \dots \dots \dots (28)$$

must necessarily be fulfilled everywhere in (α) for the last mentioned functions.

The operation of substitution furnishes simple examples of this. If we have $\omega(x) = \frac{1}{2}x$, a N.F.O. $(\alpha) = 2\sigma$ answers to the N.F.F. (σ) . Let us suppose $\frac{1}{2} < \sigma < 1$, then we have $1 < \alpha < 2$. The function $u = \frac{1}{1-x}$ forms part of the F.F. of $S_{\frac{1}{2}x}$, but does not belong to the circle (α) ; the transmuted of it is

$$v = S_{\frac{1}{2}x} \left(\frac{1}{1-x} \right) = \frac{2}{2-x}, \dots \dots \dots (34)$$

and does belong to (α)

For the series P we have here

$$P \left(\frac{1}{1-x} \right) = \frac{1}{1-x} \sum_{0}^{\infty} \binom{m}{\alpha} \left(\frac{x}{2(1-x)} \right)^m,$$

which form becomes illusory in the point $x=1$. We shall now show in a direct way, that the limit (28) does exist everywhere in (α) , and is equal to (34).

We have here

$$\begin{aligned} \varphi_m &= 1 + x + x^2 + x^3 + \dots + x^m \\ - \frac{x}{2} \frac{\varphi'_m}{1!} &= -\frac{1}{2}x - 2\left(\frac{1}{2}\right)x^2 - 3\left(\frac{1}{2}\right)x^3 - \dots - m_1\left(\frac{1}{2}\right)x^m \\ + \left(\frac{x}{2}\right) \frac{\varphi''_m}{2!} &= \left(\frac{1}{2}\right)^2 x^2 + 3\left(\frac{1}{2}\right)^2 x^3 + \dots + m_2\left(\frac{1}{2}\right)^2 x^m \\ &\dots \dots \dots \\ (-1)^m \left(\frac{x}{2}\right) \frac{\varphi^{(m)}_m}{m!} &= \dots \dots \dots + (-1) \left(\frac{1}{2}\right)^m x^m \end{aligned}$$

If these equations are added according to columns, the sum of the coefficients for the $(k+1)^{th}$ column is equal to

$$(1 - \frac{1}{2})^k = (\frac{1}{2})^k,$$

so that we arrive at

$$P(\varphi_m(x)) = \sum_{k=0}^m \binom{m}{k} \left(\frac{1}{2}\right)^k x^k$$

This expression has indeed, since $\alpha < 2$, in all points of the circle (α) a limit for $m = \infty$, the latter being equal to the right-hand member of (34).

Bacteriology. — "*Researches relating to the Etiology of Febris Exanthematicus.* By Dr. C. J. C. VAN HOOGENHUYZE. (Communicated by Prof. C. EYKMAN).

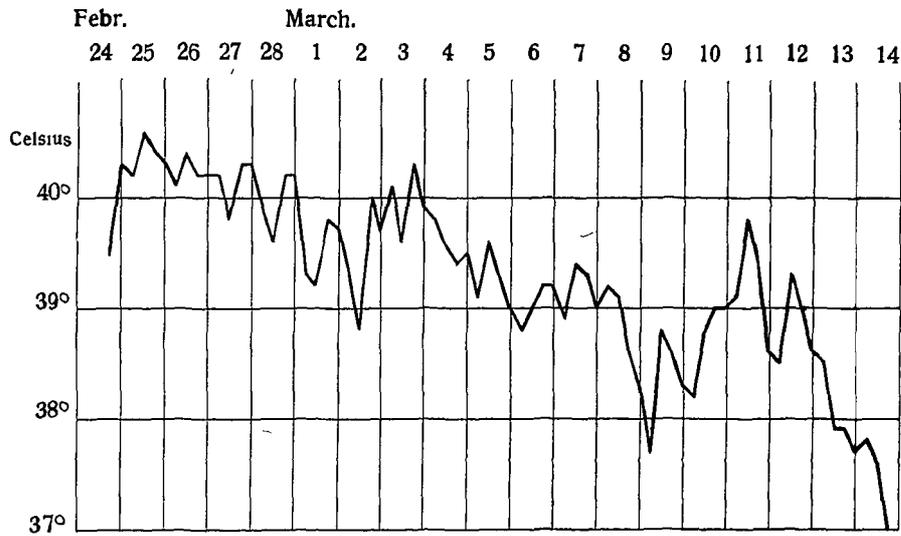
(Communicated in the meeting of June 30, 1917).

Many researchers have been engaged in studying the causation of Febris exanthematicus, and several organisms have already been looked upon as the causative agent of this disease, such as protozoa, spirilla, diplococci and diplobacilli. Considering, that even in such cases in which the researcher succeeded in growing pure cultures from the blood or from an organ, the several findings did not agree, or did not seem to agree in every respect, so that we do not know what to think of them, all these inquiries are looked at askance and it is generally acknowledged that the real etiological factor has not yet been found. Every one pursuing this line of research should, therefore, record his results for the purpose of comparison with those thus far obtained. Fortunately cases of spotted typhus are few and far between in Holland. When, therefore, some cases occurred at Amsterdam a few months ago, I seized the opportunity to study them, and determined to publish my observations for the reasons stated above, although I for one feel convinced that one investigation is not of great value. The patients were treated in the Wilhelmina-Hospital. Through the kindness of Dr. KUIPER, the Director, and of Dr. v. ZADELHOFF, the physician of the ward, I was in a position to examine the blood of one of the patients who was still very ill.

This patient F. W. R., 59 years of age, was admitted to the Hospital on Feb. 24. On the 20th he had had chills. On the 21st he was laid up with head-ache, gripes, and back-ache.

Status praesens: Patient does not look ill, does not complain; throat: somewhat red; tongue: coated and tremulous when put out; full pulse, not dicrotic; Lungs, heart: no anomalies; Bowels: present nothing particular. Patellar reflexes: high; plantar reflexes: normal. Many roseolae on chest, belly, back, arms and legs. WIDAL negative. In the urine much albumin, much urobilin. Sediment: some red, and white blood corpuscles, kidney-epithelium, some cylinders. Blood: number of leucocytes 7000. Temperature: See list I.

Temperature I. Pat. F. R.



On March 2 I drew by means of a syringe \pm 20 c.c. of blood from a brachial vein (of course with the necessary aseptic precautions). Immediately I transferred $\frac{1}{2}$ to 1 c.c. of the blood to tubes filled with 10 c.c. respectively of tapwater, 0.25 % NaCl, 0.5 % NaCl, 0.75 % NaCl., peptonewater, ascites-glycerin-bouillon, (1 c.c. ascites fluid, 9 c.c. of bouillon, 0.4 c.c. of glycerin) and 2 % ammonium oxalate, two tubes of each sort. The fluids were heated to body-temperature and in going from the laboratory to the hospital and vice versa I took preventive measures to insure security from cooling down. I made use of water and several amounts of common salt, because, if NICOLLE, CONOR and CONSEIL are right in asserting that the virus is contained chiefly in the leucocytes, I could thereby liberate the organisms by destroying the leucocytes. According to GOLDBERGER and ANDERSON, however, who made similar experiments to those of the researchers just mentioned, and who pointed to their faulty conclusions, it may be more readily assumed that the virus occurs isolated in the plasma. However this may be, I thought fit to take note of both investigations. I grew at 37° C. organisms both in aerobic and anaerobic cultures. To obtain the latter I put some pyrogallol and potassium-hydrate upon the cotton plug and shut up the tubes with rubber stoppers. Of course I also made the necessary control-experiments.

After intervals of 24 hours preparations were made of all aerobic cultures; the anaerobic cultures were examined only macroscopically, to see if there was any growth. After 3×24 hours preparations

were made also of the anaerobic cultures. The aerobic cultures yielded the following results:

Blood in water: a few diplobacilli. GRAM positive.

Blood in 0.25 % NaCl: a few diplobacilli GRAM positive.

Blood in 0.5 % NaCl: a few diplobacilli. GRAM positive.

Blood in 0.75 % NaCl: no micro-organisms.

Blood in peptone-water: no micro-organisms.

Blood in ascitesglycerin-bouillon: a few diplobacilli. GRAM positive.

Blood in ammonium-oxalate: a few diplobacilli. GRAM positive.

From the tubes, in which diplobacilli had been found cultures were made upon sloped agar. 24 hours later everything was examined again. The agar-tubes had all remained sterile. In the other tubes the following was observed:

Blood in water: a few diplobacilli, to all appearance not many more than the first time. GRAM positive.

Blood in 0.25 % NaCl: many diplobacilli. GRAM positive.

Blood in 0.5 % NaCl: many diplobacilli. GRAM positive.

Blood in 0.75 % NaCl: no micro-organisms.

Blood in peptone-water: no micro-organisms.

Blood in ascitesglycerin-bouillon: rather many diplobacilli. GRAM might be called positive as well as negative.

Blood in 2 % ammonium-oxalate: some diplobacilli, not many more than the first time. GRAM positive.

From the tubes in which diplobacilli were found again cultures were made upon sloped agar.

After 24 hours it appeared that besides the remains of red blood-corpuscles, also diplobacilli, very much like those found previously, were present in the liquid expressed from the agar of the agar-tubes, inoculated with the blood + 0.25 NaCl and the blood + 0,5 NaCl, likewise in the liquid of the agar-tubes that had been inoculated the day before. All the other agar-tubes had remained sterile. The preparations of the liquid-tubes were similar to those of the second day.

The anaerobic tubes appeared yet to be sterile.

The question now arose if what had been found in the fluid squeezed from the agar, meant growth or whether it had been evolved by inoculation. I collected the fluid from the several tubes and inoculated it into some sloped-agar tubes, made a stabculture and added broth to the rest to the ratio of 1 expression of water to 10 of broth. After 24 hours, preparations were made of the broth and many diplobacilli were found.

When watching the agar-tubes, especially those that had been

inoculated with 0.25 % and 0.5 % NaCl + blood, the surface did not any more appear to me quite clear and transparent, though I did not see any colonies either. Next day little more was noticeable. However one preparation made of it revealed diplobacilli. I now took a piece of this somewhat turbid-looking agar and ground it in broth.

In the depths of the stabculture something similar was to be seen; preparations of it contained the same diplobacilli. Of this agar I also put some pieces in broth.

Preparations made from these broth-tubes showed numerous diplobacilli. I made a subculture of some of this broth upon sloped agar. Only after 24 hours did I see a few colonies appear. Likewise a few colonies were visible upon the agar inoculated with expression-water, very much like the preceding. Repeated subcultures upon agar resulted in more colonies; though the growth was rather poor, it gradually seemed to progress.

The colonies produced looked white with incident light, were clumped and could be easily shifted bodily with a needle all over the agar-surface. It seemed as if the colonies floated upon the agar. With transmitted light they looked bluish and translucent.

The bacilli are not all exactly alike as to shape. We found short rods and longer ones. The short ones generally occur in pairs joined end to end, so that they might be called diplobacilli. Most often the centre of the longer ones is of a lighter colour, which renders the bacillus dumbbell- or biscuit-shaped. Maybe we have to do here also with two bacilli joined end to end, or all of them are single bacilli depressed in the middle? However this may be, it is evident that the two parts are linked together. In some cases we might even term them diplococci, the cocci being slightly elongated (cocci-bacilli). See Fig. 1 and 2 of the plate.

The bacilli (I will stick to that term) have no spontaneous motility. They readily stain with the ordinary dyes, most distinctly with carbol-gentian-violet, which, therefore, I made ample use of, also in my investigations of the bacilli in the digestive and intestinal tract of lice. With LÖFFLER'S methyleneblue we can see at the poles more darkly stained granules, occasionally distributed all over the body. They are Gram-positive and non-acidproof. In ascites-glycerin-bouillon, and in ordinary broth cultures, especially the older ones, other bacilli are found among the Gram-positive bacilli, that look exactly like them, but are decolorized.

The bacilli are clumped, which renders suspension difficult.

The best temperature for the growth seems to be 37°. At room-

temperature they do not grow at all. At first a culture was made every day; after some experiments the interval could be lengthened, at most to about 3 weeks, this being the longest interval after which growth seems to be possible.

Upon gelatin at 22° the growth is exceedingly tardy. No liquefaction of gelatin takes place.

Upon LÖFFLER'S serum: rather poor growth; especially the above-mentioned granules are made out here.

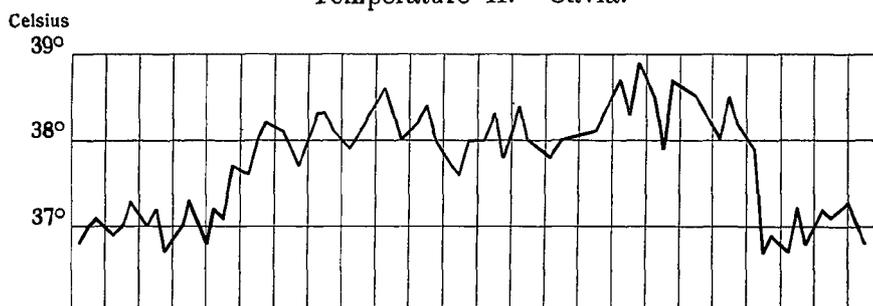
Upon Endo the growth is also poor. The colonies are white and change to light red after a few days.

In bouillon a sediment is formed. The broth does not get evenly turbid, only in the lower layers.

Indol is not produced. Milk does not coagulate. Saccharose-, lactose-, mannite-, glycose-, maltose-, raffinose-bouillon: no acid-formation, no fermentation.

In caviae, inoculated with a suspension of this broth, a rise of temperature was observed after 4 or 5 days, that persisted for a shorter or a longer space of time as is shown in List II.

Temperature II. Cavia.



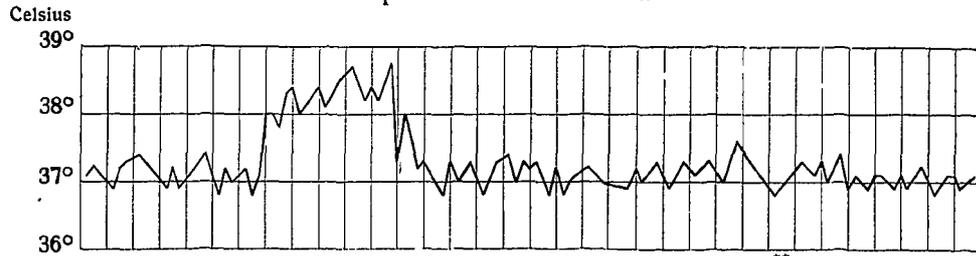
Subcutaneous injection of a suspension of the bacilli.

They then sat quietly in a corner of the hutch and appeared to be ill. To a second injection a short time after the temperature had become normal, there was no response and the temperature remained constant. To all appearance they had become immune as is shown in List III.

In order to make sure that this was not brought about by a less pathogenic condition of the cultures, also healthy caviae were inoculated at the same time. With them a reaction really took place.

We managed to cultivate the same bacilli with the same properties from the blood drawn from the heart of one of the caviae by means of a puncture and that on a day on which the temperature

Temperature III. Cavia.



* Subcutaneous injection of a suspension of the bacilli.

** Inoculated for the second time.

was very high. This experiment was conducted in the same way as described above.

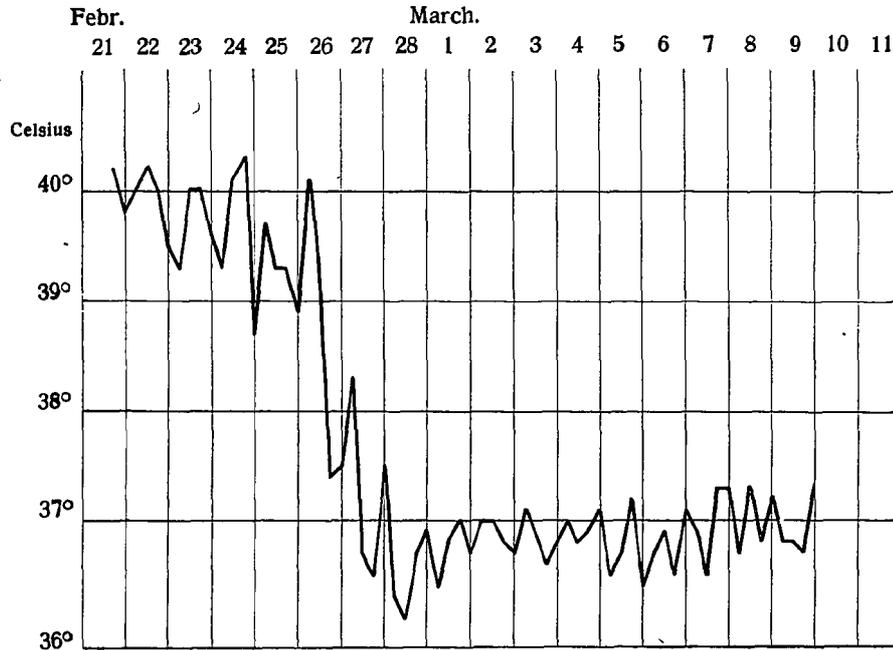
Lastly I have also been able to study the agglutination. On the 9th of March, i.e. 7 days after the blood had been drawn for the culture, I again drew some blood from the patient. The serum agglutinated the bacilli in a 1:100 dilution; the serum of two sound subjects and a sick one (with a high temperature) only in a 1:25 dilution. In a second patient, who had also suffered from typhus exanthematicus I performed an intravenous puncture 11 days after the crisis (See List IV). I did not succeed in cultivating bacilli from the blood. The serum agglutinated the bacilli described above in a 1:100 dilution. The history of the case is briefly as follows:

17 Febr. pat. (M. J. F. V. 21 years) was down with a bad head-ache, gripes, fever, pains in the arms and legs, chills. For about 3 weeks previously he had been languid. *Status Praesens*: pulse: quite full, not dicrotic; Coniunctiva slightly red. Diffuse bronchitis in both lungs; patellar reflexes very high, spleen did not seem to be enlarged, as appeared from percussion, not palpable. Scattered roseolae on chest, back, arms, legs, belly, also some in the face. Hemorrhage from the mucous membrane of the mouth; here and there spontaneous bleeding. The urine presents nothing peculiar. Number of leucocytes 8000. WIDAL negative. Diagnosis: spotted typhus.

It appeared, then, that the serum of both patients, one of whom was recuperating, agglutinated the bacilli in a 1:100 dilution; the serum of a patient suffering from another disease with high fever in a 1:25 dilution; the serum of sound subjects also 1:25.

In connection with the communications of DA ROCHA LIMA and TÖPFER I have examined some clothes-lice, taken from the body-linen of the first patient (R). I prepared as well as possible the digestive and intestinal tract from the body and ground it on an

Temperature IV. Pat. M. V.



object-glass. I was fortunate enough to demonstrate organisms, exactly similar to the bacilli described above and to those described by DA ROCHA LIMA and TÖPFER. On the photographs 3, 4 and 5 some bacilli are distinctly visible. I could not demonstrate these organisms in clothes-lice or head-lice taken from sound persons nor in house-bugs.

The only difference was the staining, after GRAM, as these organisms were easily decolorised (as DA ROCHA LIMA also tells us) whereas the cultivated bacilli were not. For want of material I was not enabled to grow cultures from the organisms found in lice.

Finally I examined several coverslips of the patient's blood, stained after GIEMSA, to detect bacilli and the bodies that various researchers discovered in the white bloodcorpuscles; here and there I saw in some leucocytes in the protoplasm beside the nucleus now punctiform bodies, now again rods with rounded ends, sometimes indented in the centre. This is exemplified in the figures 6, 7, 8, 9. It is especially the latter that remind one forcibly of the organisms described above. Staining with methyleneblue made everything clearer still.

Whether we really have to do here with bacilli which, on account of their being disposed differently in the microscopic field, present different shapes, I will not venture to decide. On slightly turning

the screw of the microscope it seems as if the point is shifted a little, so that it may be taken for a rodlet slightly inclined from the vertical. However this may be, it is at any rate remarkable to observe the resemblance in the shape of the bacilli found in the first fluids, the bacilli cultivated, the bacilli in the intestinal tract of the clothes-lice and the bodies (such I think they may be called) in the white blood corpuscles of the patient. Besides these shapes in the leucocytes I also, though rarely, detected a diplobacillus in the coverslips, after a prolonged research.

It must be observed that not in all the fluid tubes bacilli were found, although they all contained blood from the same syringe (with a control for an aseptic operation). They were found only in those tubes in which the fluid was hypotonic relating to the blood; it should also be observed that after some subcultures, the cultivation was considerably easier and the intervals between two successive cultures could be lengthened; again, that the bacilli then seemed to be less closely packed together and less pathogenic.

It is worth while to compare this finding with those of other researchers with numerous material.

In my judgment there is a great resemblance between the organisms found by DA ROCHA LIMA and TÖPFER in the body of lice, without their being able to cultivate them, and those demonstrated by me. Owing to lack of material I was not in a position to perform sections in order to observe the different epithelial cells, as described by DA ROCHA LIMA and was limited to coverslips only. This may account for my organisms lying free in the field of view. Entire epithelial cells I did not see, only fragments of them.

I am personally inclined to think after consulting the literature, accessible to me, that the bacilli detected by us when compared with cultures grown by various experimenters resemble most those of RABINOWITSCH. For the sake of brevity I shall not pass in review all the researches and only refer to the extensive publications of RABINOWITSCH, who comes to this final conclusion, that in reality all investigators have found one and the same organism, viz. short shapes growing in pairs. The slight deviations recorded are owing to the different methods of staining. The properties also agree rather well. This is also the case with the bacilli cultivated by me. Only the description of the agar-colonies do not apply to my cultures. According to him they first resemble colonies of streptococci (dew drop) and afterwards assume a pale yellow colour. My colonies are compact, white and remain so. With incident light they remind one of colonies of staphylococci. For the rest they are not at all like them,

as set forth in my description. The properties and animal experiments correspond to those of RABINOWITSCH and others. RABINOWITSCH believes that the reason why so many investigators could not produce a culture, is that the bacilli occur in the blood principally in a certain period, viz. at the conclusion of the fever-period, immediately before the crisis, so that, as he puts it, it is not the day of the beginning of the disease, but the day of the crisis that is of prime importance.

I happened to collect blood from the patient on the very day when his disease had reached its acme and his life was feared for. The following day, however, he suddenly took a turn for the better, but in consequence of several complications occurring with the disease, the temperature was not indicative of the time of the critical period.

Those who have grown these bacilli agree that it is exceedingly difficult to produce cultures. Frequently the rods were demonstrated in the microscopic preparations (e. g. in broth or expression-water), but they could not be developed any farther. RABINOWITSCH holds that the blood-serum of the patients inhibits the growth also when diluted. Very weak dilutions would, therefore, further the growth. Even the fluid expressed from the agar he considers to be a dilution. Without touching the agar surface he first puts the blood in the expression-water and only then, after shaking it well he pours it out over the agar. My success in producing cultures may be owing partly to similar dilutions in my procedure, and partly to the use of hypotonic fluids to put the blood in, and to the lucky circumstance of drawing the blood at the proper moment.

Plotz and later on POPOFF are the only investigators who detected an organism considered by them as the etiological factor of typhus exanthematicus, differing essentially from all other organisms detected, this bacillus typhi-exanthematici being obligate anaerobe.

Several investigators succeeded in cultivating organisms not only from the blood, but also from the urine and the feces of sufferers from typhus exanthematicus. They were agglutinated by the blood of the patients. HORIUCHI e.g. produced from the feces and the urine a paratyphus-like bacillus; WILSON obtained from urine and feces bacilli differing from the *Bacillus coli* only in that they did not convert lactose; PREDTJETSCHENSKY managed to grow from urine, sputum, and bronchial mucus the same diplobacilli as from the blood; KLODNITZKY grew from house-bugs, obtained in a typhus ward, a culture of small motile very virulent bacilli, called by him bacillus violentus. However he refrains from considering them as the agent exciting typhus exanthematicus. PETRUSCHKY collected from sputum rodlets which he took to be the cause of the disease; WEIL

and FELIX grew proteus-like bacilli from urine; DIENES managed to grow from two clothes-lice taken from a patient proteus-like bacilli, resembling those of WEIL-FELIX.

I will not attempt to criticize, as I am fully aware that one case cannot yield conclusive evidence. Still, it favours the supposition that in this patient the bacillus detected was indeed the cause of the disease, which had been clinically diagnosed as "typhus exanthematicus". Also in my investigations questions are still left open, owing to lack of material.

We now summarize our results:

From the blood cultures were grown that may be called diplobacilli on account of the form and the location. The colonies upon agar look white with incident light and faint-bluish transparent with transmitted light. They are detached from the agar surface and can easily be shifted bodily with a needle.

The bacilli possess no motility, take up all dyes and their appearance varies with the dye selected, (finer, coarser, granular, dumbbell- or biscuitshaped). They are Gram-positive (in older cultures occasionally Gram-negative); they are non-acidproof; they form no spores.

No growth at room-temperature. Tardy growth at 22°. They grow best at 37°.

Gelatin is not liquefied; upon LÖFFLER's serum there is only a poor growth; milk does not coagulate; the bacilli do not form acid nor indol. No fermentation in saccharose-, lactose-, mannite-, glycose-, and raffinose-bouillon.

After repeated inoculations, the properties change.

They are pathogenic for caviae (i.e. they cause a rise of temperature) [could again be cultivated from the blood of these caviae] and render them immune. Through the serum of the patient himself and that of another who was convalescent they were clumped in a 1:100 dilution; through the serum of a sufferer from another disease and two sound persons only in a 1:25 dilution.

In the digestive and intestinal tract of clothes-lice, taken from the patient, organisms were found resembling the above-mentioned bacilli and the *Rickettsia Prowazeki* of DA ROCHA LIMA. With them no culture- nor animal-experiments could be made for want of material. The Gram-staining was negative here.

In the coverslips of the blood of the patient very rarely a single diplobacillus was found. True, some forms were detected outside the nucleus in some leucocytes that reminded us forcibly of the above-mentioned organisms (also those in lice).

The Amsterdam Public Health Service Bacteriological Laboratory.

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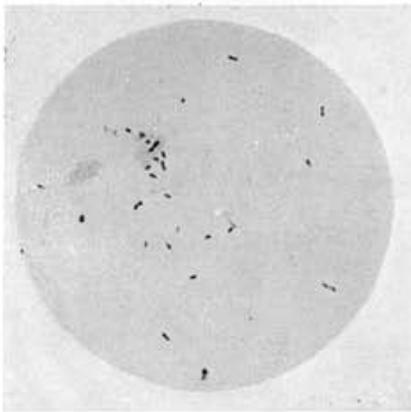


Fig. 2.

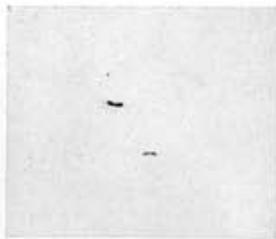


Fig. 1.

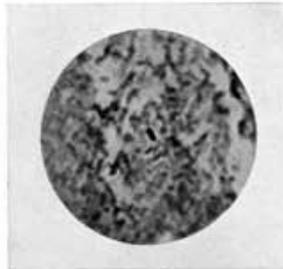


Fig. 4.

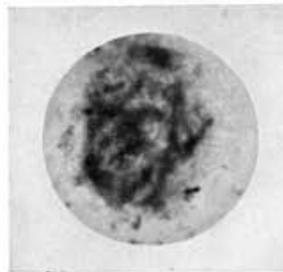


Fig. 3.

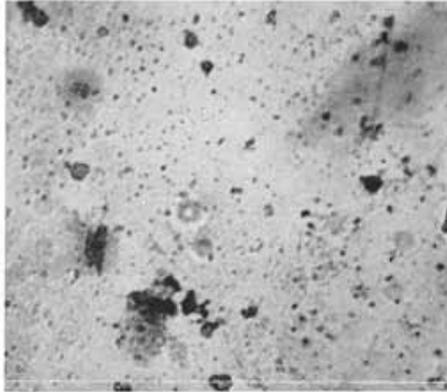


Fig. 5.

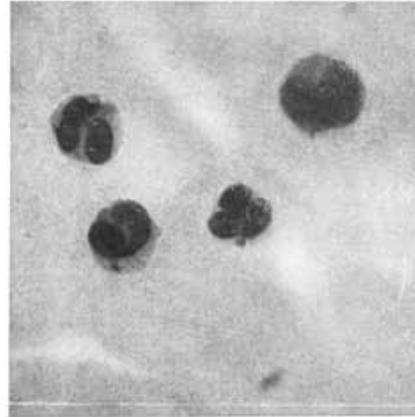


Fig. 6.

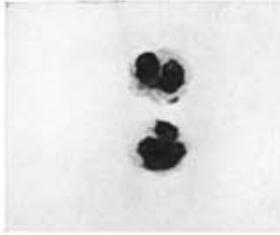


Fig. 7.

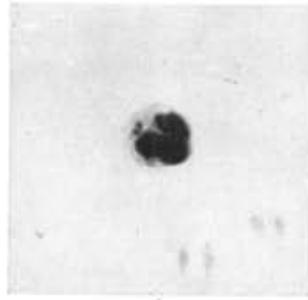


Fig. 8.

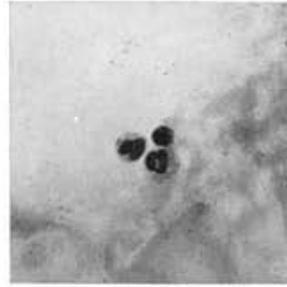


Fig. 9.

EXPLANATION OF THE PLATES.

Fig. 1. First obtained culture from blood of the patient, on agar. (Augm. 1560).

Fig. 2. Culture after inoculation on agar. (Augm. 844).

Fig. 3. Preparation of the digestive and intestinal tract from a clothes-louse of the patient, ground on an object-glass. (Augm. 1560).

Fig. 4. The same of a second clothes-louse of the patient. (Augm. 1560).

Fig. 5. The same of a third clothes-louse of the patient. (Augm. 1560).

Fig. 6. (Augm. 1540).

Fig. 7. (Augm. 1560).

Fig. 8. (Augm. 1500).

Fig. 9. (Augm. 750).

Leucocytes of the blood of the patient with several forms of corpuscles outside the nucleus.

The photos have been made by Dr. L. TH. REICHER, whom I render my sincere thanks.

Experimental Psychology. — *“Intercomparison of some results obtained in the Investigation of Memory by the Natural and the Experimental Learning Method.”* By Dr. F. ROELS. (Communicated by Prof. C. WINKLER).

(Communicated in the meeting of June 30, 1917.)

II.

This paper is to be considered as a sequel to a similar communication published in the Proceedings of the Meeting of March 31, 1917 Vol. XXV p. 1309, and treats more particularly of the way in which the experimental method benefits the spontaneous tendency to use rhythm in learning by heart.

For the method and the technique of our investigation we refer to our first communication (Ibid p. 1310).

It has long been known that, under the formal conditions of imprinting the material, rhythm tends largely to save repetitions and learning time. In daily life people are fully convinced of this; when they have to learn something by heart they use rhythm. In our experiments this tendency was strong with the natural method (I); with the experimental method (II) it is still noticeable, though less distinct. The following tables illustrate the rhythm of the first repetition of the series and also how the rhythm varies when the observer gets more familiarised with the material. The tables were constructed as follows: The duration of the repetition was split into groups, corresponding with the grouping of the material according to the rhythm used by the observer. Then I determined the time required for every syllable of the several groups by dividing the time required for every group by the number of the syllables it contained. From these timevalues the means were calculated. The intervals between two successive groups were determined from the time elapsing from the moment the last syllable of a group was pronounced to that on which the first of the following group was read. In short, we determined the mean time falling to every syllable of the group in a learning (l.) and a repetition (r) experiment; when compared with the time of the syllables consti-

tuting a group, the time required by the last syllable of a group indicates the rhythm used by the observer.

As to the tables illustrating the changes which the rhythm undergoes when the familiarity with the material increases, we have divided the number of repetitions required in learning and repeating a series into three groups of successive repetitions in the manner just described (Vide Proceedings of the meeting of 31 March 1917, Vol. XXV p. 1316). We then determined the mean time of every syllable of the various groups and intervals. R. and D. learned the series in three groups of four syllables. M. in two groups of six, each subdivided into three groups of two. The stress fell invariably on the last of the two syllables. For the rest the tables are self-evident. All time values are expressed in seconds. Tables I, II, and III refer to the rhythm of the first repetition, while Tables IV to IX show the changes in the rhythm resulting from the observer's greater familiarity with the material.

When studying the data of Table I, II and III we see directly that our observers used rhythm already at the first repetition, with I as well as with II. M. alone, seems to make an exception with II; anyhow with him the time falling to the last syllable of the group is shorter than the mean duration of the remaining syllables constituting the group. With all our observers the rhythm with I undergoes a slight acceleration from the very beginning, which is rather peculiar. (M 0.82, 0.80; R 1.07, 1.04, 1.01; D 1.02, 0.99, 0.86).

While the mean time of the syllables, constituting the various groups, is gradually diminishing from the beginning to the end, the intervals decrease for R also (1.51, 1.40); for D however they remain approximately constant (1.43, 1.45). Since M learned the series in two groups of six syllables, no data referring to him could be procured.

In the repetition experiments the duration of every syllable is, as a rule, shorter than the corresponding duration in the learning-experiments. The same may be observed regarding the intervals, viz. a decrease with all observers. The acceleration of learning in the repetition-experiments benefits the group as well as the intervals. Just as the rhythm of the learning-experiments that of the repetition-experiments is also slightly quickened from the beginning towards the end, as the acceleration, observed in the learning and in the repetition-experiments, follows, almost without exception, the order of the groups and the intervals, i. e. the farther group and interval are advanced in the series, the greater is the decrease.

With II there is in the learning-experiments a tendency to constantly increase the velocity while retaining the rhythm, as the

TABLE I. Observer M.

		Groups		Arithm mean	Mean deviation	Median
I (20)	1st	}	l	0.82	0.06	0.79
			r	0.82	0.05	0.82
	interval	}	l	1.31	0.16	1.22
			r	1.29	0.10	1.30
	2nd	}	l	0.80	0.06	0.80
			r	0.83	0.06	0.84
II (20)	1st	}	l	0.96	0.05	0.94
			r	0.94	0.06	0.92
	interval	}	l	0.84	0.09	0.80
			r	0.88	0.12	0.80
	2nd	}	l	0.80	0.09	0.79
			r	0.78	0.06	0.76

mean duration of the syllables decreases in the order of the groups. (M 0.96; 0.80; R 0.94; 0.73; 0.72; D 0.98; 0.79; 0.75). The duration of the interval decreases a little with R; with D, however, it rather increases. With a single exception only (insignificant for R, more significant for D) the mean duration of the syllables is in the repetition-experiments smaller than the corresponding time-values of the repetition-experiments. The relation of the lengths of the intervals in the learning-, and in the repetition-experiments presents, in the main, no uniformity.

For M it decreases a little; for R the intervals increase, while for D the first interval increases, the second decreases. Irrespective of the exceptions just alluded to, it may here also be observed that the acceleration, which the learning undergoes in the repetition experiments, increases in the order of the groups.

A comparison of the values for the mean deviation is of some importance as it shows us in how far the rhythm, irrespective of the peculiarities alluded to above, (acceleration in the order of the groups etc.), remains constant. Now it is manifest that with I, as well as with II, in the learning-as well as in the repetition-experiments, the mean deviation is considerably greater for the intervals than for the groups. This goes to show that the observer sticks better to his rhythm in the groups than in the intervals. It also

TABLE II. Observer R.

	Groups		Arithm. mean	Mean deviation	Median	
I (20)	1st	l	1.07	0.10	1.06	
		r	1.02	0.09	1.02	
	interval	l	1.51	0.40	1.67	
		r	1.31	0.35	1.45	
	2nd	l	1.04	0.12	1	
		r	0.95	0.10	0.95	
	interval	l	1.40	0.40	1.55	
		r	1.17	0.38	1.27	
	3rd	l	1.01	0.12	1.03	
		r	0.88	0.11	0.90	
	II (19)	1st	l	0.94	0.11	0.90
			r	0.91	0.04	0.90
interval		l	1.04	0.12	1	
		r	1.06	0.18	1.10	
2nd		l	0.73	0.08	0.73	
		r	0.74	0.09	0.69	
interval		l	1.01	0.17	1	
		r	1.05	0.18	1	
3rd		l	0.72	0.11	0.70	
		r	0.67	0.06	0.67	

appears, that the mean deviation with I as well as with II, for groups and intervals is most times greater in the learning than in the repetition-experiment; in the latter the rhythm is consequently more constant. It also appears that the experimental method is more favourable to a constant rhythm than the natural method, the mean deviation being generally smaller with II than with I. With II it is especially the intervals that are more equalized.

Concerning the influence exerted on the rhythm by an increased familiarity with the material, we see in tables IV, V, VI, VII, VIII, IX in the learning-experiments with I, an increase of the time falling to every syllable of the group (1, 2 and 3) from A to C, i.e. in the case of greater familiarity with the material. For M and

TABLE III. Observer D.

	Groups		Arithm. mean	Mean deviation	Median
I (18)	1st	l	1.02	0.17	0.97
		r	0.90	0.16	0.87
	interval	l	1.43	0.18	1.42
		r	1.31	0.20	1.32
	2nd	l	0.99	0.15	0.97
		r	0.83	0.17	0.77
	interval	l	1.45	0.20	1.32
		r	1.24	0.21	1.20
	3rd	l	0.86	0.16	0.77
		r	0.75	0.18	0.72
II (8)	1st	l	0.98	0.09	1.02
		r	1.07	0.05	1.07
	interval	l	1.04	0.19	1
		r	1.06	0.13	1.10
	2nd	l	0.79	0.05	0.80
		r	0.72	0.04	0.72
	interval	l	1.13	0.19	1.10
		r	1.09	0.14	1.02
	3rd	l	0.75	0.07	0.73
		r	0.65	0.08	0.61

R there is always a progressive increase, viz. it is larger from B to C than from A to B, whereas for D there is in two cases a decrease, in one case an increase from A to B. The tendency of the rhythm to accelerate in the order of the groups is maintained also with a greater familiarity with the material. For M and D the time invariably decreases from the first to the last group; for R the time-values of the third group are always smallest, whereas those of the first are sometimes smaller, then again greater than those of the second.

In comparing the time-values of the intervals from A to C and from 1 to 3, again a certain uniformity is to be observed. With R there is without exception an increase from A to C; with M the

TABLE IV. Observer M.

				1st group	interval	2nd group
I	1	A	A.M.	0.85	1.34	0.83
			M.D.	0.05	0.15	0.05
			M.	0.85	1.30	0.82
		B	A.M.	1	1.41	0.92
			M.D.	0.08	0.15	0.07
			M.	1	1.42	0.91
		C	A.M.	1.18	1.41	1.07
			M.D.	0.19	0.26	0.18
			M.	1.12	1.40	1.04
	r	A	A.M.	0.82	1.31	0.83
			M.D.	0.05	0.11	0.06
			M.	0.84	1.35	0.86
		B	A.M.	0.99	1.47	0.93
			M.D.	0.09	0.26	0.11
			M.	0.99	1.37	0.96
C	A.M.	1.31	1.32	1.14		
	M.D.	0.37	0.39	0.35		
		M.	1.13	1.30	0.93	

interval increases from A to B; from B to C it remains constant. With D the interval from B to C always increases; from A to B, however, it always decreases.

Leaving a few deviations out of consideration we can state that the first interval is either larger than the second or equal to it. The tendency of the second interval to decrease in relation to the first, which we found vaguely indicated in studying the tables relating to the rhythm of the first repetition, is thus seen to maintain itself all through the learning-process.

With I the data yielded by the repetition-experiments present the same uniformities, though less distinctly. A greater familiarity with the material induces a progressive increase of the time falling to every syllable of the groups 1, 2 and 3 for M, to those of groups 1 and 2 for R. The time-values for D that formed an exception

TABLE V. Observer M.

				1st group	interval	2nd group
II	1	A	A.M.	0.94	0.84	0.79
			M.D.	0.06	0.07	0.04
			M.	0.93	0.83	0.78
		B	A.M.	0.93	0.85	0.79
			M.D.	0.05	0.08	0.04
			M.	0.93	0.81	0.79
		C	A.M.	0.94	0.82	0.83
			M.D.	0.06	0.05	0.05
			M.	0.92	0.81	0.82
	r	A	A.M.	0.94	0.88	0.80
			M.D.	0.06	0.11	0.06
			M.	0.92	0.86	0.77
		B	A.M.	0.91	0.83	0.78
			M.D.	0.05	0.08	0.05
			M.	0.91	0.80	0.77
C	A.M.	0.95	0.85	0.80		
	M.D.	0.06	0.09	0.06		
	M.	0.94	0.81	0.77		

even to the general rule in the learning-experiments do not present anything uniform here either, except perhaps the average duration of the syllables of the last group, which is always smallest.

The accelerations of the rhythm in the order of the groups appears very distinctly in the repetition-experiments with R. and in a smaller degree with M. With R the decrease of the mean time for one syllable of the several groups, proceeds regularly from 1 to 3; with M a decrease reveals itself from A to B, while the time-value in A is about equal for the three groups. With D decrease in A is regular; in B and C we observe an increase from 2 to 3.

If we eliminate D, it appears that the second interval is apt to increase, in relation to the first as well from A to C as from 1 to 3. This is most distinct for R, who presents only a single exception. With M we observe an increase from A to B, a decrease from B to C, whereas the time-values for D are not uniform at all.

TABLE VI. Observer R.

				1st group	interval	2nd group	interval	3rd group
I	i	A	A.M.	1.07	1.55	1.04	1.40	1.06
			M.D.	0.12	0.37	0.12	0.39	0.21
			M.	1.07	1.62	1.02	1.55	1.08
		B	A.M.	1.15	1.60	1.18	1.50	1.05
			M.D.	0.18	0.45	0.14	0.53	0.21
			M.	1.10	1.75	1.13	1.50	1.07
		C	A.M.	1.29	1.71	1.32	1.82	1.12
			M.D.	0.52	0.78	0.39	0.99	0.50
			M.	1.05	1.40	1.14	1.45	0.84
	r	A	A.M.	1.02	1.29	0.95	1.17	0.87
			M.D.	0.12	0.37	0.11	0.40	0.13
			M.	0.97	1.50	0.93	1.25	0.90
		B	A.M.	1.04	1.44	0.98	1.75	0.68
			M.D.	0.22	0.48	0.20	0.79	0.15
			M.	1	1.20	0.92	1.65	0.65
C	A.M.	1.16	1.56	1.08	1.57	0.79		
	M.D.	0.42	0.74	0.24	1.14	0.22		
		M.	1.07	1.60	1.17	1	0.93	

Whereas in the learning-experiments with I the time falling to every syllable of the group generally increases from A to C, hardly any regular increase is discernible with II. For M e.g. the time values remain nearly constant; for R they regularly increase in the first group from A to C, while in the second and in the third groups B is greatest. For D we always observe an increase from B to C, whereas from A to B the time alternately decreases and increases.

The acceleration of the rhythm in the order of the groups is very distinct with M and R. For both observers the decrease from 1 to 3 in A, B and C proceeds regularly. With D we observe the same in A and B; in C, however, an increase is observed from 1 to 2, a decrease from 2 to 3.

Whereas the intervals for M in A, B and C are about of the same length, with R and D we observe a regular increase from A

TABLE VII. Observer R.

				1st group	interval	2nd group	interval	3rd group
II	i	A	A.M.	0.93	1.03	0.71	1.02	0.70
			M.D.	0.11	0.14	0.08	0.12	0.08
			M.	0.94	1.09	0.71	1	0.72
		B	A.M.	0.87	1.51	0.70	1.10	0.59
			M.D.	0.13	0.57	0.09	0.08	0.09
			M.	0.87	1.37	0.67	1.09	0.57
		C	A.M.	0.86	1.59	0.84	1.10	0.64
			M.D.	0.22	0.62	0.20	0.17	0.11
			M.	0.85	1.32	0.74	1.12	0.62
	r	A	A.M.	0.91	1.07	0.71	1.05	0.70
			M.D.	0.04	0.14	0.08	0.19	0.08
			M.	0.90	1.10	0.69	1.05	0.68
		B	A.M.	0.86	1.17	0.65	1.14	0.61
			M.D.	0.10	0.23	0.06	0.18	0.10
			M.	0.85	1.20	0.64	1.15	0.64
C	A.M.	0.85	1.51	0.69	1.32	0.61		
	M.D.	0.15	0.66	0.16	0.36	0.13		
		M.	0.79	1.20	0.64	1.15	0.67	

to C. The second interval evinces, here also, a tendency to decrease. Anyhow, with R it is, as a rule, smaller than the first.

Whereas in the learning-experiments with II we could hardly distinguish a regular increase of the mean time falling to one syllable of the several groups, in the repetition-experiments there is even a tendency to decrease from A to C.

Whereas with M the time-values for A, B and C are still about equal, with R we see already a tendency to decrease, and with D this tendency comes to the front unmistakably (only one exception). The decrease from 1 to 3 continues regularly; only D presents an exception.

The intervals in the repetition experiments with II increase regularly for R and D from A to C, for M they remain about constant. With R the second interval is always smaller than the first, with D it is always greater.

TABLE VIII. Observer D.

				1st group	interval	2nd group	interval	3rd group
I	I	A	A.M.	1	1.45	0.91	1.45	0.81
			M.D.	0.18	0.14	0.14	0.20	0.07
		A.	0.94	1.46	0.84	1.36	0.75	
		B	A.M.	0.90	1.40	0.87	1.36	0.83
			M.D.	0.17	0.14	0.15	0.19	0.12
		M.	0.89	1.40	0.80	1.32	0.81	
	C	A.M.	0.91	1.51	1.03	1.51	0.99	
		M.D.	0.18	0.33	0.27	0.38	0.48	
	M.	0.84	1.35	0.91	1.37	0.79		
	r	A	A.M.	0.89	1.29	0.81	1.27	0.73
			M.D.	0.16	0.19	0.16	0.15	0.17
		M.	0.90	1.32	0.80	1.30	0.70	
		B	A.M.	0.81	1.26	0.96	1.33	0.71
			M.D.	0.16	0.18	0.23	0.30	0.13
		M.	0.83	1.31	0.91	1.23	0.67	
	C	A.M.	0.82	1.40	0.83	1.22	0.79	
		M.D.	0.14	0.48	0.19	0.23	0.21	
	M.	0.83	1.20	0.82	1.20	0.73		

Considering the values of the mean deviation it appears that, just as we observed about the mean deviation in the first repetition it is considerably greater for the intervals than for the group, which proves that, just as with the first repetition, with I as well as with II, the rhythm is more constant for the groups than for the intervals all through the learning- and the repetition-process.

The rhythm adopted by our observers, in the learning- as well as in the repetition-experiments, with I and II affects the recitation in that here also the mean time falling to a syllable of a group, is generally shorter than that of the last syllable of a group, in other words the recitation also proceeds in groups and intervals (See Tables X, XI and XII, which are constructed in the same way as Tables I, II and III). We shall not enter into a discussion about the question whether this is owing to the direct tendency of the

TABLE IX. Observer D.

				1st group	interval	2nd group	interval	3rd group
II	I	A	A.M.	1.04	1.05	0.76	1.14	0.75
			M.D.	0.06	0.17	0.05	0.15	0.06
			M.	1.07	1.01	0.75	1.13	0.73
		B	A.M.	1.01	1.12	0.71	1.26	0.64
			M.D.	0.06	0.18	0.03	0.21	0.08
			M.	1	1.15	0.71	1.21	0.66
		C	A.M.	1	1.28	0.72	1.28	0.68
			M.D.	0.09	0.31	0.08	0.07	0.09
			M.	0.99	1.33	0.73	1.26	0.65
	r	A	A.M.	1.09	1.06	0.69	1.12	0.65
			M.D.	0.04	0.13	0.04	0.14	0.07
			M.	1.07	1.07	0.69	1.11	0.63
		B	A.M.	1.02	1.15	0.68	1.15	0.71
			M.D.	0.06	0.16	0.05	0.13	0.16
			M.	1.01	1.12	0.67	1.16	0.71
C	A.M.	0.99	1.20	0.66	1.24	0.70		
	M.D.	0.10	0.18	0.04	0.18	0.12		
	M.	1.01	1.19	0.64	1.29	0.72		

observers to recite with rhythm, or whether it results from the circumstance that the rhythm used in learning and repeating the series, the groups, being apperceptive wholes are easier to reproduce than the first syllable that forms the transition from the one group to the other. It is a fact that the rhythm of recitation bears a great resemblance to that of the learning and repetition-experiments. In the same way we notice in the recitation that, broadly speaking, the mean time falling to a syllable of the groups decreases in the order of the groups.

This is the case in the recitations of I and II and those of the learning- and repetition-experiments. The time required in the recitation of the last group of the series is remarkably short, a fact that we also noticed in considering the changes undergone by the rhythm in the learning process. In this respect the intervals are less uniform. This is not surprising if we consider that, as stated above, the first

TABLE X. Observer M.

	Groups		Arithm. mean	Mean deviation	Median
I (20)	1st	l	1.36	0.44	1.15
		r	1.17	0.29	1.06
	interval	l	2	1.26	1.25
		r	2.15	1.05	1.78
	2nd	l	0.97	0.31	0.87
		r	0.82	0.13	0.77
II (19)	1st	l	1.20	0.29	1
		r	1.04	0.23	1.06
	interval	l	1.26	0.54	0.92
		r	1.59	0.98	0.90
	2nd	l	1	0.24	0.92
		r	0.97	0.23	0.86

syllable of a group is much more difficult to reproduce than the others, in consequence of which the tendency to use rhythm interferes with reproduction-tendencies of different degree.

The process of the recitation agrees in another respect with that of the mean duration of the time falling to a syllable of one of the groups, viz. in this that with I as well as with II, the mean duration is almost without exception, longer in the learning-experiments than in the repetition-experiments. In a much smaller degree this also applies to the intervals, their duration being in most cases also shorter in the repetition- than in the learning-experiments.

The mean deviation is for all observers, with I and with II, in the learning- and in the repetition-experiments greater for the interval than for the groups, from which follows that here also the rhythm is kept up better for the groups than for the intervals.

The mean deviation being in the majority of cases smaller with I than with II it would seem that, broadly speaking, the natural method is more favourable than the experimental to an orderly recitation of the learned series.

CONCLUSIONS.

1. With only a few exceptions all our observers used rhythm

TABLE XI. Observer R.

	Groups		Arithm. mean	Mean deviation	Median	
I (20)	1st	l	1.03	0.30	0.96	
		r	1.10	0.39	0.90	
	interval	l	1.91	1.16	1.45	
		r	1.68	0.95	1.20	
	2nd	l	1.21	0.56	0.88	
		r	0.97	0.28	0.83	
	interval	l	1.42	0.73	1.20	
		r	1.02	0.38	0.90	
	3rd	l	0.82	0.41	0.58	
		r	0.73	0.25	0.65	
	II (19)	1st	l	1.07	0.51	0.77
			r	0.96	0.40	0.87
interval		l	2.01	1.56	1.20	
		r	1.34	0.64	1	
2nd		l	1.31	0.96	0.43	
		r	1.07	0.61	0.73	
interval		l	1.83	1.04	1.40	
		r	1.80	1.09	1.07	
3rd		l	1.03	1.03	0.65	
		r	0.72	0.31	0.58	

in the first repetition: i.e. the imprinting occurred already with the first repetition in groups and intervals.

2. The rhythm of the first repetition shows almost invariably the tendency to slightly accelerate in the order of the groups. With I (natural method) this quickening confers a benefit on the groups as well as on the intervals, both in the learning- and in the repetition-experiments, though in the latter less distinctly than in the former. With II (experimental method) this quickening is clearly demonstrable only for the groups. In the repetition-experiments the time-values of the groups and intervals are always smaller than the corresponding values in the learning-experiments. In the first repetition the experimental method is generally more favourable than the natural as to consistency in the rhythm; especially the duration of the in-

TABLE XII. Observer D.

	Groups		Arithm. mean	Mean deviation	Median	
I (18)	1st	l	0.90	0.16	0.83	
		r	0.79	0.13	0.80	
	interval	l	1.28	0.37	1.05	
		r	1.11	0.20	1.10	
	2nd	l	1.05	0.37	1.02	
		r	0.81	0.23	0.75	
	interval	l	1.60	0.65	1.30	
		r	1.99	1.06	1.40	
	3rd	l	0.96	0.21	0.95	
		r	0.72	0.16	0.72	
	II (8)	1st	l	0.99	0.37	0.82
			r	0.80	0.15	0.77
interval		l	1.43	0.55	1.25	
		r	2.36	1.24	1.80	
2nd		l	0.91	0.42	0.66	
		r	0.66	0.17	0.60	
interval		l	1.66	0.98	1.07	
		r	1.50	0.74	1.35	
3rd		l	0.79	0.39	0.65	
		r	0.90	0.69	0.47	

tervals is generally more uniform with II, though here also the rhythm is as a rule preserved better for the groups than for the intervals.

3. With respect to the changes in the rhythm with greater familiarity with the material, we observe that most often the time, falling to every syllable of the groups into which the series is divided, increases progressively as the observer gets more familiar with the material. The tendency of the rhythm to quicken in the order of the groups is kept up when the familiarity with the material increases. Barring an occasional deviation, the first interval is either greater than the second or equal to it. The tendency of the second to decrease, in relation to the first, as vaguely indicated already in the rhythm of the first repetition, is kept up all through the learn-

ing process. In the repetition-experiments the same similarities may be discerned. They are however hardly noticeable in employing the experimental method, though here also, with a greater familiarity with the material the rhythm is maintained better for the groups than for the intervals.

4. The recitation occurred in groups and intervals; the mean time falling to one syllable of the groups is here also in most cases shorter than that of the last syllable of a group.

With I and with II, both in the learning- and in the repetition-experiments the mean time falling to one syllable of the groups decreases in the order of the groups. The intervals are less uniform, which is not surprising, if we consider that the first syllable of a group is much more difficult to pronounce than the others, so that the tendency to use rhythm interferes with reproduction-tendencies in different degree.

In the recitation also the mean time, falling to one syllable of one of the groups is longer for the learning-experiments than for the repetition-experiments with I as well as with II. In a much smaller degree this holds good for the intervals; nevertheless their duration is, in the majority of cases, shorter in the repetition- than in the learning-experiments.

The rhythm of the recitation is also kept up better for the groups than for the intervals. It seems moreover that the natural method is more favourable than the experimental to a rhythmic recitation of the learned material.

Physics. — “*On the Fundamental Values of the Quantities b and \sqrt{a} for Different Elements, in Connection with the Periodic System. V. The Elements of the Carbon and Titanium Groups.*”
By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 26, 1917).

A. The Carbon Group.

1. For the calculation of the critical data and the values of a and b following from them the elements of this group offer very few data indeed. Even the situation of the melting point is still insufficiently known for carbon; of other elements the accurate knowledge of the boiling point is wanting. Yet it is exactly this group — though we have often to be satisfied with a rough estimation — that gives a fine confirmation of the fact set forth by me in the preceding papers that the values of \sqrt{a} for elements, which (at least for high temperatures) occur as *separate atoms* and not as molecules (either partially dissociated or not), will suddenly become *very much higher* than the normal (rest) values for compounds.

We already found a first example for *Antimonium* and *Bismuth*, where $\sqrt{a_k}$ (per gramme atom) present instead of the normal rest values 9, resp. $11 \cdot 10^{-2}$ the greatly increased values 32,5 and $36 \cdot 10^{-2}$. The value of $\sqrt{a_k}$ was only *partially* increased for other elements, as Arsenic, Selenium and Tellurium, owing to the fact that these elements are only partially dissociated to separate atoms at the critical temperature.

For the carbon group we find values for $\sqrt{a_k}$ which lie between 32 and $40 \cdot 10^{-2}$, so that *all* these elements appear in the form of separate atoms, as the rest values for $\sqrt{a_k}$, which would hold for compounds, lie much lower, viz. between 3 and $11 \cdot 10^{-2}$.

2. **Carbon.** The melting point lies very high, viz. at 4200° absolute. Probably this is only the sublimation point at 1 atm. pressure. According to LUMMER's interesting experiments, described in a paper published by VIEWEG: “*Verflüssigung der Kohle*”¹⁾, the carbon

¹⁾ Sammlung VIEWEG, Heft 9/10. 1914.

melts namely at the ordinary pressure (see inter alia p. 64—65) exactly at 4200° C. abs. (According to accurate spectrometrical determinations). Though the contents of the said treatise is pretty confused and incoherent from a physico-chemical point of view, and very little indeed can be concluded from what is stated for other pressures, yet this one fact — viz. $T_s = 4200$ — seems pretty firmly established. But then the critical temperature lies certainly not below 6000 à 7000° abs., and $\sqrt{a_k}$ must be at least $= 32 \cdot 10^{-2}$, when $b_k = 100 \cdot 10^{-5}$, as we found before (in I). For the formula

$$RT_k = \frac{8}{27} \lambda \frac{a_k}{b_k},$$

in which (see earlier papers) the factor λ at a temperature of 6470° (see below), where $\gamma = 2,11$, has the value 0,781, so that with $R = 1 : 273,09$ we get:

$$T_k = 80,915 \times 0,781 \frac{a_k}{b_k} = 63,19 \frac{a_k}{b_k},$$

then gives:

$$T_k = 63,19 \times \frac{1024 \cdot 10^{-4}}{10 \cdot 10^{-4}} = \underline{6470^{\circ}} \text{ abs.}$$

We remind of the fact that the factor λ is $= \frac{27}{8\gamma-1} \left(\frac{\gamma}{\gamma+1} \right)^2$, in which γ represents the reduced coefficient of direction of the imaginary straight diameter between D_k and D_0 in a D, T -diagram¹⁾.

It is now the question whether the value of γ is confirmed to some extent by another way. We derived before that $b_k : b_0 = 2\gamma$ (see "New Relations" I). As b_k is expressed in so-called "normal" units, the value of b_k must still be multiplied by 22412, and this product divided by the atomic weight A , to obtain b_k in cm^3 . per gramme. And as $b_0 = v_0 = 1 : D_0$, we get:

$$2\gamma = \frac{b_k \times 22412 \times D_0}{A},$$

so that D_0 can be calculated from

$$D_0 = \frac{2\gamma \times A}{b_k \times 22412},$$

in which (cf. also "New Relations" III) 2γ can be calculated in approximation from the formula

$$\underline{2\gamma = 1 + 0,04 \sqrt{T_k}}.$$

We, therefore, calculate the value $1 + 0,04 \times 80,4 = \underline{4,22}$ for

¹⁾ See for all this my series of papers: "A New Relation, etc." in These Proc. of March 26, April 23, May 29 and Sept. 26 1914; resp. p. 808, 924, 1047 and 451; especially I.

2γ , so that γ has the high value 2,11. [For "ordinary" substances with critical temperature of about 400° to 625° absolute (125° to 350° C.) we find for this the value 0,9 à 1]. For all other elements of the carbon group we shall find values for 2γ , lying between 4 and 3.

Hence we find:

$$D_0 = \frac{4,22 \times 12}{100 \cdot 10^{-5} \times 22412} = \frac{50,6}{22,4} = \underline{2,26.} \text{ (calculated)}$$

For *graphite* (at high temperatures all carbon forms are converted to graphite, and this is therefore the only stable form at T_k) $D = 2,10$ to $2,25$ at ordinary temperatures, according to different statements. Thus among others MOISSAN gives from $2,10$ to $2,25$, MEYER from $2,14$ to $2,25$; LE CHATELIER has found $2,255$ for artificial Acheson-graphite. The value for the limiting density D_0 , *calculated*, by us is therefore in excellent harmony with the experimental value at the ordinary temperature, which will be only very little lower.

The value of p_k is now found from

$$p_k = \frac{1}{27} \lambda \frac{a_k}{b_k^2},$$

in which $\lambda = 0,781$ (see above). Hence with $\sqrt{a_k} = 32 \cdot 10^{-2}$, $b_k = 10 \cdot 10^{-4}$:

$$p_k = 0,0289 \times \frac{1024 \cdot 10^{-4}}{100 \cdot 10^{-8}} = \underline{2970 \text{ atm.}}$$

From the formula

$$\log_{10} \frac{p_k}{p_s} = f_s^{10} \left(\frac{T_k}{T_s} - 1 \right)$$

follows at $T_s = 4200^\circ$ (T_s is properly speaking the boiling point, but probably represents the sublimation point at 1 atm. here) and $p_s = 1$:

$$3,473 = f_s^{10} \left(\frac{6470}{4200} - 1 \right),$$

from which follows $f_s^{10} = 3,473 : 0,540 = 6,43$, i.e. $f_s = 6,43 \times \times 2,303 = \underline{14,8}$. This value is very well possible, as according to one of our formulae (see "New Relations" I) $f_k = 8\gamma$, when a and b at T_k are independent of T , so that f_k would be $= \underline{16,9}$. And f_s is always somewhat smaller than f_k .

If T_k is really $= 6470^\circ$ abs., $T_k : T_s$ would be $= \underline{1,54}$ for carbon.

3. Silicium. If we assume here $\sqrt{a_k} = 34 \cdot 10^{-2}$, we get with $\lambda = 0,816$ ($2\gamma = 3,81$, see below) and $b_k = \underline{155} \cdot 10^{-5} = 15,5 \cdot 10^{-4}$;

$$T_k = \frac{66,03 \times 1156}{15,5} = \underline{4920^\circ \text{ abs.}}$$

The melting point, lying at $1426^\circ \text{ C.} = 1699^\circ \text{ abs.}$ (98,9% Si) according to DOERINCKEL (1906), $T_k: T_r$ would be $= \underline{2,90}$.

If we repeat the above check-calculation (§ 2), it follows (2γ becoming $= 1 + 0,04 \times 70,2 = \underline{3,81}$) that

$$D_0 = \frac{3,81 \times 28,3}{155 \cdot 10^{-5} \times 22412} = \frac{107,8}{34,74} = \underline{3,10}. \text{ (calculated)}$$

This value seems somewhat too high, as at the ordinary temperature for Si values have been found in the neighbourhood of 2,50 (WÖHLER gives 2,49; in RUDORF's book on the periodic system we find 2,48; etc.), but these earlier values may be too low.

For p_k we find with $\lambda = 0,816$ (see above):

$$p_k = \frac{0,0302 \times 1156 \cdot 10^{-4}}{240,25 \cdot 10^{-8}} = \underline{1450 \text{ atm.}}$$

If we assume the value 1,6 for the ratio $T_k: T_s$, T_s (the boiling point) would be about 3080° abs. V. WARTENBERG's value (1902), viz. $> 1205^\circ \text{ C.}$ (the melting point n.b. lying as high as 1426° C.), is therefore rather euphemistic.

The value $f_s^{10} = 3,161 : 0,6 = 5,27$, hence $f_s = \underline{12,1}$, would correspond with $T_s = 3100^\circ$. For f_k may be expected $f_k = 8\gamma = \underline{15,2}$.

4. Germanium. With $\sqrt{a_k} = 36 \cdot 10^{-2}$ we find ($\lambda = 0,835$, as 2γ is $= 3,58$), b_k being $= \underline{210 \cdot 10^{-5}}$:

$$T_k = \frac{67,56 \times 1296}{21,0} = \underline{4170^\circ \text{ abs.}}$$

According to BILTZ (1911) the melting point lies at $958^\circ \text{ C.} = 1231^\circ \text{ abs.}$, hence $T_k: T_r$ would here be $= \underline{3,39}$.

For 2γ is found $2\gamma = 1 + 0,04 \times 64,6 = \underline{3,58}$, so that we calculate:

$$D_0 = \frac{3,58 \times 72,5}{210 \cdot 10^{-5} \times 22412} = \frac{259,6}{47,07} = \underline{5,52}. \text{ (calculated)}$$

WINKLER found 5,47 for 20° C. , so that the agreement is again striking.

We further calculate for p_k :

$$p_k = \frac{0,0309 \times 1296 \cdot 10^{-4}}{441 \cdot 10^{-8}} = \underline{910 \text{ atm.}}$$

With $T_k: T_s = 1,6$ we should find about 2600° abs. for T_s . RUDORF gives $T_s > 1300^\circ \text{ C.}$ Remark as above for Silicium.

For f_s^{10} we calculate $2,959 : 0,6 = 4,93$, hence $f_s = \underline{11,4}$, while f_k would be $= \underline{14,3}$.

5. **Tin.** When we put $\sqrt{a_k}$ again 2 units higher, viz. $\sqrt{a_k} = 38 \cdot 10^{-2}$, we calculate with $b_k = 265 \cdot 10^{-5}$, $2\gamma = 3,44$ (see below), $\lambda = 0,847$:

$$T_k = \frac{68,54 \times 1444}{26,5} = \underline{3730} \text{ abs.}$$

At the time (1887) GULDBERG calculated the too low value 3000° abs. from various data.

For 2γ we find $1 + 0,04 \times 61,1 = \underline{3,44}$, and thus we have:

$$D_0 = \frac{3,44 \times 118,7}{265 \cdot 10^{-5} \times 22412} = \frac{408,3}{59,4} = \underline{6,87}. \text{ (calculated)}$$

At $-163,4$ COHEN and OLIE (Zeitschr. f. ph. Ch. **71**, 400; 1909) found for white tin 7,35 and for grey tin 5,77. The value calculated by us lies near that of white (tetragonal) tin, which is stable at higher temperature. TRECHMANN (1880) found the value 6,5 to 6,6 for the density of the rhombic tin, which is stable above 161° . Our value 6,9 lies, therefore, between that of tetragonal (7,3) and rhombic tin (6,6)¹⁾.

And now the vapour pressure determinations, made by GREENWOOD in 1911 (Z.f. ph. Ch. **76**, 484). Let us, however, first calculate the probable value of the critical pressure.

For this we find:

$$p_k = \frac{0,0314 \times 1444 \cdot 10^{-4}}{702,25 \cdot 10^{-8}} = \underline{650} \text{ atm.}$$

As GREENWOOD found $2270^\circ \text{ C.} = 2543^\circ$ abs. for the boiling point, the ratio would be $T_k : T_s = 1,47$, which is too low in my opinion, so that either the temperature is still higher than 3700° , or — what in connection with what will appear for lead, is by no means improbable — the boiling temperature determined by GREENWOOD has been given too high (or the vapour pressure at that temperature too low). If 2543° were correct, a value about equal to $2543 \times 1,6 = 4100^\circ$ abs. might be expected for T_k , in consequence of which also $\sqrt{a_k}$ would have to be raised to about $40 \cdot 10^{-2}$ instead of $38 \cdot 10^{-2}$.

If the value 3730° , calculated by us, is correct, the ratio $T_k : T_{tr}$

¹⁾ When we take the density of *liquid* tin at the melting point, viz. 6,99 (VICENTINI and OMODEI, 1888), as standard, we might certainly expect D_0 to be > 7 . But then it is overlooked that the solid rhombic modification, which has the density 7,2 at the melting point (232°), has the so much *smaller* density 6,5 à 6,6 at the ordinary temperature. Abnormal changes of density are, therefore, also to be expected in the *liquid* phase at decreasing temperature, if this phase could be realized below the melting point.

becomes $= 3730 : 505 = \underline{7,4}$, which is very high; with $T_k = 4100^\circ$ or still higher this ratio would even become 8 or 9.

GREENWOOD's vapour pressure determinations gave the following result.

$T = 2243$	2373	2543 abs.
$p = 0,133$	$0,345$	1 atm.

From the well-known formula $\log \frac{p_k}{p} = f \left(\frac{T_k}{T} - 1 \right)$ or $\log p =$
 $= (f + \log p_k) - \frac{f T_k}{T}$ we find:

$$f + \log p_k = \frac{T_2 \log p_2 - T_1 \log p_1}{T_2 - T_1},$$

every time from two successive observations (between which f is supposed constant), after which $f T_k$ can further be calculated from $f T_k = T(f + \log p_k) - T \log p$. Thus we find from

$$\begin{array}{l|l|l} \log^{10} p = 0,12385(-1) & 0,53782(-1) & 0 \\ T \log^{10} p = 277,8-2243 & 1276-2373 & 0 \end{array}$$

resp. $f^{10} + \log^{10} p_k = 6,681$ and $6,453$; $f^{10} T_k = 16950$ and 16410 . (GREENWOOD calculates for this the too low values $29 : 4,571 = 6,344$ and $73900 : 4,571 = 16167$).

Hence f^{10} becomes resp. $= 3,868$ and $3,640$ with $p_k = 650$ atm., $\log^{10} p_k = 2,813$, from which 4380 , resp. 4510 , mean 4450° would follow for T_k . And a modification, even a considerable one, in the assumed value of p_k has little influence on this.

The value of f_s^{10} lies here, therefore, in the neighbourhood of $3,75$, i.e. f_s in that of $8,6$. This value seems too low to us, as $2\gamma = 3,44$ already corresponds with the critical temperature $T_k = 3730^\circ$, so that f_k then would be $= \underline{13,8}$. And 2γ would be $= 3,7$ with 4500° , i.e. $f_k = 14,8$. Everything points therefore to the fact that the boiling point determined by GREENWOOD is too high, or rather that the vapour pressures determined by him, have been given too low.

If we retain the value $T_k = 3730^\circ$, calculated by us, the real boiling point temperature T_s would be $= \underline{2330^\circ}$ abs. with $T_k : T_s = 1,6$, instead of 2543° abs. as GREENWOOD gives, and the value f_s^{10} would then be $= 4,69$, i. e. $f_s = \underline{10,8}$.

6. Lead. If we assume here $\sqrt{a_k} = 40 \cdot 10^{-5}$, and $b_k = 320 \cdot 10^{-5}$ again 55 units higher than tin, though this cannot be ascertained in default of compounds, the critical temperature and pressure of which are known), we get with $2\gamma = 3,35$, $\lambda = 0,855$:

$$T_k = \frac{69,16 \times 1600}{32,0} = \underline{3460^\circ} \text{ abs.}$$

The value of 2γ is then $= 1 + 0,04 \times 58,8 = \underline{3,35}$, and we find for D_0 :

$$D_0 = \frac{3,35 \times 207,2}{320 \cdot 10^{-5} \times 22412} = \frac{694,2}{71,72} = \underline{9,68} \text{ (calculated)}$$

D has been found $= 11,4$ at the ordinary temperature, so that $9,7$ would be about 15 % too low — unless lead, like tin, is converted to a less dense modification at lower temperature. COHEN and HELDERMAN's researches (cf. among other things *Z. f. ph. Chem.* **74**, 202 (1910) and **89**, 733 (1915)) suggest already the existence of even more than two allotropic forms.

We find for the critical pressure:

$$p_k = \frac{0,0317 \times 1600 \cdot 10^{-4}}{1024 \cdot 10^{-8}} = \underline{490} \text{ atm.}$$

For the boiling point GREENWOOD (1911) found $1525^\circ \text{ C.} = 1798^\circ \text{ abs.}$; v. WARTENBERG (1908) found $1580^\circ \text{ C.} = 1853^\circ \text{ abs.}$ The two values do not differ much. If we assume the mean value $T_s = 1825^\circ \text{ abs.}$ as correct, $T_k : T_s$ becomes $= \underline{1,90}$, which is very high, and f_s^{10} becomes $= 2,69 : 0,9 = 2,99$, i. e. $f_s = \underline{6,9}$, whereas $f_k = 8\gamma = \underline{13,4}$ is expected. The value of f_s would, therefore, be much too low. And as $T_{tr} = 327^\circ,3 \text{ C.} = 600^\circ,4 \text{ abs.}$, $T_k : T_{tr}$ would become $\underline{5,76}$. Possibly the critical temperature has been assumed somewhat too high. From GREENWOOD's vapour pressure determinations a temperature would follow for T_k somewhat below 3000° . But then b_k must not be assumed to be $= 320 \cdot 10^{-5}$, but e. g. again 55 units higher, hence $b_k = \underline{375} \cdot 10^{-5}$. In virtue of the Cerium-Tantalum period, inserted after the tin, this may not be improbable. With $2\gamma = \underline{3,19}$, $\lambda = 0,868$ we should then have obtained for T_k the value $70,23 \times 1600 : 37,5 = \underline{3000^\circ} \text{ abs.}$, in perfect agreement with GREENWOOD's experiments. But a still lower value would then be calculated for D_0 , viz. $660,9 : 84,05 = \underline{7,86}$. The value of p_k would be $= 0,0321 \times 1600 \cdot 10^{-4} : 1406,25 \cdot 10^{-8} = \underline{370} \text{ atm.}$, and the two ratios $T_k : T_s$ and $T_k : T_{tr}$ would be found resp. $= \underline{1,64}$ and $\underline{5}$.

GREENWOOD's determinations now gave what follows.

$T = 1588$	1683	1798	2143	2373 abs.
$p = 0,138$	0,350	1,0	6,3	11,7 atm.
$\log^{10} p = 0,13988(-1)$	0,54407(-1)	0	0,79934	1,06819
$T \log^{10} p = 222,1-1588$	915,7-1683	0	1713	2535

A similar calculation as that for tin yields between each successive couple of observations:

$$\begin{array}{r|rr} f^{10} + \log^{10} p_k = & 6,301 & 6,672 & 4,965 & 3,573 \\ f^{10} T_k = & 11372 & 11996 & 8927 & 5944 \end{array}$$

From the two last calculated values for $f^{10} + \log^{10} p_k$ and $f^{10} T_k$ appears the inaccuracy of GREENWOOD's vapour pressure determinations, especially at temperatures higher than 2000° abs. (the same herefore as for tin). For as $\log^{10} p_k = 2,69$ to $2,57$, hence on an average about $2,63$, it would follow from the last determinations that f^{10} is $= 2,34$ to $0,94$, which is quite impossible. And if reversely we take the probable value \pm for f^{10} , the much too low values 2200° to 1500° abs. would follow for T_k from the said determinations. Accordingly, both for tin and for lead, we must reject the vapour pressure determinations above 2000 as quite erroneous. If we only take into account those below 2000° , we find with $\log^{10} p_k = 2,63$ the values $f^{10} = 3,67$, resp. $4,04$, yielding $T_k = 3100$ to 2970° , mean 3035° abs.; in excellent agreement with the value of T_k computed by us, when $b_k = 375 \cdot 10^{-5}$ is assumed (viz. 3000°). Very little in agreement, however, with the calculated value of T_k on the assumption of $b_k = 320 \cdot 10^{-5}$, viz. 3460° abs. It is really difficult to make a choice here; we do not know in how far GREENWOOD's observations below 2000° are reliable. That, however, v. WARTENBERG found an only slightly divergent value for the boiling point, is a reason to assume the middle value 1825° for the boiling point as pretty accurate. But then the critical temperature can probably not be higher than 2900° or 3100° . (According as $T_k : T_s$ is taken $1,6$ or $1,7$). If we, therefore, retain the value 3000° abs.¹⁾, which was obtained with $b_k = 375 \cdot 10^{-5}$, $T_k : T_s$ becomes $= 1,64$. As $\log^{10} 370 = 2,57$, f_s^{10} becomes $= 2,57 : 0,64 = 4,0$, i. e. $f_s = 9,2$, while the value $12,8$ is expected for $f_k = 4 \times 2\gamma$. (With $\log^{10} p_k = 2,57$ the value $3,73$, resp. $4,10$ follows for f_s^{10} from GREENWOOD's observations, which is in good harmony with the above mentioned value $4,0$).

7. Recapitulation. Combining the values of $\sqrt{a_k}$, b_k , T_k , p_k , etc., found above for the elements of the carbon group, in a comprehensive table, we get the following survey. For lead we have given

¹⁾ GOLDBERG (1887) gives also for lead the much too low value $T_k = 2000$ abs. For mercury the same: 1000° abs., which is also too low.

	$\sqrt{a_k \cdot 10^2} b_k \cdot 10^5$	T_k (abs.)	p_k (atm.)	z_i	γ	D_0 (calc.)	D_0 (found)	T_s	T_{tr}	$\frac{T_k}{T_s}$	$\frac{T_k}{T_{tr}}$	f_s	f_k	
C	32	100	6470	2970	4,22	0,781	2,26	2,255	4200	—	1,54	—	14,8	16,9
Si	34	155	4920	1450	3,81	0,816	3,10 ?	2,50	(3080)	1700	(1,6)	2,9	(12,1)	15,2
Ge	36	210	4170	910	3,58	0,835	5,52	5,47	(2600)	1230	(1,6)	3,4	(11,4)	14,3
Sn	38	265	3730 4450 ? (from Gr.)	650	3,44	0,847	6,87	6,6 à 7,3	(2330) 2543 ? (Gr.)	505	(1,6)	7,4	(10,8)	13,8
Pb	40	(320) 375	3460 ? 3000 (from Gr.)	490 370	3,35 3,19	0,855 0,868	9,68 ? 7,86 ?	11,4	1825	600	1,90 ? 1,64	5,8 5,0	6,9 ? 9,2	13,4 12,8

both the values corresponding with $b_k = 320 \cdot 10^{-5}$ and those corresponding with $b_k = 375 \cdot 10^{-5}$.

B. The Minor-group Titanium, Zircon, Cerium, Thorium.

8. Titanium. Let us in conclusion briefly discuss the minor-

group of Titanium. Here data are still more greatly wanting, as we have not even an idea of the probable values of b_k through compounds of which the critical temperature has been determined. We can, therefore, only assume them in approximation between those of the elements of the principal group. Thus we might put:

	<i>Ti</i>	<i>Zr</i>	<i>Ce</i>	<i>Th</i>
$b_k \cdot 10^5 =$	182,5	237,5	292,5	402,5
$\sqrt{a_k} \cdot 10^3 =$	35	37	39	41

With respect to Titanium we find with $2\gamma = 3,68$, $\lambda = 0,827$:

$$T_k = \frac{66,92 \times 1225}{18,25} = \underline{4490^\circ \text{ abs.}}$$

In consequence of this $2\gamma = 1 + 0,04 \times 67,0$ becomes $= \underline{3,68}$. We then calculate for D_0 :

$$D_0 = \frac{3,68 \times 48,1}{182,5 \cdot 10^{-5} \times 22412} = \frac{177,0}{40,90} = \underline{4,33} \text{ (calculated)}$$

At ordinary temperatures WEISZ and KAISER (1910) found 3,99 (amorph, 85,65 %, i.e. 3,2 % O, + 11,15 % iron) and 5,17 (molten 97,4%). MOISSAN (1895) and MEIJER (1899) found 4,87 (molten 2% C). At last HUNTER found the value 4,50 (100%) in 1910. The real value will, therefore, no doubt lie in every case between 4 and 5, so that the value calculated by us is again in fairly good agreement.

For the melting point BURGESS and WALTENBERG (1914) found 1795°, HUNTER (1910) from 1800° to 1850°. If we take the round value 1800° C. = 2073° abs., $T_k : T_r$ becomes $= \underline{2,17}$. We have finally for p_k :

$$p_k = \frac{0,0306 \times 1225 \cdot 10^{-4}}{333,06 \cdot 10^{-8}} = \underline{1130 \text{ atm.}}$$

9. **Zircon.** Here we have with $2\gamma = 3,51$, $\lambda = 0,841$:

$$T_k = \frac{68,09 \times 1369}{23,75} = \underline{3920 \text{ abs.}}$$

From this follows $2\gamma = 1 + 0,04 \times 62,7 = \underline{3,51}$, so that for D_0 we calculate:

$$D_0 = \frac{3,51 \times 90,6}{237,5 \cdot 10^{-5} \times 22412} = \frac{317,6}{52,72} = \underline{6,02} \text{ (calculated)}$$

This is again in fairly good harmony with the experimentally found value, viz. 5,95 to 6,39 (WEDEKIND and LEWIS, 1910), and 6,40 (WEISZ and NEUMANN, 1910). The former two authors worked resp. with powdery (96,5 %) and molten Zircon (91,3 to 96,5 %);

the two latter with almost pure molten material (99,7 to 100 %). The value calculated by us seems to be slightly too low. Possibly b_k may be assumed too high.

For the boiling point the exceedingly high temperature 2350° (97 %), i. e. 2623° abs., has been found by v. BOLTON (1910), and also by WEDKIND and LEWIS (1910), so that then $T_k : T_t$ would amount to $\approx 1,50$. Also from this too low amount it would follow that the critical temperature has been calculated too low in consequence of the value of b_k , which has been assumed too high.

If for $b_k \cdot 10^5$ instead of 237,5 we assume the value 210, which also holds for Germanium, T_k becomes about 4400° , and the ratio $T_k : T_t$ rises from 1,5 to 1,7, the calculated limiting density becoming slightly greater than 7, somewhat too great therefore.

We calculate for p_k :

$$p_k = \frac{0,0312 \times 1369 \cdot 10^{-4}}{564,06 \cdot 10^{-8}} = \underline{760} \text{ atm.}$$

10. Cerium. As $2\gamma = 3,39$, $\lambda = 0,851$, we calculate:

$$T_k = \frac{68,86 \times 1521}{29,25} = \underline{3580^\circ} \text{ abs.}$$

For 2γ follows from this $2\gamma = 1 + 0,04 \times 59,8 = \underline{3,39}$, so that we get:

$$D_s = \frac{3,39 \times 140,25}{292,5 \times 22412} = \underline{7,25} \text{ (calculated)}$$

6,92 (98 %) was found by HIRSCH (1912), and 7,04 by MUTHMANN and WEISZ (1904). The calculated value may possibly be somewhat too high.

As for the melting point 635° (98 %) was found by HIRSCH, and 623° C. by MUTHMANN and WEISZ, we may assume the middle value 629° C. $\approx 902^\circ$ abs. to be pretty accurate, so that $T_k : T_t$ becomes $\approx 3,97$.

For p_k we find:

$$p_k = \frac{0,0315 \times 1521 \cdot 10^{-4}}{855,6 \cdot 10^{-8}} = \underline{560} \text{ atm.}$$

11. Thorium. As 2γ appears to be $\approx 3,17$, and therefore λ is $\approx 0,870$, we get:

$$T_k = \frac{70,40 \times 1681}{40,25} = \underline{2940^\circ} \text{ abs.}$$

This makes 2γ really $\approx 1 + 0,04 \times 54,2 = \underline{3,17}$, and we find for D_s :

$$D_0 = \frac{3,17 \times 232,15}{402,5 \cdot 10^{-5} \times 2,412} = \frac{735,9}{90,21} = \underline{8,16} \text{ (calculated)}$$

This value agrees pretty well with the earlier density determinations (1863), which gave 7,7 or 7,8 — but badly with the later ones by NILSON (1882), who found 11,0, and those by v. BOLTON (1908), who even found 12,2. The value of b_k has, therefore, possibly been assumed too high.

This is also evident from the value of $T_k : T_{tr}$. For the melting point WARTENBERG (1910) found, namely, 1700 to 1755° C. (The Thorium contained only 0,15 % C.). If we assume 1727° C., i. e. 2000° abs., $T_k : T_{tr}$ would become = 1,47, which seems again too low. The same thing, therefore, as for Zircon. If instead of $402,5 \cdot 10^{-5}$ we assume for b_k the value $375 \cdot 10^{-5}$, which also holds for lead, T_k becomes somewhat higher, and then a value in the neighbourhood of 9,5 follows for D_0 , hence still too low.

Finally we find for p_k :

$$p_k = \frac{0,0322 \times 1681 \cdot 10^{-4}}{1620 \cdot 10^{-8}} = \underline{330} \text{ atm.}$$

12. Recapitulation. When we recapitulate what was found here, in a table, we get the following survey.

	$\sqrt{a_k} \cdot 10^2$	$b_k \cdot 10^5$	T_k (abs.)	p_k (atm.)	2γ		D_0 (calc.)	D_0 (found)	$\frac{T_k}{T_{tr}}$
Ti	35	182,5?	4490	1130	3,68	0,827	4,33	4 à 5	2,2
Zr	37	237,5?	3920	760	3,51	0,841	6,02	6 à 6,4	1,5?
Ce	39	292,5?	3580	560	3,39	0,851	7,25	6,9 à 7,0	4,0
Th	41	402,5?	2940	330	3,17	0,870	8,16?	8 à 12	1,5?

12. Conclusion. It follows most convincingly from all that precedes that — in order to determine the elements of the carbon group (and of the Titanium group) — the values of the *molecular attractions* $\sqrt{a_k} \cdot 10^{-2}$ must be taken *very high*, ranging from **32** for carbon to **40** for lead. These values are *very much higher* than the *residual attractions* for the *compounds* of these elements, which range from 3 to 11, as we saw before. (See I to IV). This means, therefore, simply that we have to do here with **free atoms** which exhibit a so much greater attraction than the bound atoms in the molecule.

Thus $\sqrt{a} = 0$ e.g. for carbon, which is surrounded symmetrically on all sides by atoms or atom groups, as in CH_4 , CCl_4 , C_2H_6 etc. For doubly bound C, as for C_2H_4 , C_6H_6 , $\text{C}_4\text{H}_4\text{S}$, we find $\sqrt{a} = 1,55 \cdot 10^{-5}$; whereas for triple bound C, as for C_2H_2 (likewise for CO , CO_2 , CS_2 , etc.), the *full* residual value $\sqrt{a} = 3,1 \cdot 10^{-5}$ is found (see I). But only for the *free* atoms in the *element* carbon (C_1) we find the so much higher, *ten times* higher value $\sqrt{a} = 32 \cdot 10^{-2}$.

And the small deviations between theory and experiment which still remain cannot detract from this fact — not for the other elements either. Whether the value 32 will perhaps have to be replaced by 33 in the end, or the value 40 by 41 or 42 — this does not affect the above in the least. And it is noteworthy that also the elements of the minor-group Ti, Zr, Ce, Th., of which so little is known, yet confirm this important fact in the clearest way. Besides we found this already indubiously expressed for *Antimonium* and *Bismuth* (see IV) with $\sqrt{a_k} = 32,5$, resp. $36 \cdot 10^{-2}$.

As far as the values of b_k are concerned, they appear to be the same as those which are also calculated from the compounds (if present) — which might have been expected beforehand.

In my next paper I hope to treat the exceedingly important elements of the group of the *alkali-metals*, besides those of the minor-group Cu, Ag, Au.

Clarens, May 1917.

Physics. — “*On the Fundamental Values of the Quantities b and \sqrt{a} for Different Elements, in Connection with the Periodic System. VI. The Alkali Metals*”. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of June 30, 1917)

1. After the group of the noble gases, the halogens, the elements of the oxygen and nitrogen groups, and those of the carbon group, we will, for practical reasons, first treat the group of the alkali metals, and not until after this can we treat the intermediate Beryllium and Borium groups, and the remaining minor groups with some certainty.

The task undertaken by us to compute with some certainty the values of the critical quantities, and those of b_k and $\sqrt{a_k}$, with the required accuracy, gets more and more difficult. For the alkali metals e.g. *compounds* of which the boiling point or the critical temperature are known, are entirely wanting, and thus we are deprived of a valuable test. *Nothing* is known beforehand that could be used in any way as a foundation; everything must be calculated anew, estimated, weighed, and considered. For an element as recalcitrant as e.g. Carbon or Silicium, the critical temperature of which is quite inaccessible, we know at least the value of b_k from *compounds*, from which — in connection with other data — the values of a_k , T_k and p_k can be calculated with almost mathematical certainty.

This is not the case for the alkali metals. Here nothing is known beforehand concerning b_k , and in most cases we shall therefore have to be satisfied with defining limits between which the required values of b_k and $\sqrt{a_k}$ must lie. Fortunately these limits are comparatively narrow, particularly when the course of the vapour tension curve is sufficiently known, so that the values calculated by us can yet lay claim to a satisfactory degree of accuracy.

It will appear that for the alkali metals we are very near the truth with respect to the critical temperature, when we multiply the absolute temperature of the melting point by $5\frac{1}{3}$, and that of the boiling point by 1,7. Thus we have the following survey.

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	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>
$T_{tr} =$	452,1	370,6	335,6	311,6	301,3
$T_s =$	—	1156,0	1035,3	971,1	943,1
$T_{tr} \times 5^{1/3} =$	2411	1977	1790	1652	1607
$T_s \times 1,7 =$	—	1965	1750	1651	1603
$T_{tr} \times 4^{2/3} =$	—	1729	1566	1452	1406
$T_s \times 1,5 =$	—	1734	1554	1457	1415

And now we shall see in what follows that — at least for *Na*, *K*, *Rb* and *Cs* — the real values of T_k lie between those obtained with the factors $5^{1/3}$ and 1,7, and those obtained with the factors $4^{2/3}$ and 1,5. Generally nearer to the first group. Besides we know already from former considerations that the factor by which the absolute boiling point temperature must be multiplied to obtain the absolute critical temperature, lies in the neighbourhood of 1,7. This factor can also be smaller, but it seldom becomes smaller than 1,5. For Lithium, there is reason to suppose that T_k lies probably *higher* than would follow from $T_{tr} \times 5^{1/3}$. The factor is there with pretty great certainty = 5,6.

It is certainly rather remarkable that the ratio $T_s : T_{tr}$ is so constant for the alkali metals, viz. about $3^{1/3}$.

2. Lithium. The melting point lies at $1790^\circ \text{C.} = 452,1^\circ \text{ abs.}$ According to the above we may expect the critical temperature between $452,1 \times 5^{1/3} = 2411^\circ$ and $452,1 \times 5 = 2713^\circ \text{ abs.}$ We shall perform the subjoined calculations for both values of T_k , rounded off to 2410° and 2700° .

The value of γ follows from our formula $2\gamma = 1 + 0,038 \sqrt{T_k}$. It gives with $\sqrt{T_k} = 49,09$ to $51,96$ the values 2,865 and 2,975, i.e. $\gamma = 1,43$ to $1,49$. This is accordingly the (reduced) coefficient of direction of the straight diameter between D_k and D_0 .

From formula $\lambda = \frac{27}{8\gamma - 1} \left(\frac{\gamma}{\gamma + 1} \right)^2$, with $\frac{\gamma}{\gamma + 1} = 0,589$ or $0,598$, hence $\left(\frac{\gamma}{\gamma + 1} \right)^2 = 0,347$ or $0,358$, and with $8\gamma - 1 = 10,46$ or $10,90$ we further find the values $\lambda = 0,895$ or $0,886$ for the factor λ in $RT_k = \frac{8}{27} \lambda \frac{a_k}{b_k}$ and $p_k = \frac{1}{27} \lambda \frac{a_k}{b_k^2}$. This renders $\varphi = \frac{8}{27} \lambda : R$ with

$R = 1 : 273,1$ resp. $= 72,44$ to $71,67$ (the value $\frac{8}{27} : R$ is $= 80,915$).

Let us now calculate the value of b_k . From $b_k : b_0 = 2\gamma$ follows with $b_0 = v_0 = 1 : D_0$:

$$b_k = \frac{2\gamma}{D_0}, \quad \text{or} = \frac{2\gamma \times A}{D_0 \times 22412},$$

when b_k is calculated in "normal" units, and per Gr. atomic weight. We must, therefore, know D_0 . From the relation for the ideal straight diameter (while namely the vapour density can be neglected) $D = D_0 - 2\gamma D_k \frac{T}{T_k}$ follows with $D_k = \frac{D_0}{2(1+\gamma)}$:

$$D = D_0 \left(1 - \frac{\gamma}{1+\gamma} \frac{T}{T_k} \right).$$

Unfortunately, however, the liquid density for Lithium is unknown. But $D = 0,5935$ holds for solid Lithium at 15°C . For liquid Lithium D is therefore slightly smaller than this value, perhaps 2% smaller. Thus we have:

$$\left. \begin{aligned} < 0,5935 = D_0 \left(1 - 0,589 \times \frac{288}{2410} \right) = 0,930 D_0 \\ \text{or} = D_0 \left(1 - 0,598 \times \frac{288}{2700} \right) = 0,936 D_0 \end{aligned} \right\}$$

so that D_0 becomes $< 0,638$ or $< 0,634$ (according as $T_k = 2410^\circ$ or 2700° abs.) Hence

$$\left. \begin{aligned} b_k > \frac{2,865 \times 6,94}{0,638 \times 22412} = \frac{19,88}{14310} = 139 \cdot 10^{-5} \\ \text{or } b_k > \frac{2,975 \times 6,94}{0,634 \times 22412} = \frac{20,64}{14210} = 145 \cdot 10^{-5} \end{aligned} \right\}$$

The value of b_k can therefore be at most 2% greater, i.e. from 142 to $148 \cdot 10^{-5}$. Now $b_k = 55$ for F , $= 70$ for O , $= 85$ for N , $= 100 \cdot 10^{-5}$ for C .; we might, therefore, expect for B the value 115 , for Be 130 , and for Li the value $145 \cdot 10^{-5}$. If this last value is correct, T_k would have to lie between 2400° and 2700° for Lithium, e. g. it would be about 2550° .

Now the value a_k follows from

$$a_k = \frac{T_k \times b_k}{\varphi},$$

in which $\varphi = \frac{8 \lambda}{27 R}$ (see above). This gives:

$$\left. \begin{aligned} \alpha_k &> \frac{2410 \times 13,9 \cdot 10^{-4}}{72,44} = \frac{33500}{72,44} 10^{-4} = 462,5 \cdot 10^{-4} \\ \text{or } \alpha_k &> \frac{2700 \times 14,5 \cdot 10^{-4}}{71,67} = \frac{39150}{71,67} 10^{-4} = 546,3 \cdot 10^{-4} \end{aligned} \right\}$$

from which we find:

$$\sqrt{\alpha_k} > 21,5 \text{ or } > 23,4 \cdot 10^{-2} \text{ (e.g. } \sqrt{\alpha_k} = 21,7 \text{ à } 23,6 \cdot 10^{-2}\text{)}.$$

For p_k immediately follows from (as $8 : R = 8 \times 273,1 = 2185$)

$$p_k = \frac{T_k}{2185 \times b_k}$$

the value

$$\left. \begin{aligned} p_k &= \frac{2410}{2185 \times 142 \cdot 10^{-5}} = \frac{2410}{3,103} = 777 \text{ atm.} \\ \text{or } p_k &= \frac{2700}{2185 \times 148 \cdot 10^{-5}} = \frac{2700}{3,234} = 835 \text{ ,,} \end{aligned} \right\}$$

from which $\log^{10} p_k = 2,890$ to $2,922$ follows, which we should want, when a series of vapour pressures above the melting point were known of Lithium. But of this exceptional element literally nothing more is known than the melting point and the density at 15° C . Not even the boiling point or the density at the melting point. Still less the coefficient of expansion in solid and liquid state.

3. Sodium. Here we tread on firmer ground. The melting point lies at $97,5^\circ \text{ C} = 370,6$ abs. The boiling point lies at $882,9^\circ \text{ C} = 1156^\circ$ abs. according to HEYCOCK and LAMPLUGH (1912). (RUFF and JOHANNSEN gave $877,5^\circ \text{ C}$ in 1905). Hence the critical temperature lies in the neighbourhood of $370,6 \times 5^{1/2} = 1977$, resp. $1156 \times 1,7 = 1965$, mean 1970° abs.; or, as lowest limit, in that of $370,6 \times 4^{1/2} = 1729$, resp. $1156 \times 1,5 = 1734$, mean 1730° abs. We carry out the calculations again at these two temperatures.

With $\sqrt{T_k} =$ from 44,38 to 41,59, we find from our formula (see for Lithium) $2\gamma =$ from 2,686 to 2,580, yielding $\gamma = 1,34$ to 1,29. For $\gamma : (1 + \gamma)$ we find further 0,573 to 0,563, hence for $\gamma^2 : (1 + \gamma)^2$ the values from 0,329 to 0,317, so that the factor λ becomes from 0,910⁵ to 0,919, and φ from 73,67 to 74,38.

VICENTINI and OMODEI (1888) found 0,9287 (liquid) for the density at the melting point $97,6$, so that D_0 can be calculated from

$$\left. \begin{aligned} 0,9287 &= D_0 \left(1 - 0,573 \times \frac{370,7}{1970} \right) = 0,892 D_0 \\ \text{or} &= D_0 \left(1 - 0,563 \times \frac{370,7}{1730} \right) = 0,879 D_0 \end{aligned} \right\}$$

yielding $D_0 = 1,041$ to $1,056$.

Then b_k becomes:

$$\left. \begin{aligned} b_k &= \frac{2,686 \times 23,0}{1,041 \times 22412} = \frac{61,78}{23330} = 265 \cdot 10^{-5} \\ \text{or } b_k &= \frac{2,580 \times 23,0}{1,056 \times 22412} = \frac{59,34}{23670} = 251 \cdot 10^{-5} \end{aligned} \right\}$$

We find for a_k :

$$\left. \begin{aligned} a_k &= \frac{1970 \times 26,5 \cdot 10^{-4}}{73,67} = \frac{52210}{73,67} 10^{-4} = 708,7 \cdot 10^{-4} \\ \text{or } a_k &= \frac{1730 \times 25,1 \cdot 10^{-4}}{74,38} = \frac{43420}{74,31} 10^{-4} = 583,8 \cdot 10^{-4} \end{aligned} \right\}$$

so that we have $\sqrt{a_k} = 26,6$ to $24,2 \cdot 10^{-2}$.

We calculate for the critical pressure:

$$\left. \begin{aligned} p_k &= \frac{1970}{2185 \times 265 \cdot 10^{-5}} = \frac{1970}{5,790} = 340 \text{ atm.} \\ \text{or } p_k &= \frac{1730}{2185 \times 251 \cdot 10^{-5}} = \frac{1730}{5,484} = 315,5 \text{ " } \end{aligned} \right\}$$

which renders $\log^{10} p_k =$ from 2,532 to 2,499.

The found values of γ , viz. 1,34 to 1,29, may be tested, however little, by the experimentally found value of the *coefficient of expansion* α in *liquid* state. In order to reduce α to γ we can derive the following relation. From

$$\alpha = \frac{1}{v_1} \frac{v_2 - v_1}{t_2 - t_1}$$

follows immediately:

$$\alpha = D_1 \frac{\frac{1}{D_2} - \frac{1}{D_1}}{t_2 - t_1} = \frac{1}{D_2} \frac{D_1 - D_2}{t_2 - t_1},$$

so that the quantity γ' in $D_1 - D_2 = \gamma' (t_2 - t_1)$ is found from

$$\gamma' = \alpha \times D_2, \text{ or } \alpha \text{ from } \alpha = \frac{\gamma'}{D_2}.$$

Now (reduced) $d_1 - d_2 = 2 \gamma (m_2 - m_1)$, when the vapour densities can be neglected, hence as $d = D : D_k$ and $m = T : T_k$, also $D_1 - D_2 = 2 \gamma \frac{D_k}{T_k} (T_2 - T_1)$, so that we have:

$$\gamma' = 2\gamma \frac{D_k}{T_k},$$

and

$$\alpha = 2\gamma \frac{D_k}{D_s} \frac{1}{T_k}$$

But $D_s = D_s \left(1 - \frac{\gamma}{1 + \gamma} \frac{T_2}{T_k}\right)$, and $D_k = \frac{D_0}{2(1 + \gamma)}$, so that

$$\alpha = \frac{\frac{\gamma}{1 + \gamma} \frac{1}{T_k}}{1 - \frac{\gamma}{1 + \gamma} \frac{T_2}{T_k}} = \frac{\frac{\gamma}{1 + \gamma}}{T_k - \frac{\gamma}{1 + \gamma} T_2}$$

T_2 is therefore always the higher of the temperatures, between which the experimentally determined expansibility holds. When we now apply this to Sodium, where $278 \cdot 10^{-6}$ has been found for α between 101° and 168° C. (HAGEN), we calculate ($T_2 = 168 + 273 = 441$)

$$\alpha = \frac{0,573}{1970 - 0,573 \times 441} = \frac{0,573}{1717} = 334 \cdot 10^{-6}$$

$$\text{or } \alpha = \frac{0,563}{1730 - 0,563 \times 441} = \frac{0,563}{1482} = 380 \cdot 10^{-6}$$

As the coefficient of expansion near the melting point will probably be still somewhat too small (we need only think of water, mercury, etc.), the found value 278 is probably to be raised to 334. If we have to make a choice, the *higher* of the two assumed critical temperatures, viz. 1970° , seems in any case to be nearest the truth.

If we assume that the determined coefficient of expansion really holds for the mean temperature ($101 + 168$): $2 = 134,5^\circ$ C. = 408° abs., we should have calculated the values from 330 to $375 \cdot 10^{-6}$, which are only slightly lower.

Also from VANSTONE'S density determinations we can determine the value of γ' , hence also of α . VANSTONE found namely at 110° , 184° and 237° C. resp. the values $D = 0,9265$, $0,9058$ and $0,8891$, yielding $\gamma' = 280 \cdot 10^{-6}$ between the two first, and $\gamma = 315 \cdot 10^{-6}$ between the two last. Or $295 \cdot 10^{-6}$ between the first and the third. If we assume this last value to hold at the mean temperature $173,5$, at which $D =$ about $0,909$, then

$$\alpha = \frac{295 \cdot 10^{-6}}{0,91} = 325 \cdot 10^{-6} \text{ follows from } \alpha = \gamma' : D \text{ (see above),}$$

hence very near the above calculated value 330.

If we now assume the newer value $325 \cdot 10^{-6}$ to be more accurate than the much older value 278, determined at somewhat lower temperatures, then the value calculated above from γ with $T_k = 1970^\circ$ appears to be much nearer 325 than the too high value 380, calculated with $T_k = 1730^\circ$. T_k lies therefore near 1970° , and (according to the density determinations) sooner somewhat *higher* than somewhat

lower than this temperature; e.g. $T_k = 2000^\circ$ (extrapolated 1997°).

A *second* test is furnished by the *vapour pressure* determinations. We owe the following data to HACKSPILL (1912).

$t =$	350	355	365	390	397	883 C.
$T =$	623	628	638	663	670	1156° abs.
$p =$	0,08	0,12	0,15	0,21	0,26	760 mm.
$\log^{10} p =$	0,903(-2)	0,079(-1)	0,176(-1)	0,322(-1)	0,415(-1)	2,881

According as $T_k = 1970^\circ$ is assumed or 1730° abs., we find $\log^{10} p_k = 2,532$ or $2,499$ (see above), and we have therefore, this being in mm. = 5,413 or 5,380:

$\log^{10} \frac{p_k}{p} =$	6,509	6,333	6,236	6,090	5,998	2,532
or =	6,477	6,301	6,204	6,058	5,965	2,499
$\frac{T_k}{T} - 1 =$	2,162	2,137	2,088	1,971	1,940	0,7042
or =	1,777	1,755	1,712	1,609	1,582	0,4965
Hence $f^{10} =$	3,02	2,96	2,99	3,09	3,09	3,60 → 4,67
or =	3,64	3,59	3,62	3,76	3,77	5,03 → 4,48

We see, therefore, from this that the vapour pressure factor f is pretty well constant at the lower temperatures 350 to 400° C., but at the boiling point (the values of the last column on the righthand side of the vertical line refer namely to the boiling point) it has considerably increased in both cases: from 3,1 to 3,6, and from 3,8 to 5,0. The latter increment is much too great, the more so as the *limiting value* at T_k , viz. $f_k = 8\gamma = 10,74$ or $10,32$, so $f_k^{10} = 4,67$ to 4,48, would be *smaller* in the latter case than the value at T_s , viz. 5,03, which in view of the great increase of f at higher temperatures is *quite impossible*.

We see from the above how exceedingly *sensitive* the method of the vapour pressures is, especially at higher temperatures. This is owing to this, that then $(T_k : T) - 1$ is exceedingly variable on only a slight variation in the value of T_k . In our example from 0,70 to 0,50 for a decrease from 1970 to 1730. And in consequence of this also the value of f is changed in the same degree (from 3,6 to 5,0).

We can therefore conclude from the vapour pressure determinations for *Na* with great certainty that $T_k = 1730^\circ$ will be out of the question, and that $T_k = 1970^\circ$ will be near the truth.

HEIJCOCK still gave $\frac{dt}{dp} = 0,153$ (p in mm.) at the boiling point temperature $882^\circ,9$ C. Now follows from

$$\log \frac{p_k}{p} = f \left(\frac{T_k}{T} - 1 \right),$$

when f' represents $\frac{df}{dT}$:

$$-\frac{1}{p} \frac{dp}{dT} = -\frac{f T_k}{T^2} + f' \left(\frac{T_k}{T} - 1 \right);$$

hence at the boiling point:

$$f_s = \frac{T_s^2}{T_k} \left[\frac{1}{p_s} \left(\frac{dp}{dT} \right)_s + f' \left(\frac{T_k}{T_s} - 1 \right) \right].$$

This gives with $T_k = 1970^\circ$, $T_s = 1156$:

$$f_s^{10} = \frac{(1156)^2}{1970} \times 0,4343 \left[\frac{1}{0,153 \times 760} + 0,704 f' \right].$$

We can put in approximation $0,51 : 486 = 0,00105$ for f' , so that f_s^{10} would become

$$f_s^{10} = 678 \times 0,4343 (0,00860 + 0,00074) = 295 \times 0,00934 = 2,76.$$

According to the above table, this value is too small, as it would be still smaller than the value of f^{10} at 397° , viz. 3,09. We expect, indeed, a lower value than 3,60, as the latter represents the chord in the curve $y = f(x)$, and 2,76 the tangent — but not a value so much smaller. The value $\frac{dt}{dp} = 0,153$ given by HEIJCOCK is therefore probably too high ¹⁾ — or else the value assumed for f' is too low. Also the value $T_k = 1970$ can have been assumed too low.

4. Potassium. After the above explanations we can be briefer, and simply repeat the same calculations as above.

The melting point lies at $62^\circ,5$ C. = $331^\circ,6$ abs. The boiling point at $762^\circ,2$ C. = $1035^\circ,3$ abs. (HEIJCOCK and L.). RUFF and JOH. give $757^\circ,5$ C. The critical temperature lies, therefore, at $335,6 \times 5^{1/3} = 1790$, $1035,3 \times 1,7 = 1750$, mean 1770° ; or at $335,6 \times 4^{2/3} = 1566$, $1035,3 \times 1,5 = 1554$, mean 1560° abs. These will again appear to be the limiting values.

Thus $\sqrt{T_k}$ becomes = 42,08 or 39,50, hence $2\gamma = 2,599$ to 2,501, $\gamma = 1,30$ to 1,25. This gives the value from 0,918 to 0,926 for the factor λ , and the value 74,29 to 74,90 for φ . For λ we have used $\gamma : (\gamma + 1) = 0,565$ to 0,556.

¹⁾ Or would 0,153 be a printer's error for 0,135? See Tables Annuelles of 1912, which are full of misprints. Then 860 would become 975, and 0,00934 would become 0,0105, because of which f_s^{10} would become from 2,76 to 3,09. And this value is very well possible and would — like the expansibility — point to a value of T_k which would be slightly higher than 1970, e.g. 2000^o abs.

VICENTINI and OMODEI found $D = 0,8298$ (liquid) at $62^{\circ},1$. From this follows therefore:

$$\left. \begin{aligned} 0,8298 &= D_0 \left[1 - 0,565 \frac{335,2}{1770} \right] = 0,893 D_0 \\ \text{or} &= D_0 \left[1 - 0,556 \frac{335,2}{1560} \right] = 0,881 D_0 \end{aligned} \right\}$$

from which $D_0 = 0,929$ to $0,942$.

From this follows for b_k :

$$\left. \begin{aligned} b_k &= \frac{2,599 \times 39,1}{0,929 \times 22412} = \frac{101,6}{20825} = 488 \cdot 10^{-5} \\ \text{or } b_k &= \frac{2,501 \times 39,1}{0,942 \times 22412} = \frac{97,79}{21120} = 463 \cdot 10^{-5} \end{aligned} \right\}$$

And further for a_k :

$$\left. \begin{aligned} a_k &= \frac{1770 \times 48,8 \cdot 10^{-4}}{74,29} = \frac{86380}{74,29} 10^{-4} = 1163 \cdot 10^{-4} \\ \text{or } a_k &= \frac{1560 \times 46,3 \cdot 10^{-4}}{74,90} = \frac{72230}{74,90} 10^{-4} = 964,4 \cdot 10^{-4} \end{aligned} \right\}$$

yielding $\sqrt{a_k} = 34,1$ à $31,1 \cdot 10^{-2}$.

For p_k we find:

$$\left. \begin{aligned} p_k &= \frac{1770}{2185 \times 488 \cdot 10^{-5}} = \frac{1770}{10,66} = 166 \text{ atm.} \\ \text{or } p_k &= \frac{1560}{2185 \times 463 \cdot 10^{-5}} = \frac{1560}{10,12} = 154 \text{ " } \end{aligned} \right\}$$

in consequence of which $\log^{10} p_k = 2,220$ to $2,188$.

From the formula for the calculation of the coefficient of expansion α from γ , derived above for sodium, we then find:

$$\left. \begin{aligned} \alpha &= \frac{0,565}{1770 - 0,565 \times 363} = \frac{0,565}{1565} = 361 \cdot 10^{-6} \\ \text{or } \alpha &= \frac{0,556}{1560 - 0,556 \times 363} = \frac{0,556}{1358} = 409 \cdot 10^{-6} \end{aligned} \right\}$$

And as $\alpha = 299 \cdot 10^{-6}$ has been experimentally found by HAGEN between 70° and 110° C. (mean temperature 90° C = 363° abs.), it follows from this that the value, calculated from γ with $T = 1770^{\circ}$, is nearer the truth than that value calculated with 1560° . (Just as for sodium the expansibility at 90° C. will probably be lower than the normal value at higher temperatures, so that 299 will be too small. Indeed all HAGEN's values seem to be too small. For Na 278 had to be raised to 325 through the later determinations of VANSTONE).

And now the vapour tensions. HACKSPILL has found:

$t = 264$	316	331	340	350	360	365	762° C.
$T = 537$	589	604	613	623	633	638	1035° abs.
$p = 0,1$	0,75	1,15	1,35	1,75	2,13	2,3	760 mm.
$\log^{10} p = -1$	0,875 (-1)	0,061	0,130	0,243	0,328	0,362	2,881

From the above found values of $\log^{10} p_k$ we find in mm. $\log^{10} p_k = 5,101$ and $5,069$, so that we have:

$\log^{10} \frac{p_k}{p} = 6,101$	5,226	5,040	4,971	4,858	4,773	4,739	2,220
of = 6,069	5,194	5,008	4,938	4,826	4,740	4,707	2,188
$\frac{T_k}{T} - 1 = 2,296$	2,005	1,932	1,887	1,841	1,796	1,774	0,7097
of = 1,905	1,648	1,584	1,544	1,504	1,466	1,445	0,5067
yielding $f^{10} = 2,66$	2,61	2,61	2,63	2,64	2,66	2,67	3,13 → 4,52
of = 3,19	3,15	3,16	3,20	3,21	3,23	3,26	4,32 → 4,34

From the same considerations as for Na it follows also here again very clearly that the upper series of values is better than the lower one, and that therefore $T_k = 1770^\circ$ is preferable to 1560° . The limiting values of f for T_k are viz. $f_k = 8\gamma = 10,40$ to $10,00$, or $f_k^{10} = 4,52$ to $4,34$. Probably the accurate value of T_k lies somewhat below 1770° abs.

HEYCOCK gave 0,135 for $\frac{dt}{dp}$. When we assume $f' = 0,46 : 397 = 0,0016$, the following formula follows for f_s^{10} with $T_k = 1770$ $T_s = 1035$ from the formula derived in § 3:

$$f_s^{10} = \frac{(1035)^2}{1770} \times 0,4343 \left[\frac{1}{0,135 \times 760} + 0,710 \times 0,00116 \right]$$

$$= 606 \times 0,4343 (0,00975 + 0,00082) = 263 \times 0,0106 = 2,78.$$

This value may be correct. It is larger than 2,67 and at the same time smaller than 3,13 (tangent and chord, see for Na). Perhaps T_k lies again somewhat below 1770° abs.

5. Rubidium. $38,5 + 273,1 = 311,6$ was found for the absolute melting point temperature. This multiplied by $5\frac{1}{3}$ gives $T_k = 1662^\circ$. RUFF and JOH. (1905) found for the boiling-point 691° C. = $971^\circ,1$ abs. This $\times 1,7$ gives 1651. Let us take the round value 1660. On the other hand $311,6 \times 4\frac{2}{3} = 1452$, and $971,1 \times 1,5 = 1457$, averaged and rounded off 1450.

In consequence of this $\sqrt{T_k}$ becomes = 40,74 to 38,08, hence

$2\gamma = 2,548$ to $2,447$, $\gamma = 1,27$ to $1,22$. We find therefore $0,560$ to $0,550$ for $\gamma : (1 + \gamma)$, hence according to our formula $\lambda = 0,922$ to $0,930$, and $\varphi = 74,60$ to $75,25$. Hence

$$\left. \begin{aligned} b_k &= \frac{2,548 \times 85,45}{1,648 \times 224,2} = \frac{217,7}{36930} = 590 \cdot 10^{-5} \\ \text{or } b_k &= \frac{2,446 \times 85,45}{1,673 \times 224,2} = \frac{209,0}{37500} = 557 \cdot 10^{-5} \end{aligned} \right\}$$

D_0 being $= 1,648$ to $1,673$. For, according to HACKSPILL $D = 1,475$ (liquid) for $38^\circ,5$, hence according to the formula derived by us:

$$\left. \begin{aligned} 1,475 &= D_0 \left(1 - 0,560 \frac{311,6}{1660} \right) = 0,895 D_0 \\ \text{or } &= D_0 \left(1 - 0,550 \frac{311,6}{1450} \right) = 0,882 D_0 \end{aligned} \right\}$$

We find further for a_k :

$$\left. \begin{aligned} a_k &= \frac{1660 \times 59,0 \cdot 10^{-4}}{74,60} = \frac{97940}{74,60} \cdot 10^{-4} = 1313 \cdot 10^{-4} \\ \text{or } a_k &= \frac{1450 \times 55,7 \cdot 10^{-4}}{75,25} = \frac{80770}{75,25} \cdot 10^{-4} = 1073 \cdot 10^{-4} \end{aligned} \right\}$$

giving $\sqrt{a_k} = 36,2$ à $32,8 \cdot 10^{-2}$.

We find for p_k :

$$\left. \begin{aligned} p_k &= \frac{1660}{2185 \times 590 \cdot 10^{-5}} = \frac{1660}{12,89} = 129 \text{ atm.} \\ \text{or } p_k &= \frac{1450}{2185 \times 557 \cdot 10^{-5}} = \frac{1450}{12,17} = 119 \text{ " } \end{aligned} \right\}$$

which causes $\log^{10} p_k = 2,110$ to $2,076$.

From the above values of γ we find for the coefficient of expansion α , resp. with $T_k = 1660$ and 1450 abs.:

$$\left. \begin{aligned} \alpha &= \frac{0,560}{1660 - 0,560 \times 363} = \frac{0,560}{1457} = 384 \cdot 10^{-6} \\ \text{or } \alpha &= \frac{0,550}{1450 - 0,550 \times 363} = \frac{0,550}{1250} = 440 \cdot 10^{-6} \end{aligned} \right\}$$

while HACKSPILL gives $339 \cdot 10^{-6}$ between 40° and 140° C. (mean temperature 90° C. $= 363$ abs.). Here too the first value $38 \cdot 10^{-5}$ is nearer the experimental value 34 (which will have to be raised somewhat, see for potassium and sodium) than the second $44 \cdot 10^{-5}$.

HACKSPILL gives for the *vapour tensions* of Rubidium:

$t=250$	292	305	330	333	340	346	350	353	356	365	367	698°
$T=523$	565	578	603	606	613	619	623	626	629	638	640	971° at
$p=0,06$	0,98	1,46	2,66	2,95	3,29	3,67	4,0	4,25	4,57	5,51	6,14	760 m
$\log^{10} p=0,778(-2)$	0,991(-1)	0,164	0,425	0,470	0,517	0,565	0,602	0,628	0,660	0,741	0,788	2,881

As $\log^{10} p_k$ in atm. = 2,110 to 2,076, this is in mm. 4,991 to 4,957, and we find then:

$\log^{10} \frac{p_k}{p}$	= 6,213	5,000	4,826	4,566	4,521	4,474	4,426	4,389	4,362	4,331	4,250	4,203	2,110
of =	6,179	4,966	4,792	4,532	4,487	4,440	4,392	4,355	4,328	4,297	4,216	4,169	2,076
$\frac{T_k}{T} - 1$	= 2,174	1,938	1,872	1,753	1,739	1,708	1,682	1,664	1,652	1,639	1,602	1,594	0,7096
of =	1,772	1,566	1,509	1,405	1,392	1,365	1,343	1,327	1,317	1,305	1,273	1,266	0,4933
consequently $f^{10} = (2,86)$	2,58	2,58	2,60	2,60	2,62	2,63	2,64	2,64	2,64	2,64	2,65	2,64	2,97 → 4,
of = (3,49)	3,17	3,18	3,22	3,22	3,25	3,27	3,28	3,29	3,29	3,29	3,31	3,29	4,21 → 4,

Here too the first row of values appears to be nearer the truth than the second. As f is still greatly increasing at T_s , the values past 4,21 cannot possibly remain below the limiting value 4,25 (for T_k). This limiting value is namely $p_k = 8\gamma = 10,19$ to 9,79, i. e. $f_k^{10} = 4,43$ to 4,25. Perhaps T_k lies slightly below 1660° abs.

6. Caesium. At last the last member of the group. Here the triple point is at 28°,25 C. = 301°,3 abs.; the boiling point is at 670° C. (RUFF and JOH.) = 943°,1 abs. So that T_k will lie between $301,3 \times 5\frac{1}{2} = 1607$, $943,1 \times 1,7 = 1603$, mean 1605° abs., and $301,3 \times 4\frac{2}{3} = 1406$, $943,1 \times 1,5 = 1415$, averaged and rounded off 1410° abs.

We find therefore 40,06 to 37,55 for T_k , yielding $2\gamma = 2,522$ to 2,427, $\gamma = 1,26$ to 1,21. The value of $\gamma : (1 + \gamma)$ becomes 0,558 to 0,548, so that λ becomes = 0,924 to 0,931, and $\varphi = 74,77$ to 75,36. And we find for b_k :

$$b_k = \frac{2,522 \times 132,81}{2,061 \times 22412} = \frac{334,9}{46,90} = 725 \cdot 10^{-5}$$

$$\text{or } b_k = \frac{2,427 \times 132,81}{2,090 \times 22412} = \frac{322,3}{46840} = 688 \cdot 10^{-5}$$

because $D_s = 2,061$ to 2,090. For the density at the melting-point 28°,25 HACKSPILL gives namely $D = 1,845$, so that

$$\left. \begin{aligned} 1,845 &= D_0 \left(1 - 0,558 \frac{301,3}{1605} \right) = 0,895 D_0 \\ \text{or} &= D_0 \left(1 - 0,548 \frac{301,3}{1410} \right) = 0,883 D_0 \end{aligned} \right\}$$

And we find for a_k :

$$\left. \begin{aligned} a_k &= \frac{1605 \times 72,5 \cdot 10^{-4}}{74,77} = \frac{116360}{74,77} 10^{-4} = 1556 \cdot 10^{-4} \\ \text{or } a_k &= \frac{1410 \times 68,8 \cdot 10^{-4}}{75,36} = \frac{97010}{75,36} 10^{-4} = 1287 \cdot 10^{-4} \end{aligned} \right\}$$

giving $\sqrt{a_k} = 39,4 \text{ à } 35,9 \cdot 10^{-2}$.

And for p_k we find:

$$\left. \begin{aligned} p_k &= \frac{1605}{2185 \times 725 \cdot 10^{-5}} = \frac{1605}{15,84} = 101 \text{ atm.} \\ \text{or } p_k &= \frac{1410}{2185 \times 688 \cdot 10^{-5}} = \frac{1410}{15,03} = 94 \text{ "} \end{aligned} \right\}$$

giving $\log^{10} p_k = 2,01$ to $1,97$.

The coefficient of expansion may be calculated from

$$\left. \begin{aligned} \alpha &= \frac{0,558}{1605 - 0,558 \times 337} = \frac{0,558}{1417} = 394 \cdot 10^{-6} \\ \text{or } \alpha &= \frac{0,548}{1410 - 0,548 \times 337} = \frac{0,548}{1225} = 447 \cdot 10^{-6} \end{aligned} \right\}$$

The value $39 \cdot 10^{-5}$ was found between 17° and 100° C. (mean $63^\circ,5$ C = 337° abs.) by ECKHARD and GRAEFE (1900). As these experimental values had to be raised a little nearly everywhere in order to get into agreement with the normal expansibility at higher temperatures, given by γ (the older values of HAGEN for Caesium lie still lower, viz. mean $345 \cdot 10^{-6}$), it is possible that the critical temperature of Caesium will lie between 1605° and 1410° abs.

Let us consult the vapour tensions. HACKSPILL found:

= 230	244	272	308	315	330	333	350	365	397	670° C.
T = 503	517	545	581	588	603	606	623	638	670	943° abs.
p = 0,2	0,29	0,99	2,58	3,18	4,27	4,45	6,72	9,01	15,88	760 mm.
$\log^{10} p = 0,301(-1)$										2,881
$0,462(-1)$										
$0,996(-1)$										
$0,412$										
$0,502$										
$0,630$										
$0,648$										
$0,827$										
$0,955$										
$1,201$										

We find 4,886 to 4,853 for $\log^{10} p_k$, and further:

$\log_{10} \frac{p_k}{p} =$	5,585	5,424	4,891	4,475	4,384	4,256	4,238	4,059	3,932	3,686	2,006
of =	5,552	5,391	4,857	4,441	4,351	4,223	4,205	4,026	3,898	3,652	1,972
$\frac{T_k}{T} - 1 =$	2,191	2,104	1,945	1,762	1,730	1,662	1,649	1,576	1,516	1,396	0,702
of =	1,803	1,727	1,587	1,427	1,398	1,338	1,327	1,263	1,210	1,104	0,495
hence $f^{10} =$	2,55	2,58	2,51	2,54	2,53	2,56	2,57	2,58	2,59	2,64	2,86 → 4,38
of =	3,08	3,12	3,06	3,11	3,11	3,16	3,17	3,19	3,22	3,31	3,98 → 4,22

It also appears clearly from these values of f , that the real critical temperature will lie between 1605 and 1410. The limiting values of f at T_k are $f_k = 8\gamma = 10,09$ to $9,71$, hence $f_k^{10} = 4,38$ to $4,22$. The value f_s^{10} lies slightly too far from $4,38$; the value $3,98$ lies too near it.

7. Recapitulation of this group. In accordance with the course of the vapour tension factors f we shall assume the critical temperature of sodium to be 2000° abs., i. e. $\frac{1}{3}$ of the difference between 1970° and 1730° higher than the first of these values. Further that of Potassium to be 1710° , i. e. $\frac{2}{3}$ of the difference between 1770° and 1560° abs. lower than 1770° ; that of Rubidium to be 1590° , i. e. $\frac{1}{3}$ of the difference between 1660° and 1450° lower than 1660° ; that of Caesium = 1510° , i. e. $\frac{1}{3}$ of the difference between 1605° and 1410° lower than the first value. At last that of Lithium, in virtue of the value of b_k (which we assume = $145 \cdot 10^{-5}$) halfway between 2410° and 2700° , i. e. = 2550° , so that we get the following survey.

	T_{tr}	T_s	T_k	$\frac{T_k}{T_{tr}}$	$\frac{T_k}{T_s}$	γ	b_k $\times 10^5$	$\sqrt{a_k}$ $\times 10^2$	p_k (atm.)	f $Tr.-kp.$	f_k^{10}
Lithium	452	1450?	2550	5,6	1,76?	1,46	145	22,6	806	—	5,1
Sodium	371	1156	2000	5,4	1,73	1,35	266	26,9	343	2,9 3,5	4,7
Potassium	336	1035	1710	5,1	1,65	1,29	481	33,2	163	2,8—3,4	4,5
Rubidium	312	971	1590	5,1	1,64	1,25	579	35,1	126	2,8—3,4	4,4
Caesium	301	943	1510	5,0	1,60	1,24	707	37,7	98	2,8 - 3,4	4,3

These are the most *probable* values following with pretty great certainty from the available data. The inaccuracy will at most amount to 1 or 2 %.

With regard to the values of b_k we will only observe that they

are *about* in the following ratio $1:2:4:5:6$. For $145:1=145$, $266:2=133$, $481:4=120$, $579:5=116$, $707:6=118$.

From the value of T_k and p_k for *Hydrogen*, determined just now by K. ONNES c. s., would follow the value 59.10^{-5} (per Gr. atom) for b_k , i. e. exactly *half* the middle value 118 for K:4, Rb:5 and Cs:6. So that the ratio of the b -values for H to Cs would become $\frac{1}{2}:1\frac{1}{4}:2\frac{1}{8}:4:5:6$.

Possibly the ratio values for Li and Na will later have to be rounded off to 1 and 2 on more accurate knowledge of some data.

And it appears again from the values of $\sqrt{a_k}$, for which rounded off we may write **23, 27, 33, 35, 37,5**, that all these metals occur *atomically* with the very much increased valency attractions. If they were bound to Li_2 , Na_2 , etc., only the "rest-attractions" 3, 5, 7, 9, 11 would have manifested themselves (per Gr. atom). For Li it is possible that undissociated molecules of L_2 are still present at T_k (the abnormally low value 23 would point to this), but it is also possible that this is not the case. All these questions must be left open for the present till the *whole* periodic system shall have been examined.

In a following paper the minor group Cu-Ag-Au will be treated, besides Manganese and the Iron-Platinum group.

Clarens, June 1917.

Chemistry. — “*On Milk-Sugar*”. I. By Prof. A. SMITS and J. GILLIS. (Communicated by Prof. S. HOOGWERFF).

(Communicated in the meeting of June 30, 1917).

1. *Introduction.*

When in 1880 SCHMOEGER ¹⁾ and ERDMANN ²⁾ began their investigations about milk sugar, besides the hydrate, an anhydride was known, which was obtained by heating the hydrate in a drying stove at 125°. Later on this anhydride, in contradistinction to another anhydrous modification, was called the α -form. This other anhydrous modification, the β -form, was obtained by SCHMOEGER and ERDMANN by evaporation of a saturate solution of milk sugar at the boiling temperature ($\pm 108^\circ$).

That this was another anhydrous modification than the α -form followed from this that while the α -modification is very hygroscopic, gives a clear *generation of heat* when brought into water, and yields a solution, the optic rotatory power of which *decreases* with the time, the β -modification on the contrary is not hygroscopic, dissolves under *heat-absorption* and yields a solution, the rotation of which *decreases* with the time.

HUDSON ³⁾ was the first to consider the problem offered by the milksugar, from a physico-chemical point of view. He demonstrated that whatever form of the milk-sugar is dissolved in water, the final condition is always the same, and represents an equilibrium.

HUDSON showed further that the muta-rotation has the same course as a mono-molecular reaction; he determined on one side $k_1 + k_2$, on the other side k_2 , and thus found k_1 indirectly; in this way he got $K' = \frac{k_1}{k_2} = 1,6$ for the constant of equilibrium at 11°, 2.

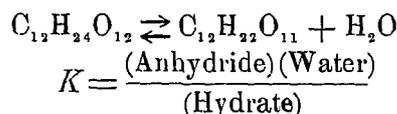
HUDSON started from the supposition that the hydrate possessed a high rotation, and the β -anhydride a low rotation, and he was of opinion therefore that the said equilibrium was to be represented by the equation :

¹⁾ Berichte 13 1915 (1880).

²⁾ Berichte 18 2180.

³⁾ Zeitschr. Phys.-Chem. 44 487 (1903).

or



or

$$K' = \frac{(\text{Anhydride})}{(\text{Hydrate})}$$

Through the slow setting in of the internal equilibrium in solution milk-sugar hydrate presents the remarkable phenomenon that the initial solubility is much smaller than the final solubility.

As, when the total concentration is not too great, it may be assumed as certain that the concentration of the hydrate in the solution in equilibrium with the solid hydrate, remains permanently the same, the constant of equilibrium will follow from the determination of initial and final solubilities, for then:

$$\frac{\text{final solubility} - \text{initial solubility}}{\text{initial solubility}} = \frac{(\text{Anhydride})}{(\text{Hydrate})} = K'$$

In this way was found $K' = 1.44$ at 15° ¹⁾, hence a value which is considerably smaller than that found from the reaction velocities, from which it therefore follows that the total concentration for this determination of K' was already too great.

From initial and final rotation of hydrate and β -anhydride also the constant K' can be determined.

HUDSON found $[\alpha]_{20}^D = 86^\circ,0$ as initial rotation for the hydrate, and $[\alpha]_{20}^D = 35^\circ,4$ for the β -anhydride. On the other hand the value $55^\circ,3$ had already been fixed for the final rotation by SCHMOEGER.

From this follows for 20° ²⁾:

$$K' = \frac{86,0 - 55,3}{55,3 - 35,4} = 1.54$$

a value which lies between the two others.

In consequence of the slow setting in of the internal equilibrium in the solution it was possible to determine the initial solution heats of the different modifications, and likewise the heats of the transformation of the hydrate and of the α -anhydride in the β -anhydride in dissolved state.

In this HUDSON and F. C. BROWN ³⁾ succeeded according to a method of H. T. BROWN and PICKERING ⁴⁾.

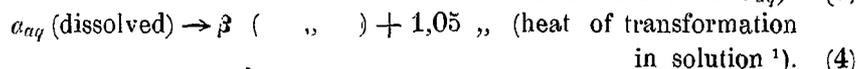
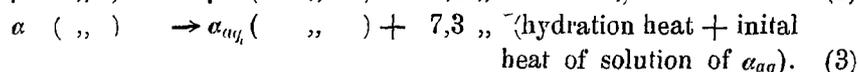
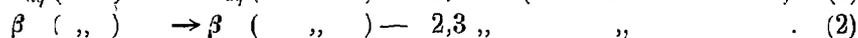
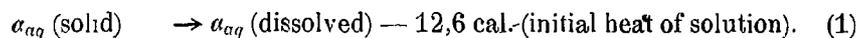
¹⁾ J. Amer. Chem. Soc. 26 1074 (1904).

²⁾ J. Amer. Chem. Soc. 30 1781 (1908).

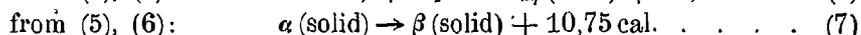
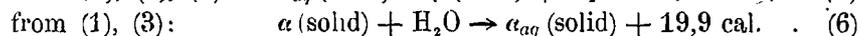
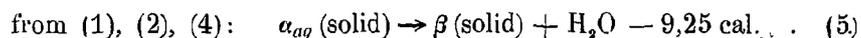
³⁾ J. Amer. Chem. Soc. 30 960 (1908).

⁴⁾ Chem. Soc. 71, 782 (1897).

The following results refer to 1 gram of anhydrous milk sugar and to the temperature of 20°.



From these data the following calculation can be made:



In these determinations HUDSON found also that the difference between initial and final heat of solution, both starting from α -anhydride and from hydrate, had exactly the same value, from which, therefore, follows that α -anhydride in contact with water hydrates immediately, and that then the following slow conversion takes place:



We also come to the same conclusion when we consider that α -anhydride and hydrate show the same initial rotation.

HUDSON has also determined the temperature where the transformation of hydrate to β -anhydride takes place, i.e. he determined the temperature at which the coexistence $S_H + S_\beta + L$ occurs.

From the final solubility of the hydrate between 0° and 89° and from two final solubilities (0° and 100°) of the β -anhydride followed 92° as transformation temperature.¹⁾

He further determined this point from the intersection of the three-phase lines of $S_H + L + G$ and $S_H + S_\beta + G$, and then the temperature of the quadruple point $S_H + S_\beta + L + G$ was found at 94°.

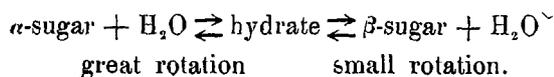
Attempts to determine the transformation point thermally and dilatometrically proved unavailing, because of the exceedingly small velocity of conversion.

On the ground of these data HUDSON in 1910 drew up a general theory of muta-rotation²⁾, which for all sugars can be given schematically as follows:

¹⁾ In this the situation of the equilibrium at 20° has been taken into account.

²⁾ J. Amer. Chem. Soc. **30** 1775 (1908).

³⁾ J. Amer. Chem. Soc. **33** 893 (1910).



The equilibrium 1 sets in with great velocity, whereas equilibrium 2 does so slowly, so that the mutarotation lies in the second equilibrium process.

2. *Experimental part.*

a. Inquiry into the stability of the occurring solid phases; determination of the transformation point Hydrate— β -anhydride + solution.

This was the state of affairs when we began our examination of the milksugar, which examination was very attractive, because here a very slow establishment of the internal equilibrium was found, which opened the possibility to get to know something about the relation between the pseudo-system and the setting in of the internal equilibrium.

In the first place we had to examine what was the stability of the solid phases, hydrate, β -anhydride, and α -anhydride in the system water-milksugar. It appears clearly from the method of preparation and the investigation of HUDSON that the hydrate is stable below 93° ; accordingly both the β -anhydride and the α -anhydride always yielded the hydrate below 93° in contact with water.

It further appeared again both from the method of preparation and from HUDSON'S investigation that above 93° , β -anhydride is the stable solid phase; accordingly the hydrate gave the β -anhydride above this temperature in contact with the saturate solution, and the α -anhydride always gave the β -modification under these circumstances.

It followed, therefore, from this that the α -form is metastable not only below 93° , but also above it.

The question is now whether there exists a transition point between the α and β -modification at higher temperatures. For this purpose the final solubility was first determined from 93° to 200° , both starting from the β - and from the α -modification.

The result was that the α -form was always first visibly converted into the β -form, and that the found points lay without exception on the solubility curve of the β -modification.

These determinations could now be made to fit in with HUDSON'S results about the hydrate, as the T, x -figures 1 and 2 express.

From the graphical representation in fig. 3, in which $\log x$ is represented as function of $\frac{1}{T} \cdot 10^3$, follows the temperature $93^\circ,5$ for

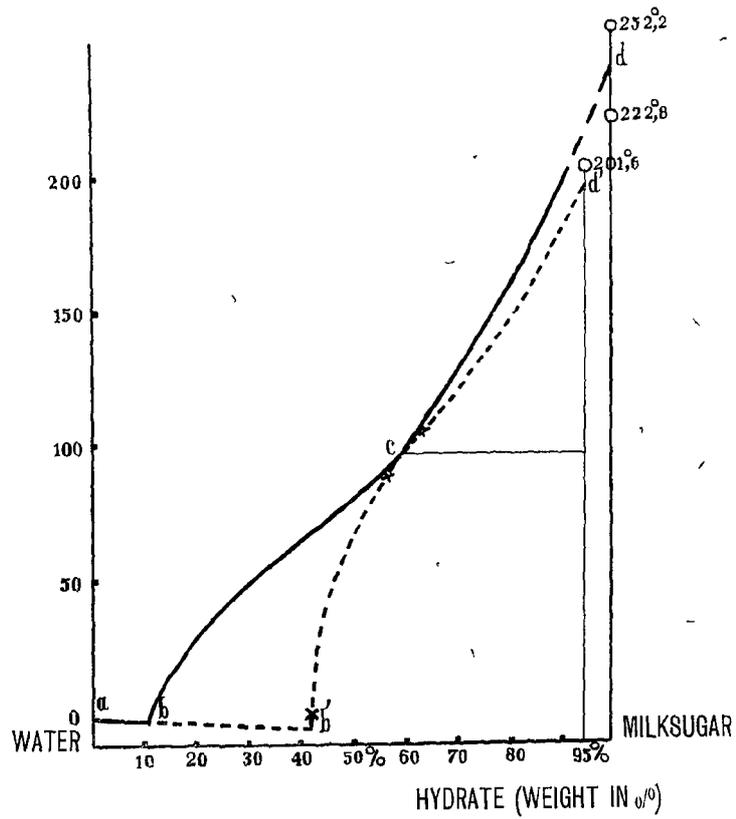


Fig 1

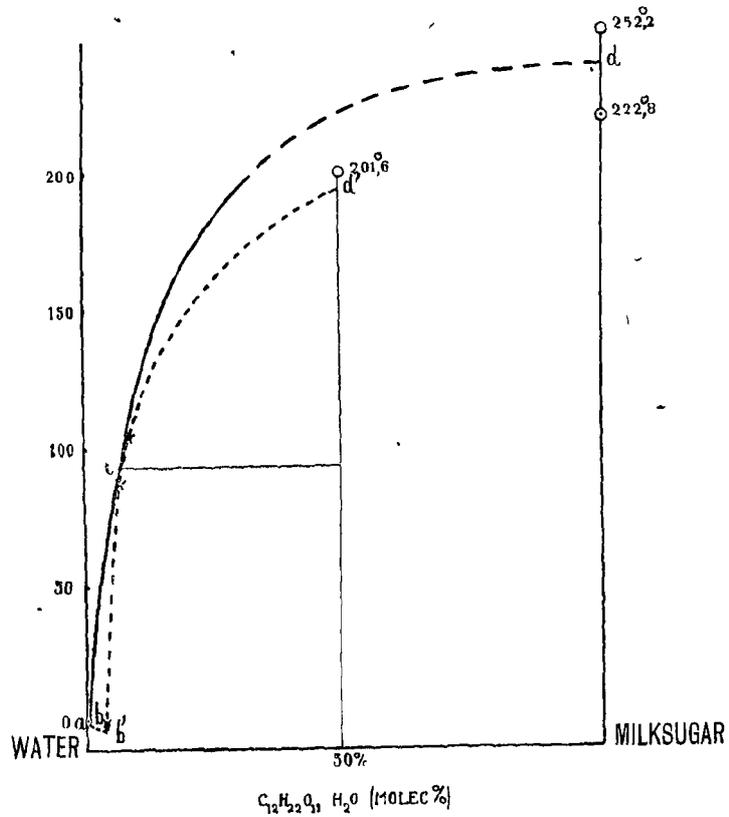


Fig. 2.

the temperature of the three-phase equilibrium hydrate + β -anhydride + solution.

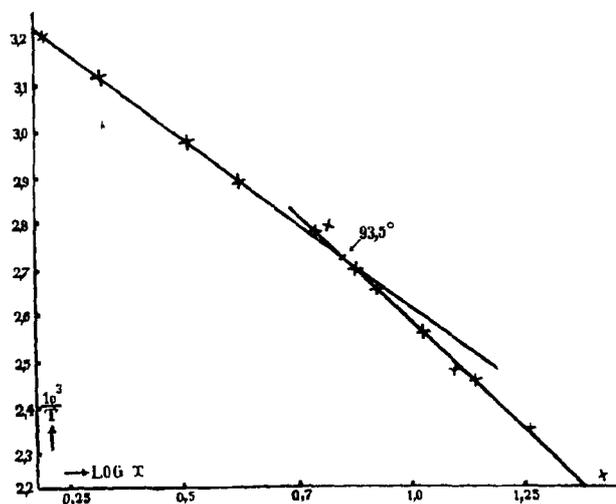


Fig. 3.

The α -modification appeared, therefore, to be metastable below 200°, and now it was the question how it is at the higher temperatures. The solubility lines could not be pursued towards higher temperatures, because the milk sugar decomposes during the time necessary for a determination.

The only thing that offered a chance of success was the determination of the melting point in exceedingly thin capillary tubes, according to the method of Soch.

This investigation gave a perfectly convincing result, for the α -modification^m melted in 2 seconds in a bath of 222°,8, while the β -modification melted in the same time in a bath of 252°,2. Hence the β -modification melted 29.4° higher than the α -form, which shows that the α -modification is metastable up to its melting-point.

On this occasion also the melting-point of the hydrate was determined according to Soch's method, for which was found 201°,6. It may serve as a proof for a very small velocity of transformation in the solid substance, when as here, the melting-point of a hydrate is to be realised more than 100° above the already discussed dehydration point.

b. The hydrate is a hydrate of the α -modification.

All this did not solve the problem offered by the milk sugar, however, by any means, for another highly remarkable peculiarity

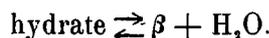
presented itself for the hydrate, a peculiarity which as far as we know, has never yet been observed for another hydrate, though it is probable that it will occur in more cases.

We found, namely, that the hydrate when heated at 125° in dry condition, always yields the α -modification, whereas in presence of the saturate solution the hydrate at the same temperature always passes into the β -modification.

To study this interesting phenomenon more closely the hydrate was brought in contact with a vessel of strong sulphuric acid of ordinary temperature at temperatures between 0.5° and 200° in vacuum. It appeared in all these experiments that the hydrate was *exclusively* converted to the α -anhydride, and this happened both below and above 93°.5.

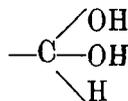
This result enables us, as we shall see presently, to consider the milk sugar problem from another point of view, which will make it possible to account for all the phenomena observed up to now in the system water-milk sugar in a simple way.

HUDSON already assumed the transformation:

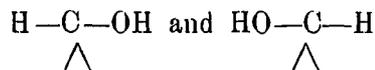


In this the expectation that the hydrate is a hydrate of the β -modification is of course implied.

Now HUDSON assumes further that the water in the hydrate is bound in this way



from which would follow that the hydrate might just as well be called a hydrate of the α -modification as a hydrate of the β -modification, because the stereochemical difference in the final carbon atom, which he assumed for the β - and β -modifications¹⁾, viz.



has perfectly disappeared in the structure formula for the hydrate.

If this were so the hydrate would be neither α - nor β -hydrate and then it could absolutely not be understood why the dry hydrate always gives α -anhydride, also above 93°, whereas the damp hydrate passes into β -anhydride above 93°.

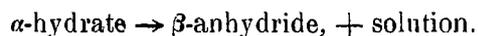
We must, therefore, certainly reject this supposition; the hydrate must be a hydrate of α and β -anhydride, and now all the experi-

¹⁾ J. Amer. Chem. Soc. 31 66 (1909).

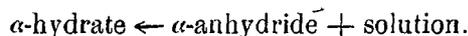
ments made by us, in which it was found that the hydrate in dry condition gives the α -anhydride at all the temperatures examined point to this *that the milk sugar hydrate is the hydrate of the α -modification.*

c. The hydrate presents a transition-dehydration point.

This conclusion throws another light on the problem: the transformation point of $93^{\circ}.5$ is no ordinary transformation point, for in this point takes place the conversion



If we had to do here with an ordinary transformation point, the conversion would be the following:



*For milksugar, however, the dehydration is accompanied with a transition of the α -modification into the β -form, so that here a phenomenon is met with, which as far as we know, has never been observed as yet. To express this particular behaviour also in the denomination of the transformation point we shall call this point henceforth the *transformation-dehydration point, resp. transition-hydration point.**

d. The system water-milksugar must be considered as pseudo-ternary. Derivation of the isotherm-diagram.

This remarkable result must be expressed in our way of representation of the system considered here.

As the occurrence of the said transition-dehydration point shows with the greatest clearness that we must consider the system water-milksugar as pseudo-ternary, we have begun collecting data for the representation of the solubility-isotherms of the system $\text{H}_2\text{O} + \alpha\text{-milk-sugar} + \beta\text{-milk-sugar}$ at a temperature below $93^{\circ}.5$.

In fig. 4 the points a and b indicate the initial-solubility of the hydrate α_{aq} and of the β -anhydride determined by HUDSON¹⁾ at the temperature of 0° . The three-phase-equilibrium $\alpha_{aq} + \beta + h$ was not determined, and was found by us by starting from these three phases, and by squirting off the liquid through a filter after 1 hour's vigorous stirring. The total concentration of this liquid was determined by evaporation and weighing, i.e. the total quantity of milksugar. In this way we find, therefore, on what line drawn parallel to the line $\alpha\beta$, the point D lies. In order to be able to indicate the place of the point D on this line, a second quantity was pressed through a filter, and then through a bent tube provided with a refrigerator, through which water flowed of the same temperature as that of the

¹⁾ J Amer. Chem. Soc. 30 1767 (1908).

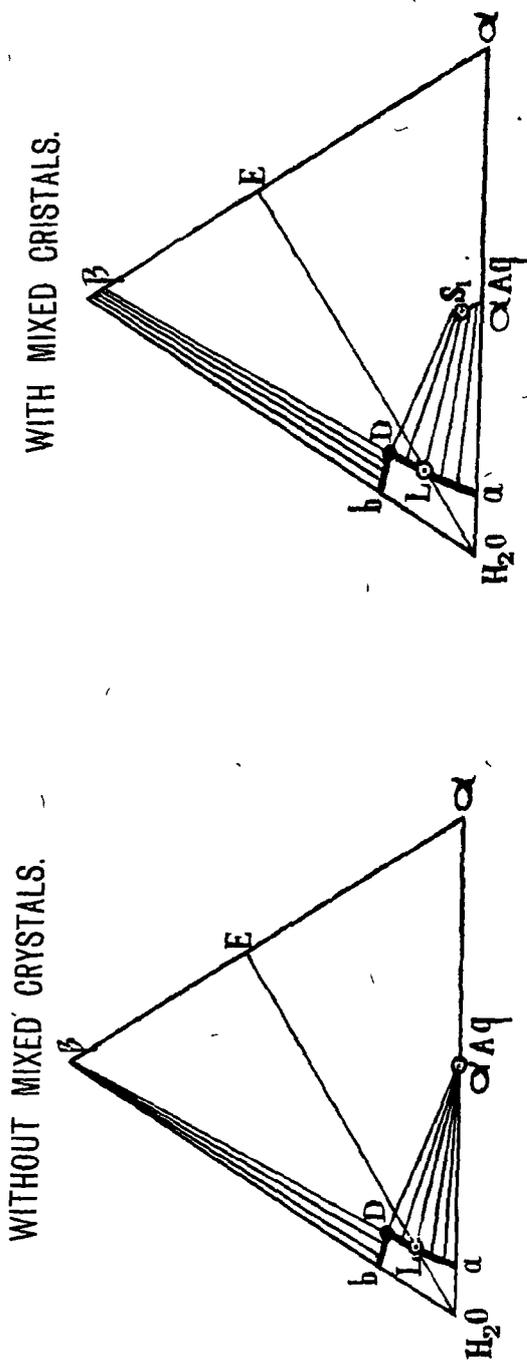


Fig. 4.

batn. Directly after it had left this tube, the solution was received in ice, to fix the equilibrium in the homogeneous liquid. By deter-

mination of the initial and the final rotation the ratio $\frac{\alpha}{\beta}$ was found.¹⁾

In the determination of the final rotation use was made of the positive catalytic influence of a drop of a solution of ammoniac.

It is clear that when the ratio $\frac{\alpha}{\beta}$ is given, it is not stated that the molecules of the two modifications α and β really occur in perfectly unhydrated condition in the solution; it only expresses what the ratio is between the concentration of α and β , leaving it quite an open question in how far these molecules are hydrated.

Thus also the point D was determined, which is the point of intersection of the isotherms of the α_{aq} and of the β -modification.

It has already been ascertained by HUDSON whether the situation of the equilibrium between α and β in solutions of different total concentration shifts with the concentration. The result was that the equilibrium $\alpha \rightleftharpoons \beta$ does not change on dilution of the solution, as was indeed to be expected in dilute solutions, as we have there to do with isomers. We can, therefore, represent these equilibria in our triangle by a straight line^e starting from the point H_2O .

As it had appeared that α_{aq} below $93^{\circ},5$ is the stable solid phase in the system water-milksugar, it was certain that the said line for the homogeneous equilibrium would have to intersect the isotherms of α_{aq} .

This point of intersection is now determined by shaking α_{aq} with water for 2 or 3 days at 0° with the aqueous solution. On analysis of this solution in the same way as this had been done with the liquid D the point L was found lying on the isotherm of α_{aq} . Hence the phases α_{aq} and L and the homogeneous equilibrium line H_2O-E denote the binary equilibrium system water-milksugar at the existing temperature.

Now it is clear that the observations must show that at $93^{\circ},5$ the equilibrium line H_2O-E must pass through the three-phase point D as Fig. 5 expresses, so that then $\alpha_{aq} + \beta \pm L$ can coexist in the binary equilibrium system.

¹⁾ The ratio between initial rotation r_0 and final rotation r_{∞} was determined at 0° for hydrate and β -anhydride mixtures of different concentration. The graphical representation of this gave a straight line, which enabled us, not only to determine the ratio $\frac{\beta}{\alpha}$ from $\frac{r_0}{r_{\infty}}$, but also to find the accurate value of the equi-

librium-constant K' at 0 , because $K' = \frac{\beta}{\alpha}$, when $\frac{r_0}{r_{\infty}} = 1$.

$K' = 1,65$ was found.

Above this temperature the equilibrium line H_2O-E must intersect the isotherm for β -anhydride, which is represented in fig. 6.

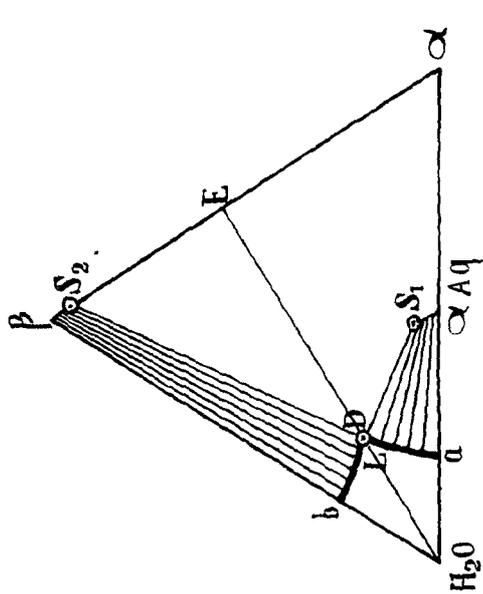


Fig. 5

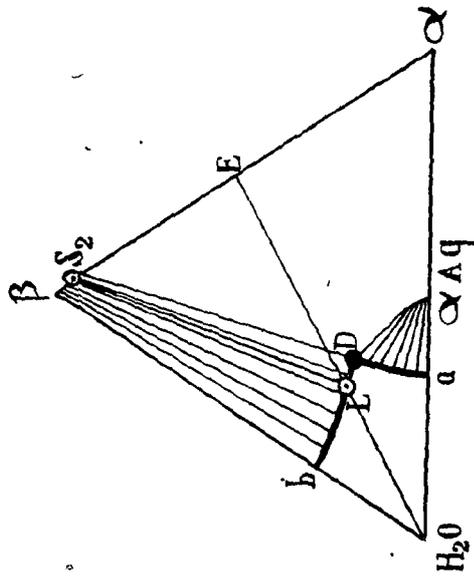
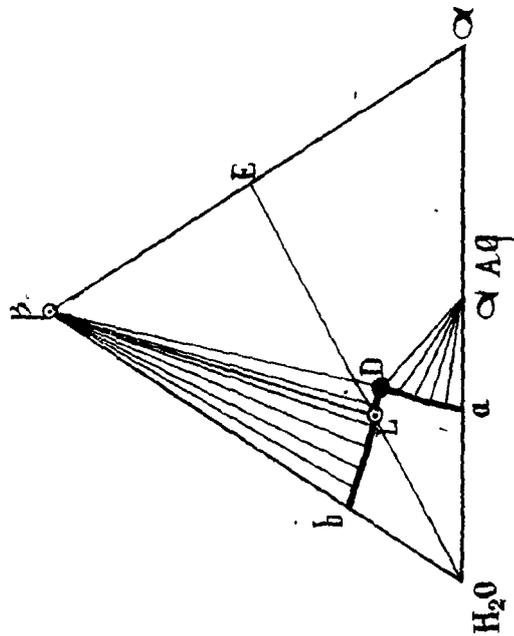
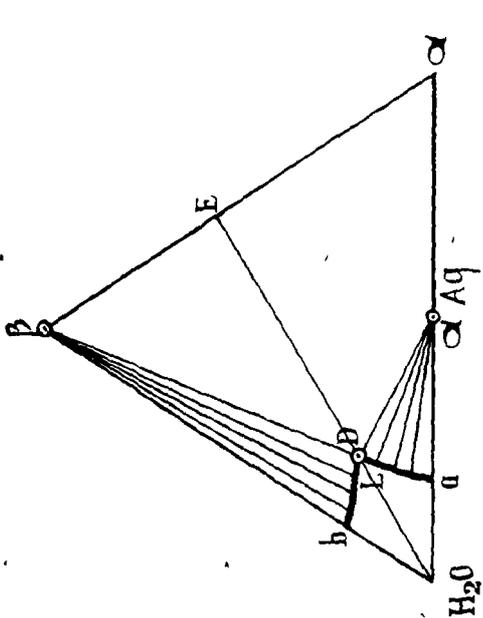


Fig. 6



a. Experimental confirmation of the validity of the pseudo ternary views.

To show that this is actually the case, it was examined how the situation of the points *D* and *L* changes with increase of temperature. The shifting of *L* with the temperature was easy to examine, and we have therefore different observations at our disposal, which, as the figures 7 and 8 show, prove that the equilibrium $\alpha \rightleftharpoons \beta$ shifts a little to the α -side on increase of temperature.

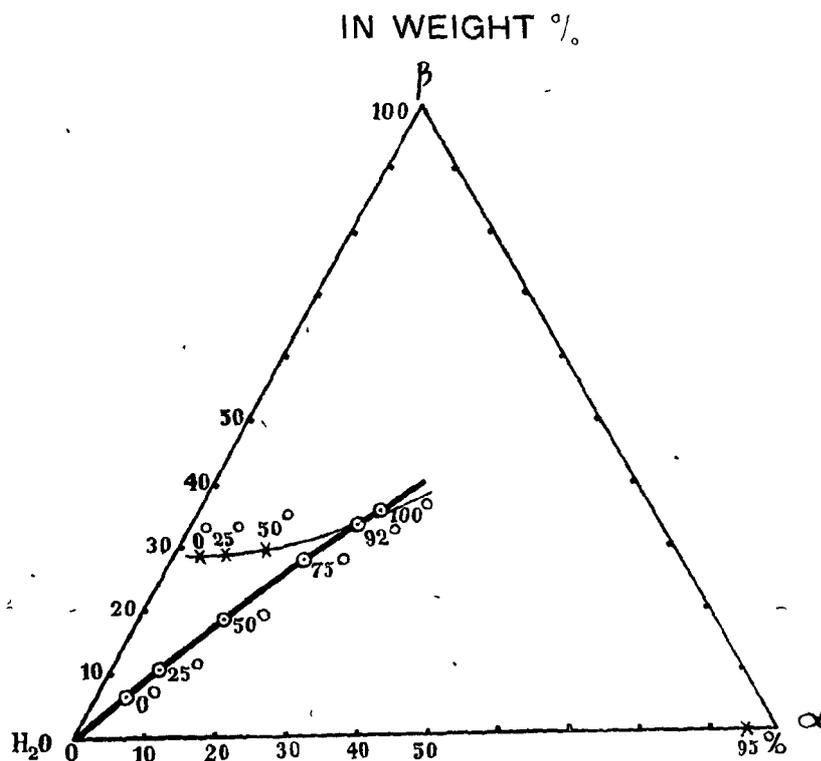


Fig. 7.

It follows already from this that also the point *D* will have to shift towards the α -side, and to a much greater extent too.

The determination of the shifting of the point *D* with the temperature does not present any difficulties at temperatures below 50°, as the velocity of transformation of β -anhydride into α_{aq} takes place slowly, so that we can take care, e. g. by continually adding β -anhydride, that there is always β -anhydride present by the side of the α_{aq} .

At higher temperatures this velocity of transformation increases,

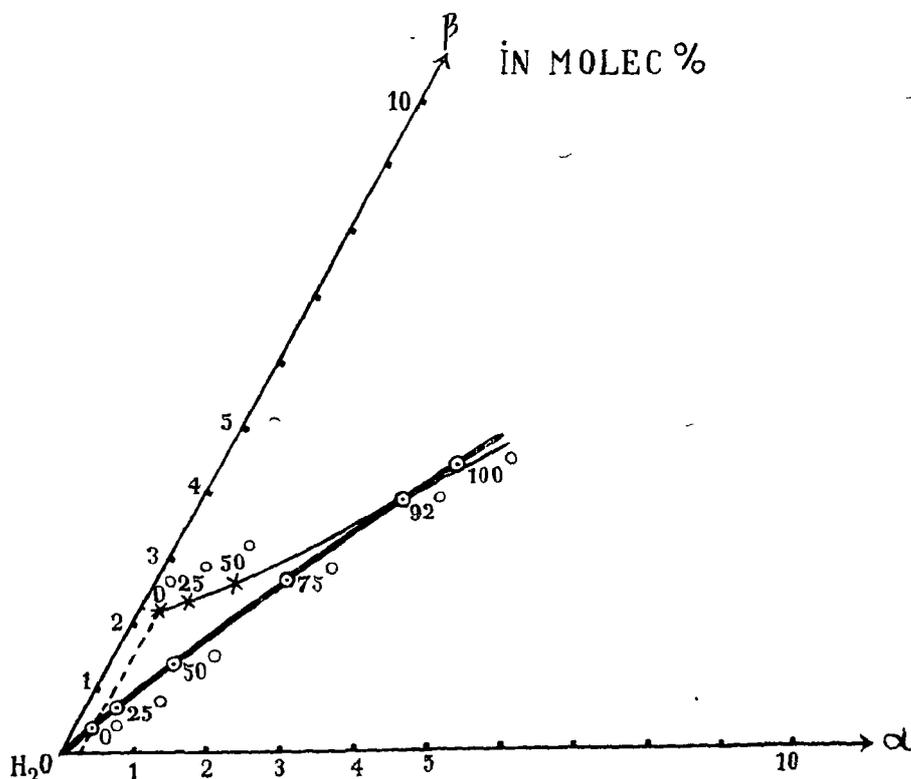


Fig. 8.

however, greatly, and on account of this 50° was the highest temperature at which a reliable observation could still be made.

As, however, appears from the figures 7 and 8, the points *D* shift exactly as had been predicted, and the line traced through the points *D* points with perfect certainty to an intersection at $\pm 93^\circ$, so that a complete confirmation of the supposition made has been obtained in this way.

We are therefore justified in saying that above $93^\circ,5$ the diagram of isotherms with the binary system of equilibrium lying in it will be as was represented in fig. 6. *(To be continued).*

Amsterdam, July 1917. *Laboratory for General and Anorg.
Chemistry of the University.*

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

VOLUME XX

N^o. 4.

President: Prof. H. A. LORENTZ.

Secretary: Prof. P. ZEEMAN.

(Translated from: "Verslag van de gewone vergaderingen der Wis- en
Natuurkundige Afdeling," Vol. XXV and XXVI).

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Proceedings Royal Acad. Amsterdam. Vol. XX.

Physics. — “*Some experiments on gravitation. The ratio of mass to weight for crystals and radioactive substances.*” By Prof. P. ZEEMAN.

(Communicated in the meeting of Sept. 29, 1917).

1. Our ideas concerning gravitation have been so radically changed by EINSTEIN's theory of gravitation that questions of the utmost interest in older theories are now simply discarded or at least appear in a changed perspective. We cannot try anymore to form an image of the mechanism of the gravitational action between two bodies, and we must return to the older theories in order to justify the suspicion, that the structure of substances might influence their mutual attraction. In most crystalline substances the velocity of propagation of light, the conduction for heat and the dielectric constant are different in different directions, and we might then suspect that the lines of gravitative force spread out from a crystal unequally in different directions.

A. S. MACKENZIE¹⁾ in America, and POYNTING and GRAY²⁾ sought for evidence of a directive gravitational attraction.

MACKENZIE proved with an apparatus like that used by BOYS in his beautiful researches on the gravitation constant, that when the axes of calcspar spheres were set in various positions the maximum difference of attraction amounted to less than $\frac{1}{200}$ th part of the total attraction.

POYNTING and GRAY proved that the attraction between two quartz spheres with parallel axes, differs less than 1 in 16000 from the attraction between these spheres with crossed axes.

KREICHGAUER³⁾ sought for a change of weight of sodium acetate when this substance crystallized from the fluid (supersaturated) state. It appeared that the change amounted to less than $\frac{1}{2} \cdot 10^{-7}$ of the total weight.

2. *The weight of quartz spheres in different positions.*

Determinations of the weight of crystals in different orientations have, I believe, never been published. Some years ago I decided upon

¹⁾ Physical Review 2. 321. 1895.

²⁾ Philosophical Transactions. A. 192. 245. 1899.

³⁾ KREICHGAUER. Verhandl. Berliner Physik. Ges. 10. 13. 1892.

carrying out such experiments, but only now, in connection with connected material I intend to give an account of the results. Weighings were made with different crystals, but the greatest accuracy was obtained in a comparison of the weights of two quartz spheres, 42 m.m. in diameter and weighing about 127 gms. Each sphere was mounted in a ring of argentan, and could be turned about a horizontal axis, the ends of which were supported by the suspending wires of the pans of the balance. The spheres were of nearly equal weight, so that it was only necessary to nearly cancel the difference of the weight of the spheres. The optical axes of the spheres hanging from the left and right arms of the balance were placed alternatively in vertical and horizontal positions by means of a simple mechanism, *allowing the necessary operations without opening of the balance case.*

From 15 different series of weighings it resulted that the *double* effect sought for is less than 0.01 mg in 127 gms. or less than 1 in 13000000.

I have much pleasure in thanking Miss C. M. PEEREBOOM, phil. nat. cand., who has taken part in the investigation, and made many weighings.

Experiments with the torsion-balance.

3. By means of the common balance we are able to ascertain the equality of two weights. In how far equal weights correspond to equal masses, in the meaning introduced in the science of mechanics, can be found out only by experiments. A rough experiment to prove the proportionality of weight and mass consists in observing the equality of the time of fall of various bodies. Much more accurate results were obtained by NEWTON's pendulum experiments (descent along a circular arc). Pendulums of equal form and hanging by equal threads, but of various composition, have the same time of oscillation. In his fundamental experiments NEWTON¹⁾ was able to ascertain the equality of the times with an accuracy of one part in 1000 and this therefore is also, at the same place, the accuracy of the proportionality of weight and mass. BESSEL²⁾ refined NEWTON's method, and came to the conclusion that a difference of attraction, experienced by various bodies of equal mass, must be less than 1/60.000 of the total attraction.

A much more accurate result was obtained by von EÖTVÖS with CAVENDISH'S torsion balance, which he brought to a high degree of

¹⁾ NEWTON. Principia.

²⁾ BESSEL. Abh. Berliner Akademie. 1830.

perfection, after many years of continuous, very refined, studies on the local variations of gravity, and which he applied also to the problem now under consideration.¹⁾ The force acting on a body at the surface of the earth is the resultant of two forces: the attraction of the earth and the centrifugal force. The direction of the resultant is dependent upon direction and magnitude of these components. At a given place of the earth the centrifugal force is directed perpendicularly to the earth's axis and dependent upon the mass. If for various substances of equal masses the attractions were different, then the resulting force for these substances would have different direction, and a couple would act on a torsion balance, the rod of which is placed perpendicularly to the meridian and carries at its ends different substances.

VON EÖTVÖS used a torsion balance with a rod, 25—50 cm. long; the torsion wire was of platinum, 0,04 mm. thick, and charged with various substances all of 30 gms. weight. The rod is placed perpendicularly to the meridian and its position relative to the case of the instrument determined accurately by means of mirror and scale. The whole instrument, rod with case, is then rotated through 180 degrees, the substance that first hung at the east side, now hanging at the west side. The position of the rod relatively to the instrument is now read again. The kind of effect considered must produce a torsion of the suspension wire. With a brass ball at one end, with glass, cork or stibnite crystals at the other end of the rod no effect was to be observed. A difference of weight of various substances of equal mass, must be for brass, stibnite and cork less than one twenty-millionth, for air and brass less than one hundred thousandth.

4. The astonishing fact of the equivalence of mass and weight, the expression of the narrow tie between the phenomena of inertia and gravitation is of fundamental importance for EINSTEIN'S theory of gravitation. This theory, only possible, if there exists a field of force giving the same acceleration to all bodies, even enables us to "create" a gravitation field by a transformation of coordinates.²⁾

The fact mentioned therefore merits to be tested in all possible directions. It has been my aim to extend the work of VON EÖTVÖS in two directions, viz.: by the investigation of *orientated* crystals and of radioactive substances. I also hoped, that I might be able to

¹⁾ V. EÖTVÖS. Ann. d. Phys. 59. 354 1897, especially p. 372—373, and Mathem. u. Naturw. Berichten aus Ungarn. 8. 64. 1891.

²⁾ EINSTEIN. Ann. d. Phys. 49. 769. 1916.

introduce some changes, securing, at any rate, the independence of my results.

An investigation of crystals seemed important to me, because von EÖRVS in his investigation of stibnite does not mention, whether attention was paid to a definite orientation. The orientation relative to the vertical however might be of supreme importance. An investigation with radioactive substances is of interest, because it enables us to verify the proposition that energy possesses mass. We know that if ΔE denotes a change of energy of a body, c the velocity of light, then to ΔE corresponds a change Δm of the mass given by the formula $\Delta m = \frac{\Delta E}{c^2}$. Because c^2 is extremely great, we can

by ordinary methods only obtain inappreciable changes of mass. We cannot hope ever to be able to measure the changes of mass caused by the effect of temperature or by chemical transformations

In the case of radioactive bodies the processes of disintegration entail losses of energy of another order of magnitude than in the case of chemical transformations. During the transformation of uranium into lead and helium an enormous amount of energy must be released. This is already the case during part of the necessary transformations, for in the course of its life one gram of radium with its transformation products including radium *F* emits about $3,7 \cdot 10^9$ calories¹⁾.

This corresponds to a change of mass equal to $\frac{3,7 \times 10^9 \times 4,18 \times 10^7}{9 \times 10^{20}} = 0,6 \times 10^{-4}$ g per gram.

If this energy possesses mass, but no weight, then pendulums with lead, helium, uranium must give values for the acceleration, differing by more than 1 part in 10,000.

Already several years ago these considerations were given by J. J. THOMSON, who also made experiments with a pendulum the bob of which was made of radium. It was, however, impossible to obtain a high degree of accuracy as the quantity of radium available was very small. Afterwards SOUTHERNS²⁾ made experiments in THOMSON'S laboratory with pendulums with uranium oxide and red lead. He came to the conclusion that the ratio of mass to weight for uranium oxide, does not differ from that for lead oxide by more than one part in 200,000.

¹⁾ RUTHERFORD. Radioactive Substances. p. 582.

²⁾ SOUTHERNS. Determination of the ratio of mass to weight for a radioactive substance, Proc. Royal. Soc. London, A. 84, 325. 1910.

Hence we must conclude, within the limits of experimental errors, that if energy possesses mass it also possesses weight. Now we can considerably restrict these limits by the use of the torsion balance and this justifies us, I think, in applying it to the investigation of radioactive substances.

5. *New experiments.* My own experiments were made with an apparatus, principally after the design of that of v. Eötvös, but of much smaller dimensions. The weights at the end of the torsion rod were each 30 grams in v. Eötvös' experiments; in my apparatus the weights were each of 1 gram. The weight of the torsion rod with mirror was only about 1,5 grams. The distance between the centres of the cylindrical weights at the ends of the torsion rod is about 10 cms. The smallness of these weights enabled me to take advantage from the properties of fine quartz wires, not yet discovered, indeed, at the time v. Eötvös began his researches.

The torsion wire in my apparatus was 22 cms. long, and about 0,01 mm. thick. The time of oscillation ranged from about 350 to 400 seconds.

In order to protect the apparatus from thermal and electrical perturbations we used, as also did v. Eötvös, double and even triple walls, of brass, about 3 mms. thick.

Manipulations with an apparatus of so great a sensibility as this torsion balance, requires exceptional stability of the surroundings. The mounting on the brick piers of the Amsterdam laboratory proved to be quite insufficient. I, therefore, resolved to construct an arrangement, probably securing the apparatus against vibrations and permitting its rotation, with scale and telescope, about a vertical axis through 180° .

The principle of this arrangement is the one used by MICHELSON and by EINTHOVEN for similar purposes.

I have much pleasure to thank here Mr. W. M. Kok, phil. nat. cand. for his assistance in the construction of this arrangement and during the continuation of the present investigation.

The principal part of the arrangement is an iron basin floating in a tank with thick oil. Tank and basin are of annular form; the central part being open, it becomes possible to suspend an apparatus from a vertical bar through the centre of the annular basin and to fix it at different heights.

A more detailed description is reserved for another occasion.

It was found that this arrangement gave excellent protection against vibrations of short period and permitted also to give slow and smooth rotations.

On the contrary the protection against vibrations of long period was very bad. Experiments with the suspended torsion balance soon taught that, even during the most quiet hours of the night, the torsion rod was never at rest. Sometimes the amplitude of the oscillations gradually diminished to zero, but then the amplitude increased again to 5 m.m., not to mention the extremely annoying nutations of the mirror, which, indeed, never ceased. Apparently vibrations of a period of 300 or 400 seconds (the period of the torsion balance) are never failing in the marshy land of Amsterdam, at least in the neighbourhood of the physical Laboratory.

It was therefore hopeless to work with the torsion balance in *Amsterdam*, and I resolved to continue my experiments in the cellar of a country house near *Huis ter Heide* (prov. *Utrecht*).

To my surprise I found that the stability of the balance, at the new station, was most excellent. The motion of the mirror, about a horizontal axis, was entirely absent and the amplitude of the oscillations always decreased with time. After about one hour the image seen in the telescope was at rest. The apparatus was placed upon a wooden table, resting on the cellar floor. Even hard stampings upon the floor in the neighbourhood of the apparatus had not the slightest effect.

Of course the temperature of the cellar was very constant. One disturbance had an effect on the observations, viz. the magnetic action due to the iron beams of the cellar vault. The constant displacement of 0,3 m.m., noticed in the experiments with quartz and recorded later on, is probably due to this cause.

In view of the accuracy aimed at in the experiments, this amount could not be neglected, though in some experiments its influence is eliminated. I therefore transferred the apparatus, first to a second place in the cellar, where presumably the perturbations would be less.

Afterwards the apparatus was placed in the vestibule. Also here the stability was excellent, but of course the constancy of temperature, though satisfactory, somewhat less. Several excellent series of observations were obtained. As they extended, however, over the whole day and the principal entrance of the house was then put out of use, I restricted these observations to a rather limited number of days.

6. For *Amsterdam* the latitude $\varphi = 52,4$ and $g = 981,3$ cm/sec. The angle α between the attraction of the earth b , and the resultant of attraction and centrifugal force a , becomes $5'42'' = 342''$.

As is easily seen from figure 1, $a = \frac{a \sin \varphi}{b}$ and hence $da = \frac{da \sin \varphi}{b^2} db = a \frac{db}{b}$, if the attraction b changes with the amount db .

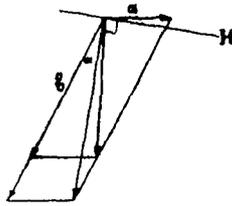


Fig. 1.

By the change of direction da , the force acting in the horizontal direction H becomes Rda , R being the resultant of a and b .

If there is a change of mass a with da , then

$$da = \frac{da \sin \varphi}{b} = a \frac{da}{a}$$

Let the difference of attraction for two substances be $1/1000000$, then $da = 0,000342''$ or in radians $1/600000000$.

In order to give an idea of the sensibility of the apparatus and to calculate the effect to be expected with a given value da , I now give some details of the arrangement, a sketch of which is given in figure 2.

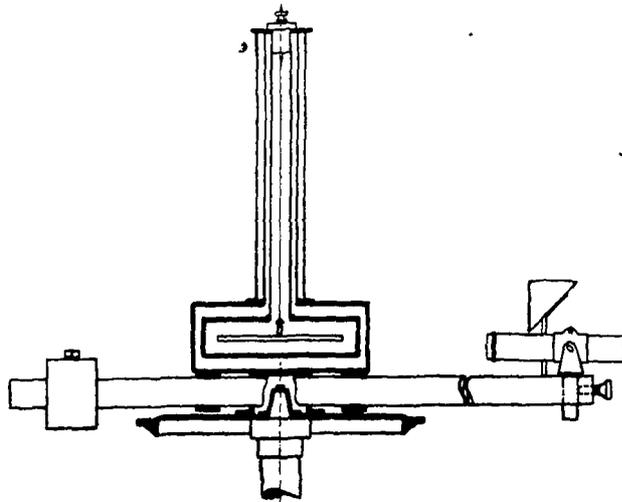


Fig. 2.

Experiment with quartz cylinders, mean weight of each 0,888 g.
Time of oscillation (complete) of torsion rod with quartz cylinders 350 sec.

Time of oscillation (without cylinders) 186 sec.

Distance of the centres of quartz cylinders 7,6 cm.

Moment of inertia of quartz cylinders $K_1 = 2 \times 3,8^2 \times 0,888 = 25,6 \text{ g. cm}^2$.

Moment of inertia rod + cylinders $K = 25,6 + 10,1 = 35,6 \text{ g.cm}^2$.

For the torsion couple S we find from $S = \frac{4\pi^2 35,7}{350^2} = 0,0115$
 $\text{cm}^2 \text{ g. sec.}^{-2}$.

Hence force per radian twist $0,0115/3,8 = 3,03 \times 10^{-3}$ dynes
 $= 3,09 \times 10^{-6}$ g.

Distance scale to mirror = 540 mm.

A displacement of 1 mm. observed in the telescope corresponds
to a rotation of $\frac{1}{2 \times 540}$.

A difference of the positions of the balance equal to 1 mm.,
when pointing first West than East, corresponds for the single effect
to a force measured by an angle of $\frac{1}{4 \times 540}$, and therefore equal to
 $\frac{3,99 \times 10^{-6}}{2160} = 1,43 \times 10^{-9}$ g.

The vertical force acting on the cylinder is 0,888 g.

If the effect is $\frac{1}{1000000}$, then we have (see above) $Rda =$
 $= \frac{0,888}{6} 10^{-8} = 1,44 \times 10^{-9}$ g.

We therefore see that with the sensibility used, 1 mm. of the
scale corresponds to an effect of 1 in 1000,000. In many cases the
result is certainly smaller than 0,1 mm.

7. *Results.* We will now summarize the results obtained. In
the first experiments the position of rest of the rod was deter-
mined from three succeeding extremities of vibration. The presence
of the observer, however, brings about a marked disturbance by
convection currents. Preference was given in the subsequent obser-
vations to the noting of the final position of rest, actually attained
after about one hour.

Experiments were made with quartz, calc-spar, lead oxide, uranium
oxide, uranyl nitrate.

Quartz. The 2 cylindrical quartz rods were 25 mm. long and
of 4,5 mm. diameter. The axis of the cylinders lay in the vertical
plane through the rod of the balance. The crystallographic axis was
perpendicular to the axis of the cylinder. I determined its position
before the beginning of the experiments, by means of observations
with the polariscope, and noted it by means of a small cross, cut
by a diamond, in the surface of the cylinder.

Experiments *in the cellar.* The annexed table gives an example
of results for cylinders with crossed and with parallel axes.

Quartz cylinders: axes \perp . Date: August. 2.

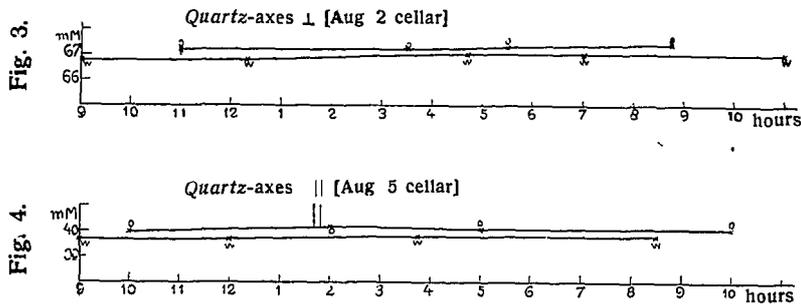
	Telescope West	Telescope East.
Reading scale	66.8	67.2
in m.m.	66.8	67.2
	67.0	67.3
	67.0	67.4
	67.0	
	<u>66.92</u>	<u>67.28</u> , hence $E > W$ 0.36.

The results are exhibited as a curve in fig. 3. The abscissae give the hours of the observations. The temperature of the instrument diminished in the course of the day a few tenths of a degree.

Quartz cylinders. Axes \parallel . Date: August. 5.

	Telescope West	Telescope East.
Reading scale	39.7	40.0
in m.m.	39.7	40.2
	39.8	40.1
	39.8	40.1
	<u>39.75</u>	<u>40.10</u> , hence $E > W$ 0,35

These results are represented in fig. 4.



These observations exhibit a difference of the readings for the position of the torsion rod after rotation of the apparatus from the E-W to the W-E position. Moreover it appears that it makes no difference whether the crystallographic axes of the quartz cylinders are parallel or crossed. At least this difference is only $0,36 - 0,35 = 0.01$ mm.

The constant difference of 0,35 mm. was traced to be probably due to the asymmetrical, magnetic action of the heavy iron beams of the cellar vault on the weakly magnetic torsion rod of hardened copper of the balance. A magnet placed in the neighbourhood of the apparatus caused a small deviation.

The balance was then transferred to *the vestibule*, a place of rather constant magnetic potential. The difference between the E-W and

W-E observations had disappeared. As an example I give again a table of results, also plotted in fig. 5 and fig. 6.

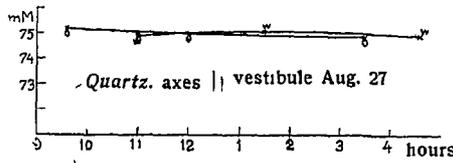


Fig. 5.

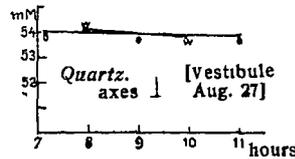


Fig. 6.

Quartz cylinders: axes // . Date: August 27.

W.	O.
74.9	75.2
75.1	75.0
74.9	74.9
<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
74.97	75.03, hence $E > W 0,06$.

Quartz cylinders: axes \perp . Date: August 27.

W.	O.
54.1	54.0
53.8	53.9
	53.8
<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
53.95	53.90, hence $E < W 0.05$

The above mentioned and further observations justify us in concluding that an influence of the orientations of a quartz crystal on the ratio of mass to weight is less than 1 in thirty millions.

Subsequent observations were made with two calc spar cylinders with the same results as obtained for quartz.

These observations were also made in the vestibule.

The results obtained are in agreement with the conclusion in § 2.

8. The torsion rod was next charged with a small glass tube with yellow lead oxide at one end, and one of the quartz cylinders at the other. A difference of the ratio of mass to weight for these substances was certainly less than 1 in twenty millions.

9. *Radioactive substances.* Observations were begun with uranium oxide, included in a thin cylindrical glass tube. The results were rather puzzling. A first series of observations in the cellar gave, in the above used nomenclature, $E > W 1,2$ mm. In this series lead oxide was compared with uranium oxide.

On August 24 I began observations with a second glass tube charged with uranium oxide. I resolved to compare this second tube

with the first in the torsion balance, expecting to find a deviation of, at the utmost, a few tenths of a mm. when observing in the cellar, and practically zero in the vestibule. An observation of August 24 in the cellar however gave, using the torsion rod, charged with the two uranium oxide tubes, a difference of $W > E$ 2,1 mm.; in the vestibule an observation of August 25 gave $W > E$ 2,2 mm.

The first tube was incidentally broken and part of the contents lost. The further experiments were made with the second tube (balanced against quartz) and gave on August 28, 29, 31 and September 2 the results $W > E$ 1, 1, 2.5, 3 mm.

The deviations found widely exceed the errors of observation. They prove (observations of August 24 and 25) that the two samples of uranium oxide are not identical. Probably both or at least one of the uranium oxides are contaminated by iron.¹⁾ By this hypothesis we may understand that the magnitude of the deviation changes with time (observations of August 28 and following days), and even exhibits contrary signs (first observations in the cellar compared with the later observations in the vestibule).

I had not yet an opportunity to test quantitatively the suggestion as to the influence of a contamination by traces of iron. This must be reserved to another occasion. Meanwhile, I have now to record observations with *uranyl nitrate*, which go far to prove that radioactive substances also follow the law of proportionality between mass and weight with great accuracy. The uranyl nitrate was included in a thin cylindrical tube and balanced against quartz. The results of observations of September 10 and 11, made in the vestibule, are plotted in figs. 7 and 8.

The curves are not quite parallel to the axis of abscissae, a case

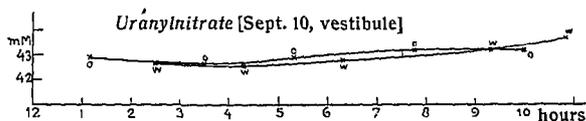


Fig. 7.

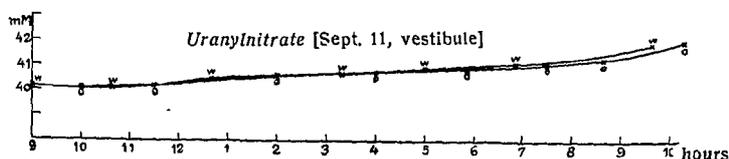


Fig. 8.

¹⁾ OWEN (Ann. d. Phys. 37, 686, 1912) finds that the three preparations of uranium, which were used in his magnetochemical experiments, contained much iron. See also there (p. 672) some remarks on the omnipresence of iron.

realized in the cellar observations Figs. 3 and 4, but exhibit a small slope due to the rise of temperature in the vestibule. This slope is however the same for the E. and W.-curves. The lines are even practically coincident for the greater part of the observations of September 11, and the small residual differences exhibit contrary signs in the observations of September 10 and 11. The observations justify us in concluding that *for uranyl nitrate a deviation of the law of the constancy of the ratio of mass and weight is less than 1 in twenty million.*

It seems extremely improbable that the behaviour of uranium should be otherwise, as far as a so fundamental property as mass is concerned, in an oxide than in a nitrate. The deviation found in the case of an oxide, is therefore most probably due to a magnetic contamination. If the deviation found in the case of the oxide were really due to a change of mass, than the nitrate should exhibit about half the effect of the oxide or about 1,5 mm., allowance being made for the quantity of uranium in the two combinations. But the effect is most certainly less than 0.2 mm.

Perhaps I may be allowed to add that electric disturbances during the observations were excluded sometimes by a short exposure of the inner case, opened to this purpose, of the balance to radium rays, sometimes by placing a few scrapings taken from the leaden box containing the radium preparation.

I have projected recently some improvements of the apparatus and the method of observation, by which I hope to be able to increase the accuracy, according to an estimation at the safe side, ten times.

I hope to return to this subject on another occasion.

Physiology. — *“Are contractility and conductivity two separate properties of the skeleton-muscles and the heart?”* By Dr. S. DE BOER. (Communicated by Prof. G. VAN RIJNBEEK).

(Communicated in the meeting of September 29, 1917).

In 1888 BIEDERMANN made experiments on skeleton-muscles, from which he concluded that under special circumstances these muscles are still irritable and have still retained their conductivity, whilst the contractility has ceased to exist. He placed the sartorius of frogs over a certain length in water. When it had lain in it for some time he stimulated the end of the sartorius that had been in contact with the water. The result was, that the stimulated part of the muscle that had been in the water, did not contract, but the other part did. ENGELMANN repeated the experiment, and obtained the same result. ENGELMANN applied this experiment likewise to the heart. He plunged the auricles of frogs' hearts for some time into water, thereupon he stimulated the auricles, and saw after doing so that the ventricle contracted, whilst the auricles did not show any contraction at all. ENGELMANN communicates his results in the following phrases: “Von der Richtigkeit der Thatsache hatte ich mich durch eigene Versuche am Sartorius curarisirter Frösche überzeugt. Die Bestätigung ist so leicht, wie das Resultat überraschend. Der Muskel wird in der ganzen Ausdehnung, in welcher das Wasser ihn seiner Contractilität beraubt, gleichsam zum Nerv. So nun auch die Muskelbündel der Vorkammern: sie verlieren im Wasser ihren Charakter als Muskeln, und behalten ihre Function als motorische Nerven der Kammer”. Further: “dass die Muskelfasern der Vorkammer auch nach vollständiger Aufhebung ihrer Contractilität doch den Bewegungsreiz für den Ventrikel noch fortzupflanzen im Stande sind, und zwar mit einer Geschwindigkeit durchaus derselben Ordnung, wie wenn das Verkürzungsvermögen erhalten wäre”.

It has now appeared to me, that the conclusions made from their experiments by BIEDERMANN and ENGELMANN, are entirely incorrect. This may appear from the following experiments which I made with regard to this problem. In the first place about the skeleton-muscles. I attached a m. Gastrocnemius of a frog to a lever and plunged the muscle into a solution of RINGER. Then I induced the muscle

to contraction by direct stimulation, and registered it by means of a stationary drum covered by smoked paper. Then I substituted water for the fluid of RINGER. After 5 minutes the point of the lever had already distinctly risen, then the drum is turned round a little way, and by direct stimulation another contraction is brought about and registered. In this way the drum is turned a little way by the hand every five minutes, and afterwards a contraction is registered on

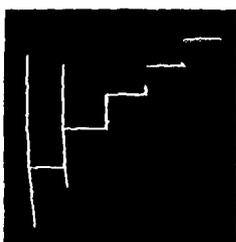
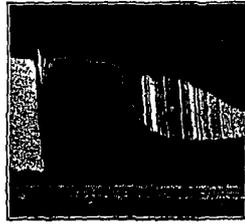


Fig. 1.

the stationary drum. The result is reproduced in Fig. 1. We see that after every five minutes the point of the lever has risen, and that after 25 minutes the point of the lever has mounted over the top of the first registered curve. Then on a stimulation the muscle no longer reacts with an abbreviation. This experiment can be explained as follows: Because the muscle has been so long submerged in water, it becomes saturated with water, swells and assumes rather a globular form. This causes the ends of the muscle to come nearer to each other, and an inflation-abbreviation is the consequence. As soon as this inflation-abbreviation surpasses the height of the "Zucking", the mechanical proportions have assumed such a character that an abbreviation can no more become manifest after a stimulation. The irritability and conductivity are intact, and the abbreviation exists already on account of the inflation. The active abbreviation of the fibrils no more approaches the ends of the muscle nearer to each other, because the inflation has already approached them at the smallest possible distance. What is decisive in this respect is the fact, that such a swollen muscle can no more dilate.

I arranged my experiments on the frog's heart in the following manner. I fastened a canula of KRONECKER through the sinus venosus in the auricles, after I had destroyed the septum atriorum and the atrioventricular-valves. Then I imbibed the heart with the solution of RINGER under the pressure of a column of water 9 mm., and registered the heart-curves by means of suspension on a drum covered by smoked paper. Then I substituted by water the fluid of RINGER. Within a short time the heart stood still and indeed at a level with the tops of the formerly registered curves (vide Fig. 2). If thereupon the heart is again imbibed with the fluid of RINGER, we can make the heart pulsate again, after the inflation-abbreviation of the heart-muscle has first diminished. The heart has, like the skeleton-muscles, sustained a rather important inflation by the imbibition with water, and the distance from the basis to the point of the

ventricle has decreased. Here also the mechanical proportions have,



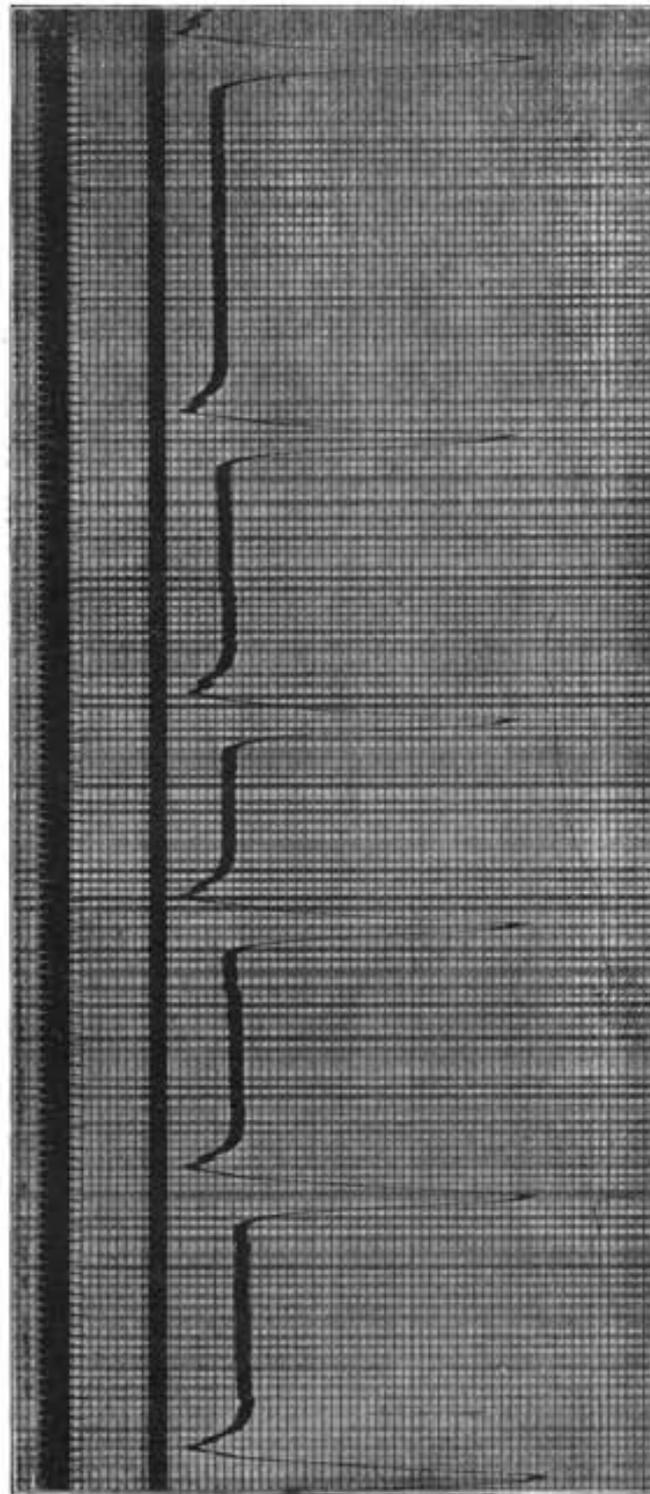
Time 1 min.

Fig. 2.

consequently assumed such a character that an active abbreviation of the heart-muscle cannot express itself. After the substitution of the water by the fluid of RINGER the restoration of the systoles sets in, but first an allongation of the heart-muscle has occurred again on account of a decrease of the inflation. Fig. 2 shows these proportions distinctly. The restoration of the systoles is not complete here, because the stagnation has lasted rather long. A complete restoration of the systoles of the ventricle can however easily be obtained by imbibing the heart for a short time with water.

Consequently the disappearance of the contractility, whilst the conductivity and irritability continue to exist, as BIEDERMANN and ENGELMANN supposed to be the case for the skeleton-muscles and the heart, are only an apparent phenomenon. In order to show, that the processes that are the causes of the contraction really take place in the heart that is swollen by water, I had recourse to the string-galvanometer. After having placed 1 unpolarisable electrode on the point of the heart and 1 on the atrioventricular limit I registered the action-currents from the imbibed (with the solution of RINGER) suspended frogs' hearts. When now I imbibed the heart with water, it stood soon still in the maximal abbreviation-state on account of the inflation. The action-currents continued for some time in the beginning of the stagnation. (vide fig. 3). In this way it was ascertained, that during the stagnation in the maximal abbreviation-state the automation and the conductivity of the heart had remained intact.

I may be allowed to devote a single word to the criticism that KAISER thought necessary to pronounce with regard to BIEDERMANN's and ENGELMANN's experiments. This physiologist attributed the results of BIEDERMANN and ENGELMANN to currentloops that should have induced to contraction from the stimulator the part of the muscle (of the heart) that had been in contact with the water. They do not deserve this criticism. My experiments, in which the stagnating imbibed frogs' hearts produced still electrograms, teach us, that in reality the processes that cause the contraction and the conductivity can continue to exist. The experiments of BIEDERMAN and ENGELMANN remain consequently unimpeachable.



Time $\frac{1}{5}$ sec.

Lever
electrogram.

Fig. 3.

Their far-going conclusions, however, which have connection with important generally physiological problems are not justified. Their experiments do not furnish the proof that conductivity and contractility are 2 separate properties, because the muscles (heart) swollen by water are already maximally abbreviated, and consequently an active abbreviation cannot become manifest.

In this short preliminary communication I wish to desist from far-going conclusions and considerations; but I observe only that no more than the contractility and the irritability, the contractility and the actioncurrent may be separated.

Last year EINTHOVEN¹⁾ has moreover pleaded in one of his essays for the connection between contractility and impulse-currents.

¹⁾ Pflügers Archiv Bd. 166, Seite 109, 1916.

Physiology. - "*The Influence of Neutral Salts on the Action of Urease*". By J. TEMMINCK GROLL. (Communicated by Prof. G. VAN RIJNBERK).

(Communicated in the meeting of September 29, 1917).

Ferments being colloids it is not impossible that the influence that electrolytes exercise on the action of enzymes must be attributed to modifications of the dispersity of the ferment.

If this were really the case, then the character of one of the two ions would have a domineering influence over against that of the other, as was likewise found by HARDY for the flaking of colloids: it appeared namely that with colloids moving cathodically, which are consequently charged positively, the anion of an electrolyte has the greater influence, whilst with colloids moving anodically the influence of the kation was domineering.

A ferment will be either a positive colloid or a negative one, and a ferment that has its action especially in alkaline surroundings, will usually be negatively charged, whilst the ferments acting in acid surroundings will be positive. We can consequently expect a great influence either of the character of the anions or of that of the kations, according to the ferment being either positively or negatively charged. Moreover with colloids the phenomenon presents itself, that both the kations and the anions can be placed in a special series according to their being able to cause a modification of dispersity either in a greater or in a more restricted degree.

With regard to the kations this series is not always entirely the same, but in the main there is no difference with various colloid-phenomena.

Some metals occasionally change place, or as FREUNDLICH remarked: "Die Reihe der Kationen ist wieder etwas verschränkt".

Usually the series of the kations is: NH_4^+ , K^+ , Na^+ , Ca^{++} , Sr^{++} , Ba^{++} , Mg^{++} .

The series of the anions is CNS' , J' , Br' , NO' , Cl' , SO_4'' .

In order to examine in how far the influence of salts on a ferment-action corresponds with that on colloid-phenomena, it is advisable to make use of an enzyme that decomposes a crystalline substrate to crystalline products of decomposition, for if one takes a colloidal

substrate, the salts might modify the substrate and make it consequently more or less susceptible to be influenced by the ferment.

The phenomenon to be studied would probably become more implicate.

The urease, the ureum decomposing ferment, which is found in soybeans is very fit for such like experiments.

The experiments were executed as follows: 3 cc of a solution of ureum ($1\frac{1}{2}$ percent) a definite number of cc of the solution of salt and water to constantly the same volumes (100 cc.) were put in a number of flasks, as a rule 7. The flasks were placed in a flat-bottomed basin in water of the temperature of the room. After the flasks had been so long in the water till the temperature in each of them had become the same, 3 cc. of the urease-preparation, according to JANSEN, was added to them. One minute elapsed between the addition of the ferment to each flask. After 50 to 60 minutes the ammonia that had been formed, was titrated with methyl-orange as indicator, every time with an interval of one minute. Consequently the action was of equal duration in each flask. It appeared at a preliminary experiment that equal results were obtained indeed in flasks of the same composition.

1. *Kations.*

The kations used were K^+ , Na^+ , NH_4^+ , Mg^{++} , Ba^{++} , Sr^{++} , Ca^{++} . Of all metals the chlorides were used.

The following results were obtained: (Vide Tab. on the next page).

If now we express the above figures graphically in such a way that the salt-concentration is indicated on the abscis, and the quantity of ammonia that has been formed on the ordinate, then irregularities strike us with two metals viz. calcium and magnesium.

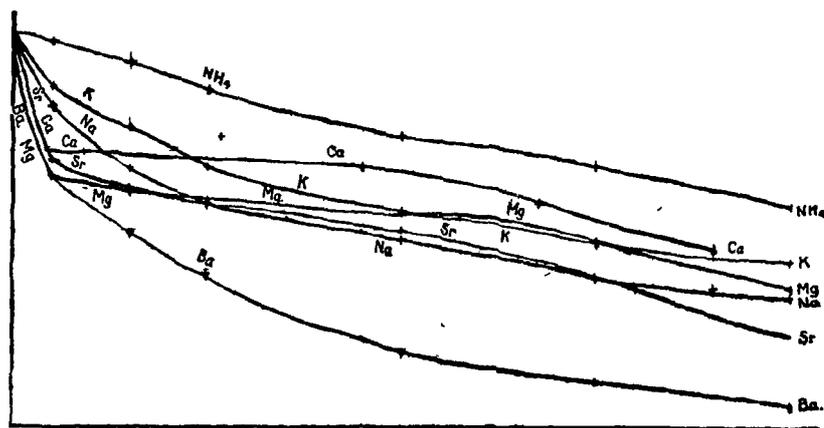


Fig. 1.

Concentration salt (grammol. per liter)	Number c.c. $\frac{1}{10}$ HCl.	Reduced	Concentration salt (grammol. per liter)	Number c.c. $\frac{1}{10}$ HCl.	Reduced
K⁺ 0	7.9	100	Ba⁺⁺ 0	8.5	100
$\frac{1}{20}$	6.8	86.4	$\frac{1}{20}$	5.4	63.7
$\frac{3}{20}$	6.0	76.2	$\frac{3}{20}$	4.2	49.6
$\frac{5}{20}$	5.2	66.0	$\frac{5}{20}$	3.4	38.9
$\frac{10}{20}$	4.3	54.6	$\frac{10}{20}$	1.7	19.5
$\frac{15}{20}$	3.7 ⁵	47.6	$\frac{15}{20}$	1.0	11.8
$\frac{20}{20}$	3.3	41.9	$\frac{20}{20}$	0.5	5.9
Na⁺ 0	7.6	100	Sr⁺⁺ 0	8.1	100
$\frac{1}{20}$	6.2	81.6	$\frac{1}{20}$	5.5	67.7
$\frac{3}{20}$	5.0	65.8	$\frac{3}{20}$	4.9	60.3
$\frac{5}{20}$	4.4	57.9	$\frac{5}{20}$	4.6	56.6
$\frac{10}{20}$	3.6	47.4	$\frac{10}{20}$	4.1	50.4
$\frac{15}{20}$	2.9	38.2	$\frac{15}{20}$	3.1	38.1
$\frac{20}{20}$	2.5	32.9	$\frac{20}{20}$	1.9	23.4
NH₄⁺ 0	8.2	100	Mg⁺⁺ 0	10.1	100
$\frac{1}{20}$	8.1	98.8	$\frac{1}{20}$	6.5	64
$\frac{3}{20}$	7.6	93.0	$\frac{3}{20}$	6.1	60
$\frac{5}{20}$	7.0	85.4	$\frac{5}{20}$	5.9	58
$\frac{10}{20}$	6.0	73.6	$\frac{10}{20}$	5.5	55
$\frac{15}{20}$	5.4	65.9	$\frac{15}{20}$	4.6	46
$\frac{20}{20}$	4.6	56.1	$\frac{20}{20}$	3.5	35
Ca⁺⁺ 0	7.9	100			
0.9 twentieth	5.5	69.8			
1.8 "	5.5	69.8			
5.4 "	5.8	73.7			
9.0 "	5.2	66.0			
13.5 "	4.5	57.1			
18.0 "	3.5	44.5			

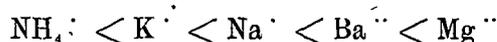
These curves indeed do not, like the others, descend regularly but show first, to about $\frac{1}{20}$ grammolecule, a considerable descent. and afterwards suddenly descend much less, so that they cut a number of the other curves.

I constantly found this sudden modification of direction at $\frac{1}{10}$ grammolecule in repeated experiments.

With regard to the other salts, they appear to retard the urease stronger in the following order :



Up to $\frac{1}{20}$ grammolecule per Liter the curve for Ca^{++} corresponds about with that of Sr^{++} , and that of Mg^{++} with that of Ba^{++} . With the experiments with colloids we do not find as a rule the whole series mentioned, the series is most complete in the experiments of PAULI about the increase of the temperature of congelment of solutions of albumen viz. :



With the exception that here Mg^{++} comes after Ba^{++} , whilst these two metals on urease to $\frac{1}{20}$ grammol. per Liter show an equal action, there is perfect agreement between the two series.

The order of succession NH_4^+ , K^+ , Na^+ , Mg^{++} occurs a.o. in experiments about the coagulation of albumen by an earthalkali salt.

The coagulation is namely favoured by salts of these four metals in the indicated order.

The series $\text{K}^+ < \text{Na}^+ < \text{Sr}^{++} < \text{Ba}^{++} < \text{Mg}^{++}$ is found at lowering the melting-point of a gelatine-gel by neutral salts.

One might draw the following normal series, from the different series that occur in literature for colloid-phenomena :

$\text{NH}_4^+ < \text{K}^+ < \text{Na}^+ < \text{Sr}^{++} < \text{Ba}^{++} < \text{Mg}^{++}$, which corresponds consequently with that which is found for the influence of the action of urease. Occasionally Ca^{++} occurs in another place in one series than in the other, now between K^+ and Na^+ , now after Ba^{++} .

This depends presumably on the concentration that has been used; it occurs likewise with urease, as the calciumcurve cuts a number of other curves above the concentration $\frac{1}{20}$ mol. per Liter.

II. Anions.

When we studied the influence of anions on the action of urease we used potassium salts. Only those acids were used the potassium salts of which are neutral, the action of urease, like other ferment-processes being very sensitive to modification of the hydri-

concentration, so that a retardation or an acceleration might be caused both by a modification of the hydrions and by the anions.

The hydrion-concentration can indeed be kept constant by means of buffer-mixtures, but as these are likewise composed of salts, borates, phosphates, citrates, we should make the results more complicated by adding at the same time other anions.

The following potassium-salts have been made use of: KCl, KI, KBr, KNO₃, KCNS, K₂SO₄.

The experiments were executed in entirely the same way as those with different kations. The obtained results were the following:

Concentration salt (grammolecule per liter)	Number of c.c. $\frac{1}{10}$ N · HCl.	Reduced	Concentration salt (grammolecule per liter)	Number of c.c. $\frac{1}{10}$ N · HCl.	Reduced
Cl' 0	7.9	100	So₄' 0	9.1	100
$\frac{1}{20}$	6.8	86.4	0.7 twentieth	7.5	82.5
$\frac{3}{20}$	6.0	76.2	2.1 "	5.9	64.9
$\frac{5}{20}$	5.2	66.0	3.4 "	5.1	56.1
$\frac{10}{20}$	4.3	54.6	6.9 "	4.0	44.0
$\frac{15}{20}$	3.75	47.6	10.3 "	3.5	38.5
$\frac{20}{20}$	3.3	41.9	13.8 "	3.1	34.1
CNS' 0	9.9	100	I' 0	14.3	100
$\frac{1}{20}$	8.7	88.9	$\frac{1}{20}$	12.6	88.1
$\frac{3}{20}$	7.6	76.7	$\frac{3}{20}$	10.9	76.2
$\frac{5}{20}$	6.7	67.7	$\frac{5}{20}$	9.95	69.6
$\frac{10}{20}$	5.9	59.6	$\frac{10}{20}$	8.7	60.8
$\frac{15}{20}$	5.3	53.5	$\frac{15}{20}$	7.8	54.5
$\frac{20}{20}$	4.7	47.5	$\frac{21}{20}$	7.2	50.3
NO₃' 0	8.9	100	Br' 0	9.1	100
$\frac{1}{20}$	7.8	87.4	$\frac{1}{20}$	7.9	86.9
$\frac{3}{20}$	6.5	72.8	$\frac{3}{20}$	6.7	73.7
$\frac{5}{20}$	5.9	66.1	$\frac{5}{20}$	5.9	64.9
$\frac{10}{20}$	4.8	53.8	$\frac{10}{20}$	4.9	53.9
$\frac{15}{20}$	4.2	47.0	$\frac{15}{20}$	4.3	47.3
$\frac{21}{20}$	3.8	42.6	$\frac{20}{20}$	3.8	41.8

If we represent these figures likewise graphically in the same way as with the kations, then we obtain a number of closely cramped curves from which appears, that with the same kation the nature of the anion has only an unimportant influence (fig. 2).

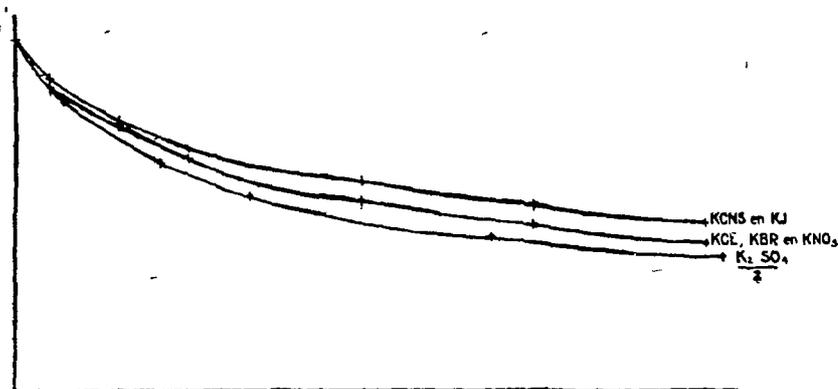


Fig. 2.

In so far as we can still speak of a regular succession it appears that CNS' and I' retard the action of urease least, and SO₄' most. Cl', Br', NO₃' lying between these, are so close to each other, that the differences do not surpass the errors of observation. As has been remarked before, we find at different colloid-chemical phenomena the series CNS', I', Br', NO₃', Cl', SO₄'.

The faculty of precipitating colloids rises e. g. in this succession.

CNS' and SO₄' are here likewise the two extremes of the series, whilst I', Br', NO₃' and Cl' lie between them. But as the differences between CNS' and I' and between Br', NO₃', Cl' are greater than at the urease-retardation, it is possible to place them in a definite succession.

The comparatively slight influence of the anions over against that of the kations is likewise the reason, why in fig. 1 the concentrations are indicated in grammolecules per Liter, whilst in fig. 2 at K₂SO₄ they are indicated in half grammolecules per Liter, consequently as the normalities.

In the first case we have e. g. for NaCl and BaCl₂, it is true, the prejudice that the action of 1 Na⁺ + 1 Cl⁻ is compared with that of 1 Ba²⁺ + 2 Cl⁻, but after the unimportant influence of the anions was proved by the 2nd series of experiments, this seems to me to be preferable to a comparison between 1 Na⁺ + 1 Cl⁻ and 1/2 Ba²⁺ + 1 Cl⁻, which would be obtained from the comparison of normal solutions instead of molar-solutions.

In Fig. 2 on the contrary e. g. KCl and K₂SO must be compared.

As now the influence of the kations is greater than that of the anions, we had better compare

1 K + 1 Cl' and 1 K + $\frac{1}{2}$ SO₄"
 than 1 K + 1 Cl' and 2 K + 1 SO₄".

It appears from a comparison of MgSO₄ and MgCl₂, which exercise about the same influence at an equal concentration of magnesia, that really for the same kation the action of 1 SO₄" corresponds with that of 2 Cl', consequently that of $\frac{1}{2}$ SO₄" with that of 1 Cl'.

Mg sulphate	Magnesium chloride	Concentration
100	100	0 grammol. p. L.
64	64	$\frac{1}{20}$ " " "
60	60	$\frac{3}{20}$ " " "
55	58	$\frac{5}{20}$ " " "
47	55?	$\frac{10}{20}$ " " "
45	46	$\frac{15}{20}$ " " "
35	35	1 " " "

We may deduce from the results that we have obtained, that for the action of neutral salts on the decomposition of ureum by urease the kations have a domineering influence, and that the succession in which those kations can be placed, in accordance with their faculty of retardation, is about the same as that which we find at the flaking and at other colloidal phenomena.

The nature of the anion has comparatively little influence; in so far as we can still observe at anions an increasing faculty of retardation, the series into which they can be placed corresponds likewise with the series occurring in colloidal chemistry.

Consequently it is possible that the influence that neutral salts exercise on a ferment-action consists in the fact that the dispersity of the ferment is modified by the ions in the same way as with other colloids.

Physiol. Lab. of the Univ. of Amsterdam.

Chemistry. — "*The Use of the Thermopile of Dr. W. M. MOLL for Absolute Measurements.*" By N. H. SIEWERTSZ VAN REESEMA. (Communicated by Prof. J. BÓESEKEN).

(Communicated in the meeting of Sept. 29, 1917).

For a number of Photochemical researches, carried out in the Phys. Chem. Lab. of the Technical University of Delft, use was made of the Thermopile and the Galvanometer of Dr. MOLL.

In order to be able to express the measured light absorptions in an absolute measure, it proved necessary to gauge the thermopile. What follows here is a preliminary communication about the measurements referring to this, the particulars of which will be published in my Thesis for the Doctorate.

The idea to gauge the thermopile by means of a Hefner-lamp or another normal lamp or also by an incandescent lamp tested e.g. by the "Physikalisch Technische Reichsanstalt" was relinquished. A direct method was preferred, (without use being made of auxiliary light sources, Hefner-lamp or other normal lamp), which could be carried out by the investigator himself in a simple way, independent of the measurements of others made in other laboratories.

Besides it would be possible, as will appear, to avoid the measurement of illuminated surfaces (here therefore a thin line of light on the thermopile) and the measurement of the distance from illuminated surface to light source, which becomes necessary in the use of a normal lamp in the indirect method.

At first it was my intention to make use of the compensation Pyrheliometer of ANGSTRÖM or of a simplified application of the principle on which it is based.

The course of procedure would have been as follows. A quantity of light in the form of a thin streak of light is made to fall on the platinum plate of the Pyrheliometer, and the electrical equivalent by compensation is measured. An electric current is namely conducted through another plate of the same shape. Behind the plates there are found thermo-elements, which have been adjusted in such a way that their electric forces work in opposite directions. Thermo-elements and plates are of the same shape. If the quantity of absorbed light in one plate is equal to the quantity of heat generated by the

electric current in the other plate, the two E.M.F. must neutralize each other, and then we may write: $I = i^2 r$, in which I represents the quantity of light absorbed per time unit, i the electric current, r the electric resistance in the plate. When I has been measured in this way, the pyrheliometer is removed and the thermopile is put in its place.

If U_I is the deviation that the galvanometer gets in consequence of this, then:

$$kU_I = I = i^2 r, \text{ hence } k = \frac{i^2 r}{U_I},$$

k is a constant. In this way the pile and the galvanometer are gauged, k indicates the quantity of energy falling on the thermopile, which causes the unity of deviation.

In a conversation on this subject Dr. MOLL suggested a great simplification in December 1915. Instead of the pyrheliometer a blackened platinum plate might be placed immediately before the pile. Then no special apparatus is required for the gauging, but a plate is simply slid before the pile, which plate is subsequently illuminated, then an electric current is passed through it, while the corresponding deviations in the galvanometer are measured.

Dr. MOLL was so kind as to give me a quantity of Wollaston plate, for which I express my indebtedness to him here, and through which he enabled me to work out and apply his excellent idea.

The mode of procedure was now as follows:

A plate was slid before the pile, an electric current was conducted through it.

Let us then call the deviation in the galvanometer belonging to the thermopile, U_i .

The strength of the current led through the plate, i .

Its resistance r .

We then write:

$$U_i k' = i^2 r (1)$$

Then a beam of light originating from some constant source of light or other, for which in my case a Nernst-lamp served, was thrown on the plate.

Let us call the deviation of the galvanometer U_I and put the quantity of light $= I$, then:

$$U_I k' = I (2)$$

Now the quantity of light has been gauged, k' is eliminated from (1) and (2) and we get:

$$I = i^2 r \frac{U_1}{U_i} \dots \dots \dots (3)$$

Then the plate is removed, and the same I is thrown directly on the thermopile. We then get:

$$l = U_1 k \dots \dots \dots (4)$$

if U_1 denotes the deviation which the galvanometer now gets.

From (3) and (4) now follows:

$$k = \frac{i^2 r}{U_i} \frac{U_1}{U_i} \dots \dots \dots (5)$$

in which k again represents the quantity of energy required to impart the unity of deviation to the thermopile.

Now the thermopile and the galvanometer have been gauged.

As now the sensitiveness of Dr. MOLL's thermopile is variable over the width of the pile, it must be defined at the gauging of the pile which spot has been gauged. For the same reason it is not indifferent with what width of beam of light we work. To obtain an idea on both points, the sensitivity of the pile was determined as function of the width of the pile, and at the same time of the length of the pile.

For this purpose a very narrow beam of light, 0.2 mm. wide and 5 mm. long emitted by a Nernst-lamp, was thrown on the pile.

The rays fell at right angles to the latitudinal direction of the pile. The latter stood on a heavy block of wood, which could be displaced in a direction normal to the direction of the rays. A simple arrangement was applied to measure the displacements.

At every position of the piece of wood a number of readings were made of the deviation given to the galvanometer, when the beam of light fell on the pile. Then the pile was shifted vertically, so that another spot in the longitudinal direction of the pile could be treated. Also for the new longitudinal position the function of the latitude was determined.

At last the lines were obtained which are adjoined here.

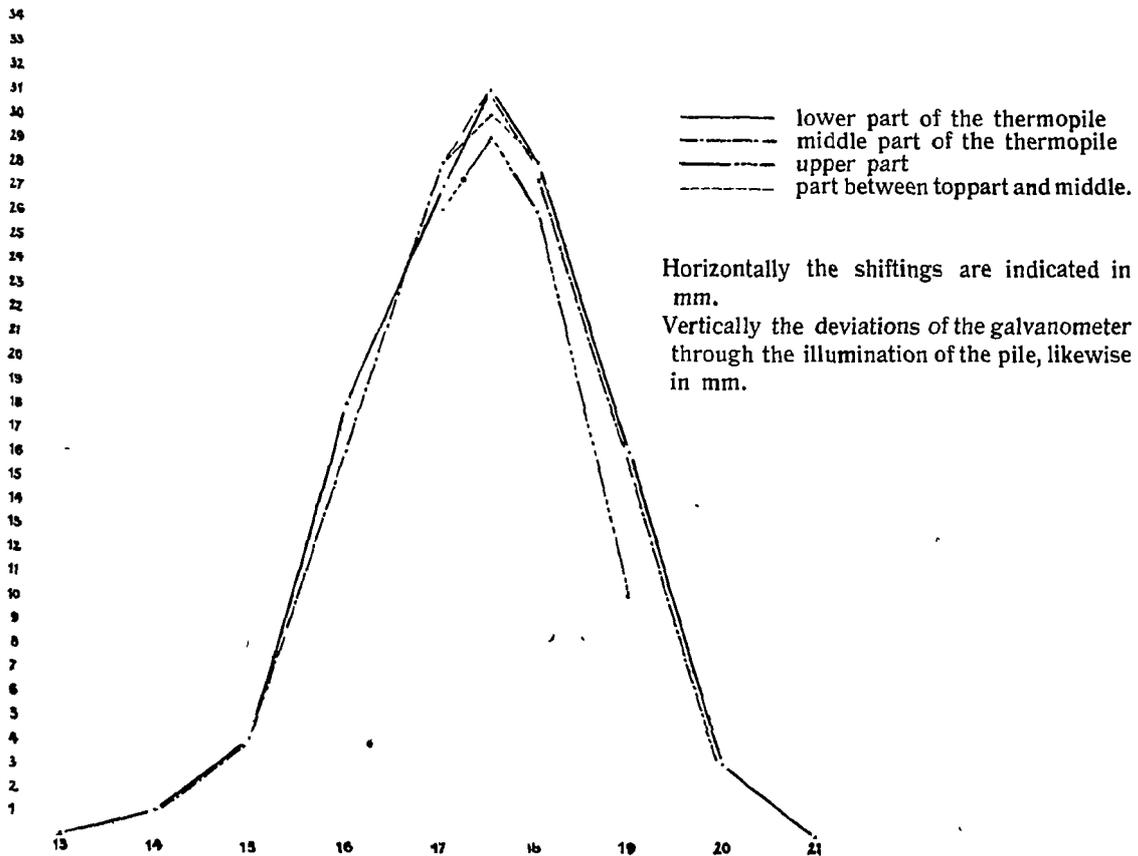
The thermopile was made in the year 1914 by the firm KIPP and SON at Delft (May, year 1914).

The thermoelements were made of copper-constantan. The pile was ± 20 mm. long and 8 mm. wide. The pile had to be repaired once, but showed still a sufficient uniformity.

It follows from the steep course of the curves how greatly the sensitiveness of the thermopile depends on the latitudinal direction of the pile.

	Lower part of the thermopile.										Middle part of the pile.									
Displacement in mm. normal to the direction of the rays of light.	13	14	15	16	17	18	17.5	19	20	21	13	14	15	16	17	18	17.5	19	20	
Deviations of the galvanometer in mm.	0	±1	4	18	27	28	31	16	3	0	±1	4	16	28	28	31	16	3		

	Upper part of the pile.								Part between the top and the middle.												
Displacements in mm. normal to the direction of the rays of light.									17	18	17.5	19							17	18	17.5
Deviations of the galvanometer in mm.									26	26	29	10							28	28	30



The necessity of sharp adjustment at a definite spot is very evident here. If e.g. we have gauged the thermopile at adjustment 16, and if we use the pile later at adjustment 17, it follows from the table that errors can be made of the order of 50%, at least when again beams of 0.2 mm. are used.

Hence a displacement of only 1 mm. can already have a great influence. It is also clear that the deviation is greatly dependent on the width of the used beam of light.

When we consider e.g. 2 beams that send the same quantity of energy to the thermopile per second, the centres of which coincide in the maximum of sensitivity of the pile, but the widths of which differ, and may be successively 1 and 3 mm., it follows from the table that in the case of the narrow beam a deviation is obtained about 20% greater. In this calculation the mean values of the sensitivities have been used.

It follows further from the graphical representation that the thermopile has been made very uniform. The maximum sensitivities all lie at 17,5 mm. This uniform and sharp appearance of the sensitivity maximum enables us now to use this as criterion of adjustment.

The procedure in this is as follows: The function of width is determined with the beam to be used, as has been done above; from this it is possible to determine accurately with what adjustment the beam can show the greatest deviation. Then we adjust the thermopile in the required position, after which we carry out the desired measurements.

This operation, which can take place quickly, is carried out before the gauging as well as before the use of the thermopile.¹⁾

In this way the difficulties with the adjustment have been solved.

With regard to the width of the beams it may be observed that in these experiments use was made of a blackened platinum plate 1 mm. wide, which was at a distance of 1 mm. from the thermopile.

This plate can now be used in a simple way to make also the beams of light about 1 mm. wide.

In the gauging the used beam of light was obtained by cutting out by means of a screen from a larger parallel beam of light originating from a Nernstlamp. The screen is provided with screen doors, so that the beam to be used can be made broader and smaller.

¹⁾ With regard to this adjustment Dr MOLL informed me lately, that for relative measurements he also works with the greatest sensitiveness, by rotating the thermopile to and fro. As a very accurate adjustment is necessary for the gauging, I prefer to determine for this the function of width in order to determine the maximum adjustment graphically from the different points that have been found.

When first we make the beam fall over the edges of the plate that is placed immediately before the thermopile, we see on the thermopile, besides the illuminated plate, 2 lines of light, with the shadow of the plate between them.

We now slide the doors towards each other, till the two lines of light have just disappeared from the thermopile, which can be very sharply observed. Accordingly the beam of light now falls exclusively on the plate before the pile.

When the thermopile is used the width is made equal to about one mm. in a corresponding way, only instead of screen doors use is made here of a cylinder lens.

With regard to the accuracy we observe that it follows from the table that 2 beams of equal intensity, but of the widths 1 and 0,5 mm., both adjusted at the maximum, will show about a difference of deviation of 2.5 %. It follows from this that if we perhaps make the widths equal to about 0.1 mm. in this way, no great errors will henceforth be made with this either.

The question whether the above given formulae may really be applied here, is fully entered into in my Thesis for the Doctorate. Nor will the constructions be discussed here, which were executed to my great satisfaction by the chief instrumentmaker of the laboratory, Mr. JOH. DE ZWAAN.

As a further elucidation of the investigation we shall proceed to give a numerical example.

Voltage of source of light	U_I	U_I	U_I/U_I	mean value
110 Volt	74.1 m.M.	172 m.M.	0.436	0.434
106 "	61.0 "	137.5 "	0.451	
102 "	47.3 "	109.0 "	0.434	
98 "	36.2 "	86.8 "	0.417	

i	U_i	Generated heat in cal. per sec. $i^2 r \times 0.24$	$\frac{i^2 r \times 0.24}{U_i}$ in $\frac{\text{cal.}}{\text{mm.}}$	mean value
0.015 amp.	179.9 m.M.	$0.015^2 \times 2.47 \times 0.24$	7.42×10^{-7}	7.40×10^{-7}
0.020 "	324.4 "	$0.020^2 \times 2.47 \times 0.24$	7.30×10^{-7}	
0.025 "	500.4 "	$0.025^2 \times 2.47 \times 0.24$	7.49×10^{-7}	
0.030 "	720 "	$0.030^2 \times 2.47 \times 0.24$	7.41×10^{-7}	

By making the Nernstlamp burn at different tensions, the gauging could always be carried out for different intensities of light. Likewise different intensities of current were always used. These were measured in a milliampère meter of "Koeler". The resistance of the platinum plate was measured with the Wheatstone bridge.

The values 2,43 Ω , 2,50 Ω , and 2,48 Ω , hence on an average 2,47 Ω were found for r , the electric resistance.

$$k = \frac{i^2 r}{U_I} \times \frac{U'_I}{U_i} \dots \dots \dots (5)$$

$$= 7.40 \times 10^{-7} \times 0.434 = 3.2 \times 10^{-7} \text{ cal. per second.}$$

i.e. that a deviation of 1 mm. is caused by 3.2×10^{-7} cal. per second. It should be stated here that the distance from the galvanometer mirror to the lath amounted to 174.3 mm. in these measurements.

I owe a few words of cordial thanks to Prof. Dr. W. REINDERS, who enabled me to carry out this investigation in the Phys. Chem. Lab., and for the encouragement he gave me during the work.

Delft, July 15, 1917.

Chemistry. — “*On Milksugar*”. II. By Prof. A. SMITS and J. GILLIS.
(Communicated by Prof. S. HOOGWERFF.)

(Communicated in the meeting of Sept. 29, 1917).

The Ternary Pseudo T, x-figure.

When we draw up the pseudo-ternary *T, x*-figure, we come to the following representation. (Fig. 9).

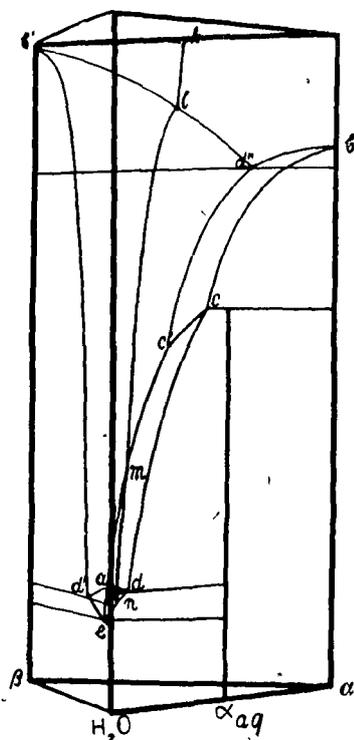
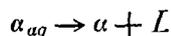


Fig. 9.

In the side plane for α -anhydride— H_2O we know the initial solubility from 0° to 25° (determined by HUDSON loc. cit.); further the situation of the eutectic point at -0.3° and 0.27 mol. % α (point *d*).

We found the melting point of α at $222^\circ,8$ and that of α_{aq} at $201^\circ,6$. With regard to the real transformation point of α_{aq} , i. e. the point where under the pressure of 1 atm. the following conversion takes place:



we have been able to ascertain that it lies above 100° ; for when α -anhydride was brought at 100° in a saturate milk-sugar solution, a marked generation of heat still took place as a proof that at this temperature hydration of the solid α -anhydride still occurs.

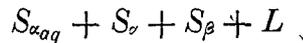
If instead of a saturate milk-sugar solution pure water of 100° is taken, this generation of heat is not observed, because the velocity of solution is very great at this temperature, and the negative heat of solution then hides the smaller positive heat of hydration from us.

In the side plane of the system β -anhydride-water we know the initial solubility at 0° , the eutectic point *d'* lying at $-2^\circ,3$ and 2,2 mol. % β , and further the melting point of H_2O (point *a*), and the melting point of β -anhydride *b'*, lying at $252^\circ,2$.

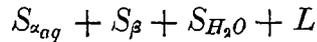
In the side plane for α -anhydride + β -anhydride we only know the melting point b and b' of α and β -anhydride, it being assumed here that there occurs a eutectic point (point d'').

The melting surfaces in the space are clearly visible in the spacial figure. At the place where the melting surfaces or solubility surfaces intersect, there arises a three-phase line, and at the place where these three-phase lines meet — and this meeting always takes place by three three-phase lines at the same time — there arises a quadruple point.

Two quadruple points may be pointed out here in our spacial figure, first the point c' lying above $93^{\circ},5$, where coexist:



and secondly the ternary eutectic point e , where coexist:

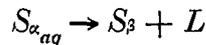


lying according to the calculation at $-2,6^{\circ}$.

The T, x-spacial figure of the binary system.

In the ternary pseudo figure described here lies the binary system. We get this system, when we draw the surface of equilibrium for the equilibrium $\alpha \rightleftharpoons \beta$ in aqueous solution at different total concentrations and different temperatures through the axis for the component H_2O .

This surface of equilibrium intersects the melting point surface of β -anhydride along the line lm , from which it follows that in the binary system water-milksugar the saturate solutions in stable state coexist with β -anhydride from m to l . A change sets in in this in the point m , for below this point the equilibrium surface does not intersect the melting point surface of β -anhydride, but the melting point surface of α_{aq} , so that it is clear from this that the point m represents the found remarkable *transition dehydration point* lying at $93^{\circ},5$, and for which on supply of heat the transformation



takes place.

Further the said surface of equilibrium of course intersects also the ice-plane, and the line of intersection here indicates the melting point line of the ice in the binary system. This melting point line of the ice and the melting point line of the hydrate intersect in n (at $0,65^{\circ}$ and $\pm 0,6$ mol. %), where the surface of equilibrium meets the eutectic line de of the pseudo-ternary system.

It should be pointed out here that the shape of the surface of equilibrium could be derived from the final solubility of $S_{\alpha_{aq}}$ and S_{β} from 0° to 170° , and further from the projection of this line on the ground plane over the temperature range 0° to 100° .

Theory of the mutarotation.

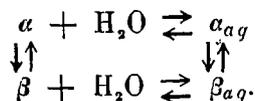
On the ground of the new views to which we were led by our experimental investigation, we now arrive at a theory on mutarotation which is essentially different from that drawn up by HUDSON.

As follows from the here given explanation of the behaviour of the system water-milksugar, this system must be considered to be pseudo ternary, in which water is then a component and α and β milksugar are the pseudo components. From this it follows immediately that it must be assumed that these different sorts of molecules occur side by side in the liquid phase, in which the phenomenon of the mutarotation takes place. We know further that for milk-sugar a hydrate α_{aq} is known in solid state. This alone would already point to the presence of this hydrate also in the solution, for which, as we have seen, other phenomena plead too.

Now it is evident that when the α -anhydride can combine with water to a hydrate, this will also be the case with the β -modification. That we do not know this hydrate in solid state, does not plead at all against this assumption, for this tells us only in this connection, that the solubility of the β_{aq} must be greater than that of β -anhydride, which is just the reverse for the other pseudo-component.

In favour of the assumption of β_{aq} in the solution pleads further that for maltose, a substance which also presents mutarotation, the β_{aq} is known in solid state¹⁾, but the α_{aq} is not, and also that here, therefore, we find exactly what is still wanting for the milk sugar.

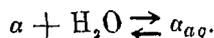
We assume, therefore, that in the aqueous solution the following equilibrium sets in:



In this symbol there are two conversions of which we can say that they take place with great velocity.

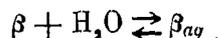
First the reaction.

¹⁾ J. Amer. Soc. 31 76 (1909) en 32 p. 894 (1910).



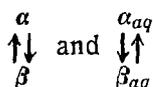
This follows from what was stated in the first communication.

With regard to the conversion



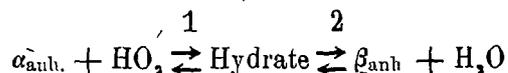
we must refer to the system H_2O -maltose, in which it was also found that this reaction proceeds very rapidly. Hence it might be said that for the sugars the hydration equilibrium seems to set in very rapidly, and on this ground we assume that the hydration equilibrium of β -anhydride sets in very quickly.

In this way we come, therefore, to the conclusion that the setting in of the equilibria



must be held responsible for the mutarotation, in other words that the establishment of these equilibria takes place *slowly*.

In this view the difficulty that lies in the mutarotation theory of HUDSON, and is also acknowledged by himself, is entirely obviated. HUDSON namely assumed that we should have to do with the following equilibria:



in which the equilibrium 1 sets in with great velocity and 2 very slowly.

On account of this view HUDSON is forced to assume that for maltose exactly the reverse takes place, and that it is there exactly the equilibrium 2 that sets in very rapidly, and that 1 sets in very slowly.

HUDSON says about this: "Why the monohydrate should change instantly to the α -form for some sugars, but to the β -form for others, is entirely unknown, and is a most interesting problem."

HUDSON's view was somewhat forced, as he was obliged to assume for two perfectly analogous reactions, viz. hydrations of stereoisomers, that one proceeds very rapidly, the other very slowly. According to our view it is assumed that the reaction velocity of the said perfectly analogous conversions differs but little, whereas a great difference is assumed to exist between reaction velocities, one of which is a hydration and the other an intra-molecular conversion.

Mutarotation would, therefore, not be due to a slow dehydration process in the sugar series, as was assumed by HUDSON, but to the slow

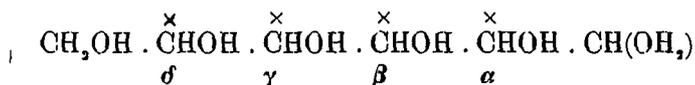
unsubstituted sugars, but also for the glucosides, the acetates, the hydrazons, and the compound sugars, so that this gives a very weighty support to the validity of the assumed structure for the α - and β -modifications.

HUDSON, however, has overlooked a very important point as far as the structure of the sugar mono-hydrates is concerned.

In this he has not been very consistent, as he assumes e.g. for the sugars lactose, glucose, arabinose, and galactose as rotation for the α -modification (a rotation which is not directly to be determined because the α -modification of those sugars passes into hydrate on contact with water), that calculated from the rotation of the hydrate, for which he gives the structure as follows e.g. for glucose:



This formula cannot be correct, as in this way the asymmetric final carbon atom of TOLLENS's formula disappears, which means that the rotation of this hydrate will no longer be $A + B$, but only B' , which quantity is equal to the algebraic sum of the rotations of the asymmetric carbon atoms indicated by \times :



and this sum is no longer equal to B , because the asymmetric carbon atom has changed now too.

The observed regularities for the aldoses are, therefore, no longer to be explained in this way. We should e.g. have for glucose:

$$\begin{array}{l} \alpha\text{-hydrate:} \quad \quad \quad B' \\ \beta\text{-anhydride:} \quad - A + B \end{array} \left. \begin{array}{l} \text{sum} \\ - A + B + B' \end{array} \right\}$$

On the other hand we have e.g. for the ethylglucosides α and β (both anhydrides)

$$\begin{array}{l} \alpha\text{-ethylglucoside:} \quad + A' + B \\ \beta\text{-ethylglucoside:} \quad - A' + B \end{array} \left. \begin{array}{l} \text{sum} \\ 2B \end{array} \right\}$$

Hence the sum of the molecular rotations of the α and β glucose cannot be equal to that of the α and the β ethyl glucoside, 23200 and 25230 being found, hence a pretty good agreement. The same thing holds for galactose and ethyl galactoside, for which is found 34700 and 36400.

For other glucosides e.g. methyl-d-glucoside, methyl-d-galactoside, and methyl-d-xyloside, of which the β -modifications of the two first contain resp. $\frac{1}{2}$ H₂O and 1 H₂O, and of the third the α and β modifications are anhydrous, HUDSON's law holds good in spite of

this, though the rotations of these substances are taken as if they were really anhydrous.

It is therefore evident that the optical superposition takes place here whether these substances contain water or not, and that for all the asymmetric final carbon atom with the lacton ring occurs.

Accordingly we arrive at the result in this way *that for the unsubstituted aldoses e. g. glucose, galactose, milksugar etc. the presence of H₂O does not change anything at all in the structure of the asymmetric final carbon atom.*

No more, therefore, than for methyl glucoside will the water be bound to the final carbon atom in glucose itself. We may now question how it is that HUDSON notwithstanding this inconsistency, has arrived at satisfactory results. The answer to this question is very simple. In his calculations for the rotation of the anhydride HUDSON has namely taken the rotation of the hydrate, which is only allowed when the water is bound in such a way that it cannot influence the rotation of the final carbon atom.

If e. g. milk sugar hydrate is a molecular compound of C₁₂, H₂₂, O₁₁, with one mol. of water, and quite to be compared with CuSO₄.H₂O, then it is clear that the water bound to the sugar molecule does not affect its rotation or only very slightly. If we, therefore, know the rotation of α -milk sugar hydrate, this rotation is the same as that of milk sugar anhydride, as nothing has been changed in the grouping of the active carbon atoms, and thus it may be understood that though HUDSON has executed his calculations with the rotations of hydrates, they have yet led to good results; but in this way it has been proved very convincingly that the hydrates do not contain the group $\text{—C}\begin{matrix} \text{= (OH)} \\ \text{— H} \end{matrix}$.

SUMMARY.

The results of this research may be summarized as follows:

1. The final solubility curve was determined between 89° and 200°, starting both from β -anhydride and from α -anhydride, and this curve, in connection with HUDSON'S determinations, proved the existence of a break at 93°.5.

2. From the fact that α -anhydride is always converted into β -anhydride above 93°.5, and also from the melting-points of α -anhydride (222°.8) and of β -anhydride (252°.2) determined for the first time follows with certainty that above 93°.5 the α -modification is metastable.

3. It could be established by dehydration experiments of the solid hydrate at different temperatures that this hydrate is a hydrate of the α -modification.

4. It was demonstrated by experiment that $93^{\circ}.5$ in the system water-milksugar is no ordinary transformation point, but a point that we propose to call a *transition-dehydration point*, as at this temperature the hydrate of the α -modification under the pressure of 1 atm. *dehydrates and is also converted to the β -modification*.

5. The observed phenomena have suggested that for milksugar two kinds of molecules α and β have to be assumed, on account of which the system water-milksugar must be considered to be pseudo-ternary. Of this system the isotherms have been determined under the pressure of 1 atm. at different temperatures. By also indicating the curve which represents the situation of the equilibrium between α and β milksugar at different total concentrations the situation of the binary equilibrium diagram at different temperatures could be pointed out in the pseudo ternary system, which enabled us to explain in a simple way all the phenomena observed.

6. Then the pseudo ternary T - x -figure of the system $H_2O + \alpha$ milksugar + β milksugar with the surface of equilibrium lying in it was constructed.

7. A new theory was drawn up for the mutarotation, and in conclusion it was still proved that the monohydrates in the sugar series cannot contain the group $-\overset{=}{\underset{H}{C}}(\text{OH})_2$.

Amsterdam, June 29, 1917.

Anorg. Chem. Laboratory
of the University.

Chemistry. — *“Influence of different compounds on the destruction of monosaccharids by sodiumhydroxide and on the inversion of sucrose by hydrochloric acid. III. Constitution-formula of the hydroxybenzoic acids and of sulfanilic acid”*. By Dr. H. I. WATERMAN. (Communicated by Prof. J. BÖESEKEN).

(Communicated in the meeting of September 29, 1917).

Benzoic acid, salicylic acid and meta- and para-hydroxybenzoic acid.
In a previous communication ¹⁾ I have proved that in alkalic solution phenol behaves as monobasic acid. It can be expected that in alkalic solution benzoic acid will act as monobasic acid. This expectation has been confirmed by the experiments.

According to the said properties of phenol on the one hand, benzoic acid on the other hand it might be supposed that in alkalic solution the three hydroxybenzoic acids would behave as two-basic acids. It has been proved that this is only the case with meta- and para-hydroxybenzoic acid. Salicylic acid on the contrary in alkalic solution acts as mono-basic acid. The results of the referential experiments are united in table I^a and I^b.

From the polarisation at the beginning of the experiments is proved that neither benzoic acid nor the three hydroxybenzoic acids have considerable influence upon the polarisation of glucose (table I^a and I^b). Whilst the presence of 5 cm³ of 1,06 normal sodium-hydroxide-solution after 3½ hours has lowered polarisation from +11,1 to respectively +5,8 and +5,9 (N^o. 5 and 8, I^a), the addition of 1 milligram-molecule of salicylic acid and benzoic acid has caused that the polarisation has only been lowered to +6,4 and +6,6 (N^o. 6 and 7, I^a).

Analogous results were obtained with the same experiments after ± 6½ hours; under the influence of 5 cm³ of 1,06 normal NaOH-solution the polarisation has here been lowered to respectively +3,3 (N^o. 5) and +3,1 (N^o. 8), at N^o. 6 and 7 only to +3,9 and +4,0.

1 milligrammolecule of the said acids compensates the action of something less than 1 cm³ of 1,06 normal NaOH-solution; salicylic acid and benzoic acid behave therefore as about monobasic acids. If salicylic acid would act as two-basic acid, the polarisation of N^o. 6 (I^a) after 3½ and 6½ hours should not be respectively +6,4

¹⁾ These Proceedings, April 27, 1917. Vol. XX p. 98.

and + 3,9 but about + 7,6 and + 5,4. The intensity of yellow-colouring too was herewith in agreement.

The colour of N^o. 6 and 7 (I^c) after 24 hours was, nearly equal to that of N^o. 4 (I^c).

TABLE Ia. Benzoic acid ¹⁾ and salicylic acid ¹⁾ in alkalic solution.

Number	Added	Numb. of cm ³ 1.06 N. NaOH added.	Polarisation (2 d.m.) in grades VENTZKE			Colour of the solution after 24 hours
			at beginning	after + 3 1/2 hours	after + 6 1/2 hours	
1	40 cm ³ of a solution containing + 5% glucose	0	+ 11.2	+ 11.1	not determined	colourless
2	id.	2	+ 10.7	+ 8.9	+ 6.9	rather pale yellow
3	id.	3	+ 10.2	+ 7.6	+ 5.4	pale yellow
4	id.	4	+ 10.3	+ 6.9	+ 4.1	deep pale yellow
5	id.	5	+ 9.9	+ 5.8	+ 3.3	yellow
6	id.	138 milligr. salicyl. acid = 1 milligr. molecule	+ 10.1	+ 6.4	+ 3.9	deep pale yellow
7	id.	122 milligr. benzoic acid = 1 milligr. molecule	+ 10.1	+ 6.6	+ 4.0	deep pale yellow
8	id.	5	+ 9.9	+ 5.9	+ 3.1	yellow

Diluted to 50 cm³. and placed in thermostat with watermantle. Temp.: 33°-34°

¹⁾ Preparations from the laboratory-collection.

From the results united in table I^b it follows that with N^o. 5 and 9, where 5 cm³ of 1,06 normal NaOH has been added after three hours the polarisation has been lowered from +11,4 to +5,3 (N^o. 5 and 9, I^b).

The presence of 1,06 milligrammole of meta- and para-hydroxybenzoic acid has caused that the polarisation has been lowered only to +7,5 and +7,7 (N^o. 7 and 8, I^b) about equal

TABLE Ib o-, p-) m-) and p-) hydroxybenzoic acid in alkalic solution.

Number	Added	Numb. of cm ³ , 1.06 N. NaOH added	Polarisation (2 d.m.) in grades VENTZKE		Colour of the solution after ± 21 hours
			at beginning	after 3 hours	
1	40 cm ³ of a solution containing ± 5% glucose	0	+ 11.4	not determined	colourless
2	id.	2	+ 10.9	+ 8.5	pale yellow
3	id.	3	+ 10.5	+ 7.5	yellow
4	id.	4	+ 10.1	+ 6.2	yellow-brown
5	id.	5	+ 9.9	+ 5.3	brown
6	id. 146 mgr. salicyl. acid = 1.06 milligrammole	5	+ 10.0	+ 6.4	yellow-brown
7	id. 146 mgr. m hydroxybenzoic acid = 1.06 mgr. mol.	5	+ 10.2	+ 7.5	yellow some-thing deeper than n ^o . 3
8	id. 165 mgr. p. hydroxybenzoic ac. = 1.06 mgr. mol. 2)	5	+ 10.4	+ 7.7	yellow
9	id.	5	+ 9.8	+ 5.3	brown

1) Preparations of "KAHUBAUM".

2) C₆H₄(OH)COOH. 1 Aq.

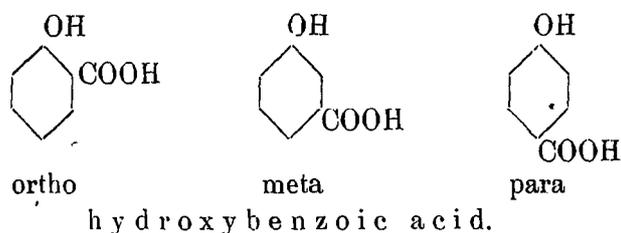
Diluted to 50 cm³, and placed in thermostat with watermantle. Temperature 33°–34°

to the polarisation of N^o. 3 (I^b), where 3 cm³ of 1,06 normal NaOH-solution had been added. 1 milligrammolecule of m.- and p.-hydroxybenzoic acid compensates therefore the action of 2 cm³ of normal NaOH-solution.

To avoid every accidental deviation in the comparison, experiment N^o. 6 (I^b) served, from which could be concluded once more that in alkalic solution salicylic acid behaves as monobasic acid.

The intensity of colour of the solutions, which with these experiments (I^b) was observed after 21 hours was in rather good agreement with these results.¹⁾

In the above we have met a difference in properties of salicylic acid on the one hand and the meta- and para-hydroxybenzoic acids on the other hand, which is not expressed by the usual constitution-formula:



Indeed this difference had been stated in other directions, viz.:

1st. The slight solubility of salicylic acid in water and the strong solubility in oil.²⁾

2nd. The slight liability to attack of salicylic acid by organisms, compared with the strong liability to attack of the meta- and para-hydroxybenzoic acids.²⁾

3rd. The antiseptical action of salicylic acid, which is strongly connected with the properties mentioned under 1 and 2.²⁾

Furthermore in such compounds the presence of hydroxylgroups increases the solubility in water and decreases the solubility in oil.

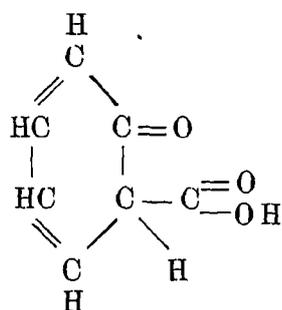
Finally in many cases the augmentation of the number of hydroxylgroups causes that the compounds can be attacked easier by organisms.²⁾

These considerations necessitate to reject the usual constitution-

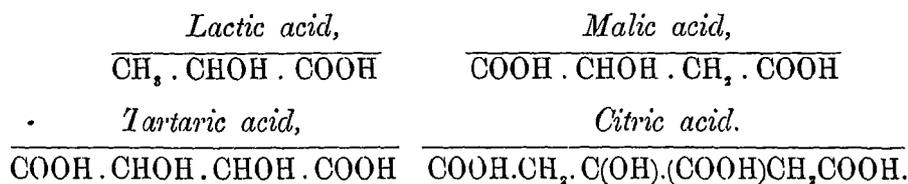
¹⁾ It must be remarked that the observations of intensity of colour have no absolute but only a relative value; the results of a series of experiments therefore can only be compared mutually and not with experiments belonging to another series. To a certain degree this is also the case with the polarisation because the temperatures at the beginning of the experiments are not always the same but depend on the temperature of the laboratory.

²⁾ J. BOESEKEN and H. I. WATERMAN, These Proc. November 25, 1911 p. 608.

formula of salicylic acid, because this formula contains a hydroxyl-group in the nucleus next to the carboxylgroup.



A formula as proposed by BRUNNER ¹⁾ is in accordance with the just mentioned properties of the salicylic acid.

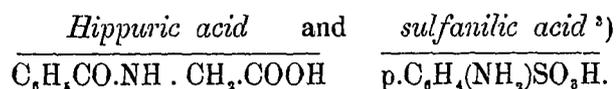


The research of these four acids was quite in agreement with their constitution-formula, in connection with my experiments described before.

In alkalic solution the alifatic alcohols, such as methylic alcohol and aethylic alcohol, have no acidic properties. ²⁾

It could be expected that lactic, malic, tartaric, and citric acid would behave as respectively one-, two-, two- and three-basic acid in accordance with the presence of an equal number of carboxyl-groups.

The referential experiments are united in table II.



Although about these compounds with certainty nothing could be foretold in accordance with the neutral character of acetamide ($\text{CH}_3 \cdot \text{CONH}_2$) and urea ($\text{CO}(\text{NH}_2)_2$) in acidic and alkalic solution ⁴⁾ it could be expected that the aminogroup of the benzoxylamino-acetic acid would not enable this compound to fix hydrochloric acid under the circumstances of my experiments. Therefore it might be supposed that hippuric acid in acidic solution behaves neutral, in

¹⁾ Compare A. F. HOLLEMAN, Die direkte Einführung von Substituenten in den Benzolkern; Leipzig, 1910, p. 180.

²⁾ Chemisch Weekblad 14, 119 (1917).

³⁾ The used preparations were from the laboratory-collection.

⁴⁾ These Proceedings, June 30, 1917.

TABLE II. Lactic acid, malic acid, tartaric acid and citric acid in alkalic solution.

IIa. Malic acid and tartaric acid.¹⁾

Number	Added	Numb. of cm ³ . 1.06 N. NaOH added		Polarisation (2 dm.) in grades VENTZKE		Colour of the solution after ± 24 hours.
				At beginning	After ± 6½ hours	
1	40 cm ³ of a sol. cont. ± 5% gluc.	3	Diluted to 50 cm ³ . and placed in thermostat with water- mantle. (Temp. 33°-34°).	+ 10.3	+ 5.7	pale yellow
2	id.	5		+ 9.8	+ 3.6	yellow
3	150 mgr. tartaric acid = 1 m.grammolecule ²⁾	5		+ 11.0	+ 5.7	pale yellow
4	134 milligr. malic acid = 1 milligrammolecule ²⁾	5		+ 10.0	+ 5.2	pale yellow

IIb. Lactic acid and citric acid.¹⁾

Number	Added	Numb. of cm ³ . 1.06 N. NaOH added		Polarisation (2 dm.) in grades VENTZKE		Colour of the solution after ± 24 hours.
				At beginning	After ± 6 hours	
1	40 cm ³ of a sol. cont. ± 5% gluc.	0	Diluted to 50 cm ³ . and placed in thermostat with watermantle. (Temperature 33°-34°).	+ 11.0	+ 11.4	colourless
2	id.	2		+ 10.7	+ 6.4	rather pale yellow
3	id.	3		not determined	+ 4.8	pale yellow
4	id.	4		not determined	+ 3.8	yellow
5	id.	5		+ 9.6	+ 2.6	yellow-brown
6	210 milligr. citric acid (+1Aq.) = 1 mgr molec.	5		+ 10.7	+ 6.1	rather pale yellow
7	90 milligr. lactic acid = 1 milligrammolecule	5		+ 10.2	+ 3.6	yellow
8	id.	5		+ 9.9	+ 2.8	yellow brown

¹⁾ The preparations employed were from the laboratory collection.

²⁾ The polarisation caused by tartaric acid and malic acid is slight.

alkalic solution as monobasic acid because this compound possesses one carboxylgroup.

The referential experiments were in agreement with this expectation.

When we suppose that sulfanilic acid possesses the open constitution-formula we might expect that this compound should behave in alkalic solution as monobasic acid and in acidic solution as monacidic alkali.

However it was proved that in acidic solution sulfa-

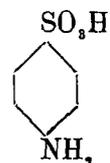


TABLE IIIa. Hippuric acid and sulfanilic acid in alkalic solution.

Number	Added	Numb. of cm ³ . 1.06 N. NaOH added	Polarisation (2 dm.) in grades VENTZKE		Colour after \pm 24 hours
			at beginning	after \pm 6 hours	
1	40 cm ³ . of a solution containing \pm 5% glucose	0	+ 11.0	+ 11.4	colourless
2	id.	2	+ 10.7	+ 6.4	rather pale yellow
3	id.	3	not determined	+ 4.8	pale yellow
4	id.	4	not determined	+ 3.8	yellow
5	id.	5	+ 9.6	+ 2.6	yellow-brown
6	id. 209 milligr. sulfanilic acid = 1 milligram-molecule (\pm 2 aq.)	5	+ 10.2	+ 3.6	yellow something deeper than no. 4
7	id. 179 milligram hippuric acid = 1 milligrammolecule	5	+ 10.1	+ 3.7	yellow, something deeper than no. 4
8	id.	5	+ 9.9	+ 2.8	yellow-brown

Filled up to 50 cm³ and placed in thermostat with watermantle. (Temp. 33°—34°.)

nic acid behaves neutral and in alkalic media as monobasic acid.
The referential experiments are united in table III^a and III^b.

TABLE III^b. Hippuric acid and sulfanilic acid in acidic solution.

Number	Added	Number of cm ³ 1.01N HCl added	Polarisation (2 dm.) in grades VENTZKE		
			after 18 $\frac{3}{4}$ hours	after \pm 26 hours	after 67 hours
1	50 cm ³ of a sol. containing 260 Gr. sucrose p.L.	0	+49.5	+49.4	not determined
2	id.	2	+22.1	+15.2	-6.5
3	id.	3	+12.6	+5.3	-11.5
4	id.	4	+6.2	-0.8	-13.0
5	id.	5	+1.0	-5.0	-13.7
6	209 millig. sulfanilic acid = 1 milligrammolecule	5	+1.0	-5.3	-13.7 ²⁾
7	179 milligram hippuric acid = 1 milligrammolecule	5	+1.2	-5.0	-13.7

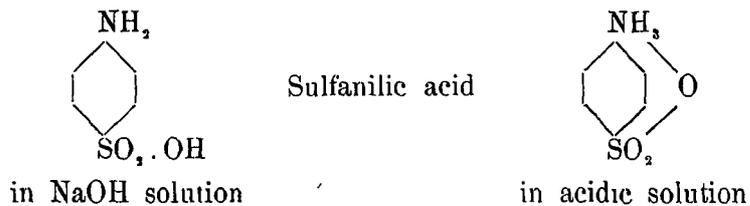
1) At beginning of the experiment not quite dissolved. After 3 hours the sulfanilic acid was practically dissolved; then the hippuric acid was not quite dissolved, after 18 $\frac{3}{4}$ hours all was dissolved.
2) The liquid was coloured pale yellow.

From the experiments 6 and 7 (III^a) we see that after \pm 6 hours polarisation has been lowered to respectively +3,6 and +3,7. This number is almost equal to the polarisation of N¹. \pm after the same time. From which it may be concluded that 1 milligram-

molecule of sulfanilic acid and hippuric acid each compensate the action of something less than 1 cm³ of 1,06 normal NaOH-solution. In alkaline solution they act practically as monobasic acid.

The mentioned acids practically have no influence on the inversion of sucrose by hydrochloric acid (III^b)

This gives rise to the supposition for sulfanilic acid in alkaline solution of the "open" constitution-formula, in acidic solution of the "closed" formula.



Dordrecht, August 1917.

Chemistry. — "*The Structure of Truxillic Acids.*"¹⁾ By A. W. K. DE JONG. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of Sept. 29, 1917).

Up to now the following truxillic acids are known, α , β , γ , δ , ϵ truxillic acid and β cocaic acid, which belong to two series, because the members of one series cannot be converted to those of the other without previous depolymerisation to cinnamic acid.

The γ acid belongs to the series of the α truxillic acid; it is formed by heating of the α truxillic acid with acetic acid anhydride²⁾; the β -cocaic acid, which is formed by melting from α truxillic acid with KOH,³⁾ belongs to the same series.

The second series is derived from β truxillic acid, which through melting with KOH passes into δ truxillic acid⁴⁾. The last acid yields ϵ truxillic acid through heating with acetic acid anhydride; the ϵ truxillic acid possesses the same melting point as γ truxillic acid; a mixture of the two acids melts, however, about 20° lower, from which the difference of these acids can already appear. Also in the solubility of their salts there are found great differences.

By the formation of α truxillic acid from α normal cinnamic acid⁵⁾ and of β truxillic acid from β normal cinnamic acid⁶⁾ it is known that one of the 4 following structural formulae, corresponding with the 4 different ways in which 2 molecules of cinnamic acid can combine under formation of a tetramethylene ring, belongs to these truxillic acids.

These 4 structural formulae belong to 2 series viz. the two first to one, and the two last to the other series. The members of these series cannot be transformed into each other without previous depolymerisation to cinnamic acid.

We know from LIEBERMANN'S researches that β truxillic acid yields benzil⁷⁾ on oxidation with potassium permanganate, from

1) Ber. 22, 2255; Ber. 23, 2516; Ber. 26, 834; Ber. 27, 1410.

2) LIEBERMANN, Ber. 22, 2240.

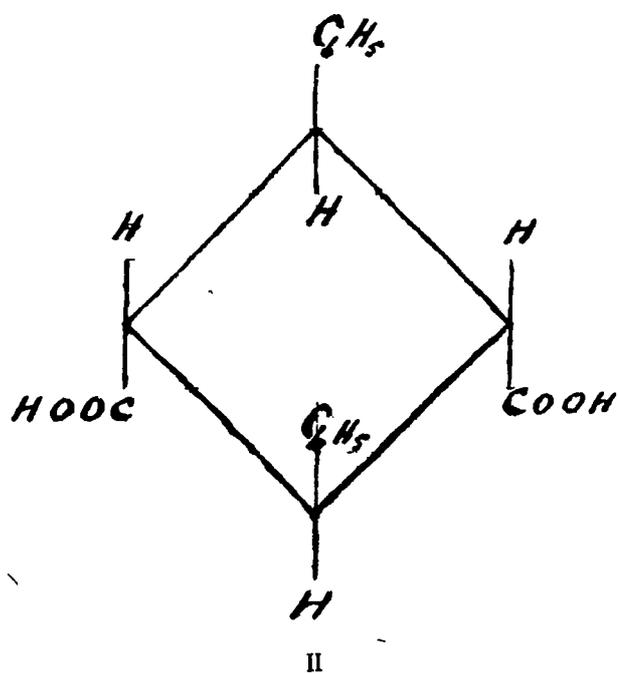
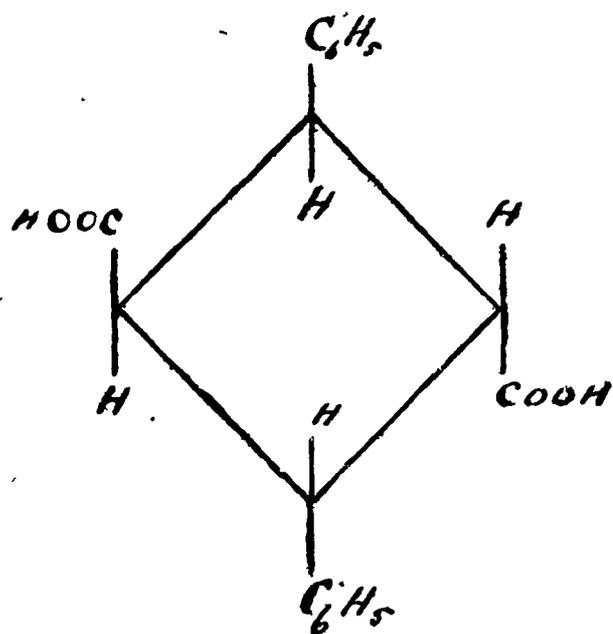
3) HESSE, Ann. 271, 202.

4) LIEBERMANN, Ber. 22, 2240.

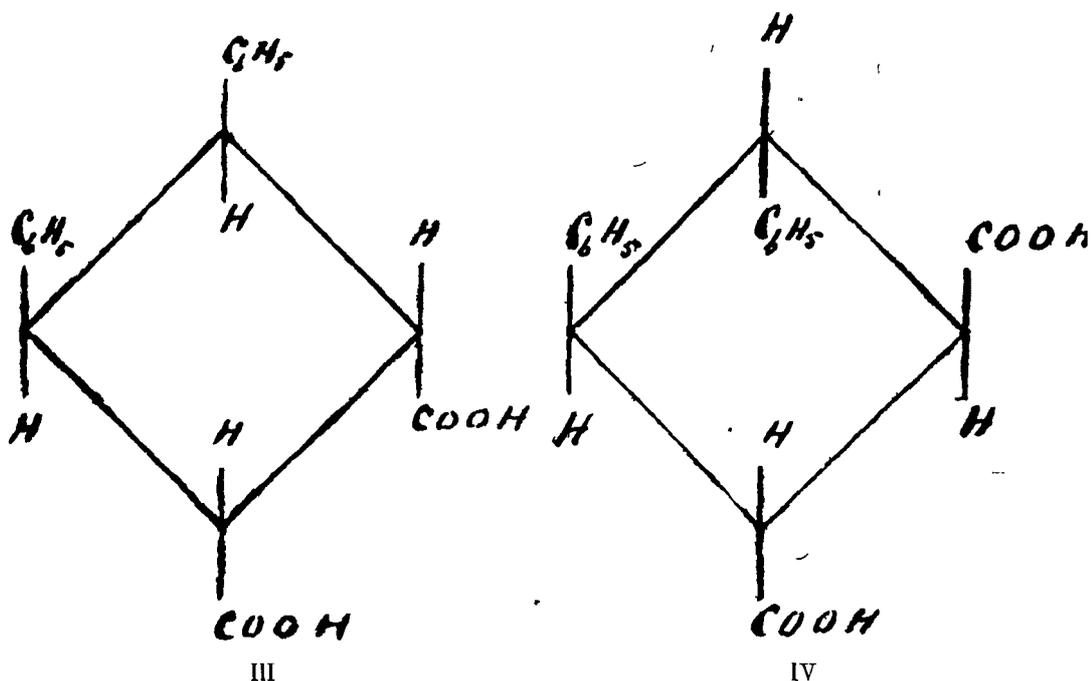
5) RUBER, Ber. 35, 2908.

6) These Proc. 1915, Vol. XVIII p. 181.

7) Ber. 22, 2253.



43*



which it appears that for this acid the C_6H_5 -groups must be found at 2 adjacent C-atoms, so that in connection with the formation from normal cinnamic acid one of the formulae III or IV must be assigned to this acid.

The β truxillic acid forms an internal anhydride¹⁾, and is not changed into another truxillic acid by heating with acetic acid anhydride²⁾. It appears from this that the COOH groups are placed on the same side of the closed-chain of four carbon atoms; hence we must give formula III to the acid.

Through melting with KOH δ truxillic acid is formed from β truxillic acid³⁾; this acid cannot have arisen from the former by displacement of one COOH or one C_6H_5 , from one side of the ring to the other side, because then in the former case δ truxillic acid with acetic acid anhydride would have to yield β truxillic acid, and in the other case δ truxillic acid would not be changed by heating with acetic acid anhydride, neither of which is conformable to the facts. It must, therefore, be assumed, that 2 groups exchange places at the same time, viz. a C_6H_5 group and a COOH group, because, as is easy to see, the formation of ϵ truxillic acid from δ

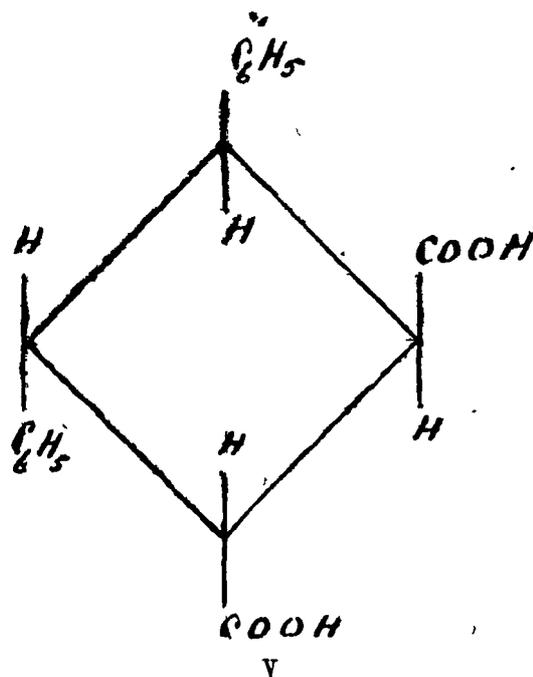
¹⁾ Ber. 22, 834.

²⁾ Id. 2240.

³⁾ l. c.

truxillic acid through heating with acetic acid anhydride could not be explained in another way.

These exchanges of place of a C_6H_5 - and a $COOH$ -group from one side of the closed-chain to the other side can also take place for the groups of 2 adjacent C-atoms of the four ring, and also of 2 C-atoms placed opposite each other. In one case formula IV is obtained, and in the other case the following formula is valid.



This formula is built up from 2 molecules of allo-cinnamic acid.

The δ truxillic acid now is formed from normal cinnamic acid, viz. through the illumination of the stable lead salt of this acid.¹⁾

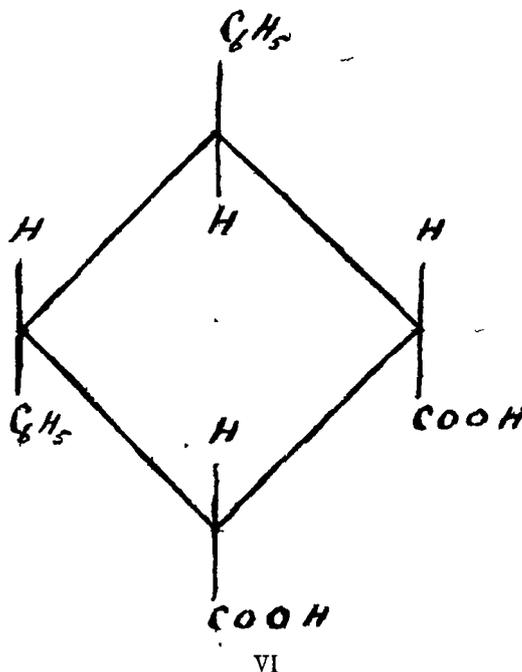
0,466 gr. of cinnamic acid, as lead salt, gave 0,075 gr. of truxillic acid and 0,095 gr. of δ truxillic acid after 27 hours' illumination.

The formula IV must, therefore, be assigned to the δ truxillic acid, whereas the ϵ truxillic acid possesses the following formula (See form. VI following page).

By heating with hydrochloric acid at 180° and also by melting with KOH it is changed into δ truxillic acid. These two acids are in the same relation to each other as fumaric and maleic acid, ϵ is the cis-acid, δ the trans-acid.

¹⁾ Shortly an extensive paper will be published about the action of solar light on cinnamic acid salts.

It is clear that one of the 2 structural formulae I or II must be assigned to the α truxillic acid.



This acid does not give an internal anhydride,¹⁾ and is converted by heating with acetic acid anhydride into γ truxillic acid,²⁾ which acid is again converted into α truxillic acid by heating with hydrochloric acid.³⁾ These two acids possess therefore a similar isomerism as the cis- and trans-acids, in which the α truxillic acid possesses the trans-form. In the γ truxillic acid the COOH-groups are on one side of the ring, this not being the case for the α truxillic acid. Accordingly this latter acid must possess formula I, and the γ truxillic acid is formed from the α truxillic acid by displacement of one COOH-group, which causes its structural formula to assume the following form. (See formula VII).

The β cocaic acid arises from α truxillic acid by heating with KOH.⁴⁾ Through heating with acetic acid anhydride it is not changed into another truxillic acid. In this acid the COOH-groups must therefore be situated on one side of the ring, just as in γ truxillic acid. It can however, not have arisen from α truxillic acid by

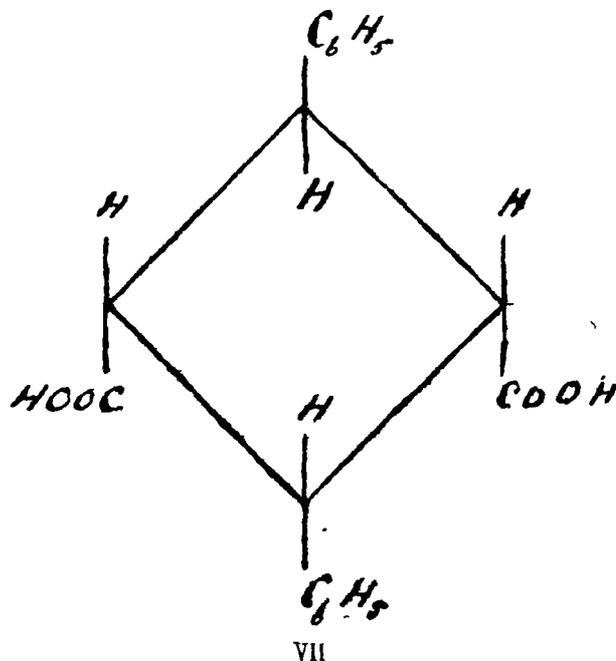
¹⁾ Ber. 26, 834.

²⁾ Ber. 22, 124.

³⁾ Ber. 22, 2245.

⁴⁾ l. c.

displacement of a COOH-group alone, because then it would have to be converted into α truxillic acid by heating with hydrochloric acid, whereas it is not changed by this operation. There must,



therefore, two groups viz. a C_6H_5 - and a COOH-group have been displaced from one side of the ring to the other in the formation of β cocaic acid from α truxillic acid. This can take place in two ways, in which in one case formula II arises and in the other case all C_6H_5 - and COOH-groups will lie on one side of the ring.

Formula II is built up of 2 molecules of normal cinnamic acid, and the other formula is formed from 2 molecules of allo cinnamic acid. The β cocaic acid was found on illumination of the stable barium salt of normal cinnamic acid together with ρ truxillic acid.

0,593 gr. of cinnamic acid, as barium salt, yielded 0,168 gr. of β truxillic acid and 0,092 gr. of β cocaic acid after 27 hours' illumination.

It appears therefore from this, that formula II must be assigned to β cocaic acid. Besides it is very improbable that a substance for which the heavy groups are all found on one side of the ring would arise by melting with KOH.

After what has been said about the conversions of the 6 truxillic acids, the following rules may be given.

1. The truxillic acids for which 3 large atom groups are situated on one side of the ring are converted through heating with KOH or HCl to truxillic acids with 2 heavy atom groups on one side.

2. By melting with KOH those forms arise for which the heavy atom groups are situated alternately on one side or on the other of the ring.

3. The truxillic acids for which 2 heavy atom groups are placed on one side of the ring are not changed into another truxillic acid through heating with hydrochloric acid.

In the foregoing exposition it has been assumed that the truxillic acids possess a tetramethylene ring. The proof for this has not yet been furnished; their properties found up to now can very well be reconciled with this conception.

I hope shortly to be able to communicate the results of an investigation in this direction.

Geology. — “*Old Andesites*” and “*Brecciated Miocene*” to the east of *Buitenzorg (Java)*. By Dr L. RUTTEN. (Communicated by Prof. Dr. C. E. A. WICHMANN).

(Communicated in the meeting of September 29, 1917).

In their “*Geology of Java and Madoera*”¹⁾ VERBEEK and FENNEMA deal with the development of the Neogene formations about as follows:

During the oldest period of the Miocene numerous and very extensive eruptions took place all over Java; the eruptive rocks were for the greater part andesites. Where they emerge they are in many cases difficult to distinguish from the andesites of the present volcanoes; in other cases, however they differ from the recent andesites in being weathered to a greater depth.

In a subsequent period the old volcanoes were denuded again considerably, their detritus forming round the volcanic nuclei a system of stratified breccia, conglomerates and andesitic sandstones (m 1), which may locally be found to be interstratified with clay and sometimes with limestone or marl.

This period was succeeded by one in which fine-grained layers, especially marls, were deposited upon the old miocene breccia and conglomerates (m 2).

Subsequently in the most recent part of the Miopliocene especially limestones were formed (m 3).

Now after the Tertiary had been folded, the present volcanoes arose in Java and spread their discharge over vast areas of the tertiary strata, which had meanwhile been considerably denuded.

In the period m 1 and m 2 only few volcanic eruptions occurred; in the period m 3 there was no volcanic activity at all.

It is obvious, that the authors, who were thrown upon their own resources when called upon to construct, in comparatively few years, a geological map of an island, four times larger than Holland and difficult to traverse over long distances, had to make a number of working hypotheses on the stratigraphy, the tectonic and the geological history of the island, if they would make anything of their injunction. It will be well, therefore, to look upon their maps and profiles of Java — in which their views of the neogene, as

¹⁾ R. D. M. VERBEEK and R. FENNEMA, *Geology of Java and Madoera*. 1896.

described above, have been laid down graphically — first and foremost as the embodiment of their working hypotheses, which in some details are reliable, but whose general trustworthiness must be called in question.

The maps and profiles cannot be unreservedly accepted. Only more prolonged and more minute investigations than V. and F. were able to perform, will have to demonstrate for every part of the island whether the writers are right in their generalising assertions about the geology of Java, or whether their mapping has to undergo a thorough revision.

On the geological map of Java old andesites, brecciated and marly miocene and recent eruptive rocks have been indicated to the east of Buitenzorg ¹⁾. A number of excursions made in this district enable me to form an estimate of this mapping.

Up to about 4½ km. before the Poentjakpass the great highroad from Tjiandjoer to Buitenzorg, runs over the young, volcanic mantle of the Gedeh-Pangrango-massif. According to the geological map it then crosses a mountain ground of old andesites and basalts, which in the South leans against the Northern declivities of the Pangrango, and extends towards the North, broadening rapidly, as far as nearly 15 km. north of the Poentjakpass. The southern part of these old eruptive rocks (G. Gedogan, Djoglok, Soemboel and Gegerbentang) is, according to the geological map, as it were, pinched off from the more northern tracts by the young volcanic massif of the G. Limo. In the landscape these "old andesites" do not seem to be distinguishable from the "young volcanoes". Nor do the large number of andesite blocks on the Batavia-side of the Poentjak, visible from the tea-gardens, look less fresh than those found on the slopes of the Gedeh. It appears, then, that after traversing the district once no evidence whatever can be adduced, to show the existence of two volcanic massifs of entirely different age.

The other arguments brought forward by VERBEEK and FENNEMA in their "Geology of Java and Madoera" to support their hypothesis that in this region the old miocene eruptive rocks are detached from the young volcanoes, are not quite satisfactory. In the French edition (p. 506) we read: "Autant qu'on ait pu juger par les affleurements insuffisants, les sédiments tertiaires semblent reposer au Nord et à l'Ouest sur l'andésite et contre celle-ci". It seems, therefore, that, as regards the normal superposition of the tertiary sediments on the old andesites — which would indeed prove the age of the

¹⁾ Sheets AII, AIII, BII, BIII.

latter — the writers themselves are not quite satisfied. Further on they assert that several eruptions must have taken place in the great old-andesite-massif, and try to substantiate this view by pointing to the facts that, petrographically, the rocks differ rather much, and that remains of different crater-rims are still extant. One of the peaks, however, of these “old” crater-rims — the Goenoeng Limo — is according to the writers a young volcano, while with respect to a second peak — the G. Kentiana — they also suggest the possibility of a younger date, “mais les autres points d'éruptions appartiendront sans doute à l'ancien massif andésitique”. (p. 506).

No conclusive arguments for the high antiquity of the “old” andesites, east of Buitenzorg, are to be found in the text; on the other hand indications are found in the work to show that the writers themselves were wavering in their opinion, and there is, moreover, one important fact that seems to point to a later date. Indeed VERBEEK and FENNEMA also allude to traces of rather distinct crater-rims inside the massif. If, in addition, we consider that, as they suppose, the “old volcanoes” had to furnish the material for all the strata of the miocene breccia and conglomerates to a thickness of sometimes thousands of meters, and if we also keep in view that, after the miocene, the Tertiary of Java, has undergone at least one intense plication, we can hardly realise that volcanoes should have outlived a very lengthy period of denudation and an intense plication so long as to contain even now distinguishable crater-rims.

These considerations, which force themselves upon the geologist who travels from Tjiandjoer to Buitenzorg, induced me to make excursions with a view to farther inquiries into the relative age of the Tertiary and the eruptive rocks round about Buitenzorg. From Sept. 1914 to May 1917 I spent 21 days in fieldwork.

It stands to reason that a minute study of the Sedimentary Tertiary round Buitenzorg can a priori be expected to yield sufficient evidence to decide whether the “Old Andesites” are really older than the sedimentary Tertiary and, consequently much older than the volcanic mantles of Gedeh and Salak, or whether all eruptive rocks about Buitenzorg are coeval. If the “Old Andesites” belong to pre- or old miocene, the miocene strata round these massives must be very coarse-grained; they must include many fragmentary materials from the old volcanoes near them, they must be “brecciated”, as indeed also V. and F. have suggested. If, however, the oldest part of the sedimentary Tertiary in the neighbourhood of the “Old Andesites” appears to be fine-grained and free from or poor in volcanic discharge,

we can only assume that the andesites were not formed before the deposit of the Tertiary. Again, if the large masses of the old eruptive rocks existed before the folding of the Tertiary, we can expect the tectonic of the Tertiary in the neighbourhood of these massifs to adapt itself in some measure to the large eruptive masses. If, however, the folding of the Tertiary is older than the "Old Andesites", the general tectonic appearance if the Tertiary continues undisturbed up to the eruptive masses. Besides, if the sedimentary Tertiary is younger than the "Old" Andesites we may look for the "Old Andesites" normally disposed, underlying the sedimentary Tertiary in its deep-seated plications. If the Andesites are subsequent in age, we can hardly expect to find their points of emergence in a country so difficult to traverse, but in their neighbourhood the sedimentary Tertiary might show traces of contact-metamorphism, whereas enclosures of sedimentary Tertiary might be found in the Andesites. Facies and tectonic of the sedimentary Tertiary may therefore yield valuable material. We can a priori expect little from a direct comparison of the "Old Andesites" with the recent eruptive rocks in their vicinity. V and F. have already alluded to it that the "Old Andesites" of Java differ from the recent Andesites only in being more intensely weathered. If, however, we reflect that the weathering of some recent volcanoes has advanced so far (as instanced by the slopes of Salak and Gedeh) that from the volcanic tuffs colloid matter has been derived, still including recognisable andesite fragments, of a waxy softness, we can realise, that generally the "Old Andesites" can hardly be weathered to a still greater depth.

Now let us discuss the results of our local inquiry in the direction alluded to:

When starting from the country-seat Tjiloewar on the road from Buitenzorg te Batavia towards the South-east,¹⁾ one first moves along brownish-red grounds in which occasionally andesitic blocks are revealed at the surface; they are the typical weathering products of the recent Salak-Gedeh tuff breccia and agglomerates. Prior to reaching the river Tji Keas one descries on some hills yellow grounds, which at the Tji Keas prove to be the weathering product of a bluish-grey, bulbous shaly hard clay (shale), containing in some places little Foraminifera (Rotalidae, Globigerinidae). On the Tji Keas a Globigerina-containing marl-bank occurs in this badly stratified clay (shale), so that the strike and the slope can be measured (N 60°.0, 10°). In some places the clay — generally fine-grained —

¹⁾ See the accompanying map and profiles.

is slightly sandy: the residue appears to contain many pyrite-granules and quartz-splinters, while plagioclase, amphibole, pyroxene and andesitic ground mass are decidedly wanting. Between Tji-Keas and Tji Teureup we find again at the detached hillock Pr. Bondol perfectly analogous clays sloping towards the North at an angle of 14° . A road runs from the Pr. Bondol towards the south, crossing the ridge of the Pr. Maoeng (See map). When I visited this district, the road was under repair, it was even partly torn up, which had required a great deal of digging, so that the disclosures were very interesting. Up to a short distance from the ridge of the Pr. Maoeng the presence could be ascertained of the hard, greyish blue, bulbous shaly clay, getting plastic in a moist condition, yellowish-white when weathering, and constantly declining towards the North. The strike is invariably about N. 70° E, the slope increases from N. to S. from about 15° to beyond 55° . At first we are surprised to see in all brooklets and on the hills immense fragments of andesite, but on closer investigation we discover that they have nothing to do with the rocks of the interior of the hills, as they are the relics of a recent tuff-breccia formation. In one regress of the road we could beautifully observe how a red volcanic area, interspersed with andesitic fragments, overlay discordantly vertically erected, denuded tertiary clay that had been weathered white.

A geological survey is largely impeded by the circumstance that all over the environs of Buitenzorg suchlike young volcanic agglomerates overlay the Tertiary, because in many cases the solid stone is found only in deep indentations of the river. Perhaps this is why *V* and *F* have indicated so many "miocene breccia" in this district.

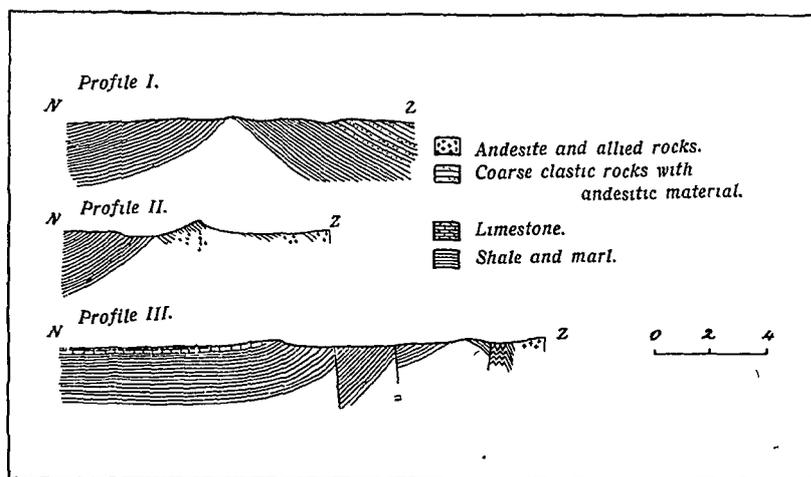
At the watershed of the Pr. Maoeng the regress of the road is 10 m. deep; here also are we confronted with the typical blue clay, now, however, declining 28° towards the South. Here we are in the heart of an anticline, in whose northern arm we have encountered a very uniform clay-formation of 1500—2000 m. thickness. The clay in the kernel of the anticline also appeared to be next to quartzless and completely devoid of andesitic matter.

On the Southern slope of the Pr. Maoeng again the Tertiary clay may be noted repeatedly, now sloping down southward. Whereas, however, in the northern arm of the anticline the strike was rather constantly N. 70° E. it becomes in the Southern arm N. 70° W. to N. 50° W.; it seems, then, as if the anticline again dips towards the South. South of the confluence of the Tji Djajanti and the Tji Keas disclosures of Tertiary rocks are over some distance

many fresh plagioclase-splinters and magnificent idiomorphic biotite laminae.

Where the valley of the Tji Keas breaks Southward into the uplands about $1\frac{1}{2}$ km. to the south of the embouchure of the Tji Djajanti, the disclosures reappear; they are the familiar, somewhat marly hard clays, which, however, here include bands of marl, sandstone, and conglomerates, which incline 30° — 45° towards the South. The strike is $N\ 65^{\circ}\ W$. On this level, then, which lies stratigraphically at least 1700 m. above the core layers of the Pr. Maoeng anticline, we find for the first time numerous coarse clastic bands intercalated into the tertiary formation. The marl is not fossiliferous, the sandstone and the conglomerates are calcareous, and all stones are very rich in andesitic constituents. In a small affluent of the Tji Keas, running Southward, it is admirably revealed that in still more elevated levels, true andesitic tuff-breccia succeed, which, in their turn, alternate with sandstones and clays. In the most Southern affluent of the Tji Keas, the Tji Bedoeg, we again encounter hard shales, including besides bands of andesitic sandstones, conglomerates and breccia, also a layer of Globigerina marl and a thin bank of coralligenic limestone. In the latter Lithothamnia and Amphistegina occur. The direction is $N.\ 55^{\circ}\ W.$, the slope 30 — $31^{\circ}\ S$. The southmost disclosure of the Tertiary I found in a rivulet north of Gadok, where the andesitic sands and tuffs dip 20° Southward.

In the profile described above we have encountered a tertiary



formation whose lowermost portion consists of homoplastic clays that bear no or hardly any volcanic matter. Their marine origin

is proved by the sporadic Foraminifera. Higher up the clays are gradually pushed back by coarse-clastic layers, built up of volcanic material, while the most recent layers of the plicated Tertiary consist exclusively of volcanic sands and tuff-breccia, dipping beneath the Gedsch-massive at a slight angle.

The clay-formations can be traced towards the East up to the spot where VERBEEK has roughly indicated the western limit of the "Old Andesites" — i. e. along the upper course of the Tji-Teureup. Between the rivers Tji-Djanjanti, Tji Teureup, and Tji Keas, the bulbous shale, free from volcanic material, can again be seen wherever the solid rocks emerge. Between the upper-course of Tjikeas and Tji-Teureup, over a zone of little breadth but of 1 km. length (direction about N. 20° W.) many huge "wool-packs" (some of them 100 m³) of andesite are lying in or on the clay-formation, forming an immense field of blocks. It cannot be made out, whether these blocks — like the numerous smaller andesite fragments occurring all over the area (cf. page 601) — are the remains of a discordant young covering of tuff-breccia, or whether they are the line of outcrop of an andesite dyke breaking through the clay-formation.

In the upper-course of the Tji-Teureup we find the familiar clay-rocks, here including Globigerina and moreover slightly silicified, so that it can be ground. It slopes down towards the South-west amidst disclosures of andesite-rocks which, downstream, pass into a granular-crystalline, diorite-like rock. It is interesting to note that the hollows of the Globigerina are often silicified. A most peculiar brecciated limestone, including Lepidocyclina and Amphistegina, occurs in concordant arrangement with this clayrock. It is made up of irregular limestone fragments, some of them highly crystalline, cleft by thin intermediate layers of the clayrocks just described. It seems as if the limestone has been broken to pieces during the plication of the mountain ground and particles of the plastic clay have been intercalated by pressure. So we see that close to the contact with the old andesites; nay, surrounded by them on nearly all sides, we find a tertiary formation, absolutely devoid of volcanic material.

The claystones occurring here, differ from the shales, found more to the West, in being more consolidated on account of only a slight silicification.

When going down the Tji Teureup, encountering all the way normal, imperfectly stratified shales, we approach the magnificent,

cone-shaped Goenoeng Pantjar, 870 m. in height, recognized from afar as a typical volcano, and, indeed, indicated on V and F's map as "Old Andesite". This is highly surprising as, with the exception of a few huge Andesite blocks — perhaps the outcrop of a dyke — we can only descry, either round or on the mountain, bluish white, more or less silicified shales, again without any trace of volcanic material. Moreover we find on the western base another calcareous sandstone, built up mainly of quartz-splinters. In this rock volcanic material is also lacking. The pebbly shale is so hard in some places, that the natives use it as flint. In Profile II we assumed, that the nucleus of the coniform G. Pantjar is constituted by an andesite mass, occasionally also a granular crystalline rock (see notes of interrogation) and that the silicified shale, a silicification perhaps due to contact-metamorphism, covers the volcanic nucleus, as a mantle. Two geysers on the northern slope of the G. Pantjar lend support to this view.

In the Tji Teureup as well as in a rivulet east of the G. Pantjar loose fragments of Andesite were found, which unmistakably include tertiary shale. Though it seems reasonable to look for the origin of these andesite blocks in the southern massif of the "Old Andesites", still it may be possible that they arise farther away in the Gedeh massif. On this account their discovery is not conclusive for the relatively recent date of the "Old Andesite".

In the profile across the G. Pantjar (N^o. 11) the axis of the Pr. Maoeng anticline is found rather to the North of this mountain, as shales sloping southward were still noted to the N.E. of the G. Pantjar. In the northern arm of the anticline lies in this profile the G. Hambalang which, like the more eastern G. Karang, looks from afar — e.g. from the road Batavia-Buitenzorg — like a plane distinctly sloping northward. On the G. Hambalang the disclosures of the Tertiary are few and far between, as it is largely overlaid by volcanic material of a recent date. Due east from the G. Hambalang the Tji Leungsi exhibits an almost uninterrupted disclosure of the Tertiary. On its left bank, at one place in the youngest parts of the clay-formation, a Cycloclypei-coral limestone has been intercalated, which towards the east rapidly increases in thickness, emerges there through the steep south slope of the G. Karang as a white outcrop, and spreads horizontally to the North of G. Karang all over the area as far as Kalapa Noengal (Profil III). These lime-stones contain besides Cycloclypeus also *Lepidocyclina* and *Amphistegina*.¹⁾

¹⁾ At one place in the youngest part of the shale-formation the Cycloclypeus lime stones are covered by peculiar felspathic sands.

Also to the south of the G. Karang, does the Tji Leungsi, which flows here through a narrow cleft, present an almost continuous disclosure of Tertiary. Again we observe everywhere the bluish-grey, occasionally marly shales, containing locally many calcite dykes and septarian nodules, composing the whole formation; volcanic material is absolutely wanting down to the core of the anticline, so beautifully disclosed here, the eastern elongation of the Pr. Maceng anticline. It is true though, that discordant, thick river-sediments of volcanic material are here seen to overlie the denuded shales. This material comprises some huge blocks, most likely remains of a young tuff-breccia, which formerly overlay the whole area of shales. In the profile of the Tji Leungsi the core of the anticline described, is arched nearly horizontally; farther on the South arm, however, many disturbances are to be seen, while still farther, quite near the shales — some kilometers west of the Tji Leungsi — the solid andesite rock can be detected. Generally the shales dip in the direction of the andesite.

A last series of researches was made east of the Tji Leungsi — in the basins of the Tji Djanggal and Tji Pamingkis. In the Tji Pamingkis we find below the embouchure of the Tji Handjavar only the typical clay-formations of a peculiar position; the strata are sloping mainly to the east. Here the vast anticline, which we saw emerging from the West, east of Buitenzorg, may be supposed to dip again towards the east.

In the upper course of the Tji Djanggal shale was found sloping towards the south at only about 10 m. from the steep blocks of hornblendic andesite and its breccia. This again bears witness to the fact that the shale dips in the direction of the andesite, but it is still a matter of conjecture whether the andesite overlies the shale or whether it is separated from it by shifting. Perfectly analogous phenomena were noted between the Tji Djanggal and the Tji Handjavar in a small river, the Tji Soerian. Here we see moreover distinctly in some places that the hornblendic andesite breccia rest on shale. It may also be, though, that such brecciated masses have glided down from the neighbouring mountains and are now, as a secondary formation, superposed on the clay-formation, so that also this observation does not afford conclusive evidence for the relatively recent date of the "Old andesites", although it lends plausibility to the view.

Finally a very interesting observation was made in the Tji Handjavar, west of the steep, coneshaped Goenoeng Handjawong, 970 m. in height. On its left bank, at the base, we find consolidated andesite rock, superposed on this a fine-grained, greyish-green breccia

of little thickness, this again being surmounted by very thick, coarse blocks of breccia. All the breccia are sloping towards the West and the whole arrangement seems to be the normal one, resulting from their being deposited as effusiva of the G. Handjawong. In the fine-grained breccia — an integral and transported component of the "Old andesites" — numerous, small enclosures of tertiary shale were found.

In the foregoing we saw then that by far the greater part of the sedimentary Tertiary, east of Buitenzorg, is built up of a very fine-grained clay-formation, in which volcanic material is all but wanting or completely so. Higher up, however, coarse clastic banks of volcanic material found their way to the surface. It appears, then, that the state of matters is just the reverse of VERBEEK and FENNEMA's hypothesis. They supposed the deep-seated portions of the Tertiary to be "brecciated", the upper portions to be "marly". This paralyses their main argument for the high antiquity of the "old andesites".

Let us now summarise our arguments against a high antiquity of these rocks :

1. In no place in the deepest plications of the Tertiary did we encounter disclosures of andesite.

2. The fact that in many places, close to the andesites, a sedimentary formation, free from volcanic material, was found, goes very much against a higher antiquity of andesites than of sediments. For this contact the only explanation could be furnished by an extremely complicated system of shifts — of which there are no indications — if the andesites were older than the sedimentary Tertiary.

3. The fact that in several places, near the contact, the tertiary clays dip in the direction of the andesite goes very much against a higher antiquity of andesite than of shales.

4. The silicification of shales at the G. PANTJAR can be explained satisfactorily only when assuming that the andesites are younger than the shales.

5. The occurrence of clay-enclosures in loose andesite fragments west and east of the G. PANTJAR also points to a recent date of andesite.

6. The fact that between Tji Djanggel and Tji Handjawan andesite breccia are in some places superposed on shales is best explained by assuming that the andesites are younger than the sediments.

7. Lastly the discovery of enclosures of shale in breccia of the "Old Andesites" at the G. Handjawong proves unequivocally that

the "Old Andesites" originated only after the deposit of the Tertiary clay-formation.

CONCLUSION.

The old andesites east of Buitenzorg are younger than the encircling sedimentary Tertiary. The bulk of the sedimentary Tertiary east of Buitenzorg is developed as a clay-formation: only in the recent levels breccia and allied rocks occur. Now it is still a moot point whether the "Old Andesites" are the places of eruption, from which the conglomerates and the breccia of the young Tertiary, included in the folding, were extruded, and consequently are a little older than Gedeh-Salak, or whether they are contemporaneous with these volcanoes. That they are less high and that their volcanic shape is less perfect, would seem to favour the first view. This question, however, can be positively solved only through minute researches in this volcanic region, so difficult to traverse, and through petrographic investigations in connection with them.

In the above we have pointed out, for one district, that the geological map of Java, requires a thorough revisal. It would not be difficult, even by dint of comparatively little fieldwork, to enlarge the number of instances. We do not mean to censure the makers of the "Geological map". Those who hold that respect is due to the men who performed a comprehensive task with only little assistance, may still feel called upon to point to the shortcomings resulting from a superficial examination. The only fault of the authors is, that in publishing an illusive map, indicating in every place "continued" formation outlines, and accompanied by a great many profiles, they have made us believe that we really possess a rather detailed geological survey of this island. This is why after the investigations by V. and F. the necessity of further geological work in Java has been given hardly a moment's consideration.

May this paper tend to produce the conviction that a minute revision of the geological survey of Java, is of prime importance for geological science. In practice a similar wish has frequently been expressed, but in vain.

Buitenzorg, 1 Jan. 1917.

Mathematics. — “*Some Considerations on Complete Transmutation.*”

(Fourth Communication). By Dr. H. B. A. BOCKWINKEL. (Communicated by Prof. L. E. J. BROUWER).

(Communicated in the meeting of December 21, 1916.)

18. In this paper we shall discuss the general theorem of Taylor for the functional calculus, a particular case of which, that we, as such, called MAC LAURIN'S theorem, was discussed in the preceding paper. Before proceeding to this, we shall, however, treat an important proposition of the normal additive transmutation of which we shall avail ourselves in the future.

The proposition in question is a special case of another that holds in general for a continuous transmutation and which, generally expressed, states, that such a transmutation *keeps* its additive property with regard to an *infinite* sum. The proposition is as follows

If a series the terms of which are functions that form part of the F.F. of a continuous additive transmutation T , converges uniformly in the N.F.F. towards a function u , which also forms part of the F.F., the series the terms of which are equal to the transmuted of the first mentioned terms, converges uniformly in the N.F.O. towards $T(u)$.

For if we have

$$u = u_0 + u_1 + \dots + u_m + \dots,$$

such that the series converges *uniformly* in the N.F.F. of T , this means: corresponding to any given, arbitrarily small amount δ there is an integer N such that in the *whole* N.F.F. of T

$$\left| \sum_n^{\infty} u_m \right| < \delta, \quad \text{for } n > N$$

Further, on account of the continuity of T , there corresponds to any arbitrarily small amount τ an amount σ such that, if v be a for the rest arbitrary function of the F.F.

$$|T(v)| < \tau \quad \text{in the N.F.O. of } T,$$

if

$$|v| < \sigma \quad \text{in the N.F.F. of } T.$$

Thus there corresponds to any arbitrarily small amount τ an integer N , such that we have in the N.F.O. of T ,

$$\left| T \left(\sum_n^{\infty} u_n \right) \right| < \tau, \quad \text{if } n > N.$$

Now we have, on account of the additive property of T , in the numerical field of operation

$$T u = T u_0 + T u_1 + \dots + T u_{n-1} + T \left(\sum_n^{\infty} u_n \right),$$

from which it follows in connection with the result just arrived at, that we also have in that field

$$T u = \sum_0^{\infty} T u_m,$$

the series converging *uniformly* there. Thus the proposition has been proved.

If T is a *normal* transmutation both the N.F.F. and the N.F.O. are a circle with centre x_0 . The radii of these two we call respectively (σ) and (α) . The *characteristic* expansion of u is in that case the one in a power series

$$u = c_0 + c_1 y + \dots + c_m y^m + \dots, \quad (y = x - x_0).$$

Then, if we call ξ'_m the function in which $(x-v)^m$ is transformed by T (the latter *exists* and is *regular* in (α) since the rational integral functions form part of the F.F. of a normal transmutation), we have in (α)

$$T(u) = c_0 \xi'_0 + c_1 \xi'_1 + \dots + c_m \xi'_m + \dots,$$

and the series converges there *uniformly*. This is the proposition we referred to and which we may express as follows:

If T be a normal additive transmutation, of which the circle (α) forms the N.F.O., and the circle (σ) the N.F.F. the transmuted Tu of a function u of the F.F. may be found by applying the transmutation term by term to the power series, in which u may be developed in the domain (σ) , and the result is a series that converges uniformly within (α) .

19. We shall now discuss the *generalisation* of TAYLOR'S theorem for the functional calculus.

This is concerned with the development of the transmutation T , applied to a product $w = vu$, according to powers of Du , if the transmuted Tv of v and an enumerable infinite number of other quantities, which may be called the derivatives of the transmutation

T applied to v (the name has been introduced by PINCHERLE) are known; a development of Tv in the point $w = v$, or in the vicinity of $w = v$, as we might say, while the special development, according to powers of Dw , might be called one in the point $w = 1$. (Cf. the general development of a function $f(x)$ in the point $x = a$ and the particular one in the point $x = 0$).

We again make the following suppositions:

1. T is normal such that the N.F. is a circle (α) with centre a_0 , while the functions of the F.F. belong to a circle (σ) , concentric with (α) .

2. The series P belonging to T is complete in (α) with corresponding domain (β) .

It will further be easy in the future to suppose that as a pair of associated fields of T each such pair of fields of P comes into consideration, which involves that for (σ) may be taken any circle greater than (β) (see N^o. 12, 2nd communication). Possibly (β) itself cannot be taken as N.F.F. together with (α) as N.F.O. (N^o. 13); but in any case we have now according to the functional theorem of MAC-LAURIN, $Tu = Pu$, for all functions belonging to (β) , because, if u belongs to (β) , it also belongs to a somewhat larger circle. According to the final observation in N^o. 15 (3rd communication), if T were not yet defined for all these functions, we might extend the F.F. of T over them by simply writing for these functions $Tu = Pu$. And if T should be defined a priori for a certain part of the functions belonging to (β) , such that we had for them $Tu \neq Pu$, T would not be continuous in the total field, and in that case we should not retain this T in the considerations we are concerned with here, but put another operation in its place, which for the functions mentioned is identical with P .

If therefore w be a function belonging to (β) , we shall have in the domain (α)

$$Tw = Pw \equiv \sum_0^{\infty} \frac{a_n w^n}{n!}.$$

Now we have, since $w = vu$, according to the formula of LEIBNIZ

$$w^{(n)} = v w^{(n)} + n_1 v' u^{(n-1)} + \dots + v^{(n)} u$$

consequently

$$T w = \sum_0^{\infty} \frac{a_n}{n!} (v w^{(n)} + n_1 v' u^{(n-1)} + \dots + v^{(n)} u).$$

In each member of this last series, from and after the one for which $n = m$, occurs a term with $v^{(m)}$; taking these terms

together, we can, at least *formally*, represent the transmuted $T'w$ as follows

$$T'w = \sum_0^{\infty} m \sum_0^{\infty} k a_{m+k} \frac{u^{(m)}}{m!} \cdot \frac{v^{(k)}}{k!} \cdot \dots \dots \dots (35)$$

We shall now assume that u and v both belong to (β) , and then prove that the doubly infinite series in the right-hand member converges *absolutely*; then, as is known, the validity of the change in the grouping of the terms, has been proved, and consequently the correctness of the last formulá.

If u and v belong to (β) , they belong also to a somewhat greater circle (ρ) with a radius $\rho = \beta + \delta$, ($\delta > 0$). If further the maximum modulus of u as well as of v on the circumference of (ρ) be smaller than M , we have in the domain (α)

$$\left| \frac{v^{(k)}}{k!} \right| < \frac{\rho M}{(\beta - \alpha + \delta)^{k+1}}, \quad \frac{u^{(m)}}{m!} < \frac{\rho M}{(\beta - \alpha + \delta)^{m+1}} \dots \dots (36)$$

Since, further, the transmutation is complete in (α) with corresponding domain (β) , there corresponds to any given arbitrarily small number ε , an integer n_ε valid¹⁾ for the whole domain (α) , such that

$$|a_n| < (\beta - \alpha + \varepsilon)^n, \quad \text{for } n > n_\varepsilon \dots \dots (37)$$

Consequently we have for $k \geq n_\varepsilon$, corresponding to *any* integer m (not negative) and in all points of (α)

$$\left| a_{m+k} \frac{v^{(k)}}{k!} \right| < \frac{\rho M (\beta - \alpha + \varepsilon)^m}{\beta - \alpha + \delta} \cdot \left(\frac{\beta - \alpha + \varepsilon}{\beta - \alpha + \delta} \right)^k \dots \dots (38)$$

If we now assume ε chosen smaller than δ , the left-hand member of this inequality is in the domain (α) comparable with the general term of a decreasing geometrical series of constant positive terms. The series

$$a'_m = \sum_0^{\infty} k a_{m+k} \frac{v^{(k)}}{k!} \dots \dots \dots (39)$$

converges therefore *absolutely* (and uniformly) in the domain (α) . Since the first series in (35) arises from it by multiplying the terms by the factor $u^{(m)} : m!$, which is independent of k and limited in (α) , the latter converges as well absolutely in (α) for *all* integral (not negative) values of m .

There still remains to be proved the convergence of the series

¹⁾ See the so-called uniformity supposition in the 2nd paragraph of N^o. 4, 1st communication.

$$\sum_0^{\infty} b_m \left| \frac{u^{(m)}}{m!} \right| \dots \dots \dots (40)$$

in which

$$b_m = \sum_0^{\infty} \left| a_{m+k} \frac{v^{(k)}}{k!} \right| \dots \dots \dots (39a)$$

The inequality (38) holds also, according to (37) and the first part of (36), for all integral (not negative) k , and in all points of (α) , if $m > n_\epsilon$. We therefore have in (α)

$$b_m < \frac{\rho M}{\delta - \epsilon} (\beta - \alpha + \epsilon)^m, \text{ for } m > n_\epsilon, \dots \dots (41)$$

from which it follows in connection with the second part of (36) that, from and after some fixed term, the terms of the series (40) are in the whole domain (α) comparable with those of a decreasing geometrical series of positive terms not depending on x . The series (40) therefore converges uniformly in (α) , and thus the absolute and uniform convergence of the system of two successive series in (35), and consequently the validity of this formula has been proved.

According to (39) we can write that formula as follows:

$$Tw \equiv T(vu) = \sum_0^{\infty} a'_m \frac{u^{(m)}}{m!} \dots \dots \dots (42)$$

This form is the development in question of $T(vu)$ in a "series of TAYLOR". In order to accentuate the analogy we introduce the following symbolism. The development

$$Tv = \sum_0^{\infty} \frac{a_k v^{(k)}}{k!}$$

suggests to represent the transmutation T by the symbol

$$T = \sum_0^{\infty} \frac{a_k D^k}{k!}$$

If this symbol is differentiated with respect to D as if it were a power series in that letter, and if we represent the arising symbol by T' , we have

$$T' = \sum_0^{\infty} \frac{a_{k+1} D^k}{k!}$$

Going on in this way we find, by indicating the result of m -fold repeated differentiation by $T^{(m)}$.

$$T^{(m)} = \sum_0^{\infty} \frac{a_{m+k} D^k}{k!} \dots \dots \dots (43)$$

According to (39) we can consequently write

$$a'_m = T^{(m)}(v) \dots \dots \dots (44)$$

and for formula (42)

$$T(vu) = \sum_0^{\infty} \frac{T^{(m)}(v)}{v!} D_u^m \dots \dots \dots (42')$$

Since the symbol indicating the operation $T^{(m)}$ has arisen by m -fold repeated differentiation from the symbol for T , we may call the operation $T^{(m)}$ the m^{th} derivative of T ; PINCHERLE introduces this name, though in another way. We further observe that the transmutation D answers in the functional calculus to the function $y=x$ in the theory of functions, because the derivative of D is equal to 1, that of D^m to $m D^{m-1}$, and the $(m+1)^{\text{th}}$ derivative of D^m equal to zero. In consequence of this we may call the transmutation indicated by a rational integral function of the symbol D a *rational integral operation*. Infinite power series in D represent then what we may call a *transcendental operation*.

The formula (42') is now clearly recognizable as a *development in the series of TAYLOR*, that is a development of Tv in the point v according to powers of the simplest operation D , calculated for the increase u ; we have to take the term *increase with u* in the meaning of *geometrical increase*, that is *multiplication by u* . We may also speak then of the development of Tv in a *geometrical vicinity of functional point $w=v$* . For $v=1$ the series passes again into the particular one found before; it appears in that case that the coefficient a_m is equal to $T^{(m)}(1)$, that is the m^{th} derivative of T applied to the functional origin $w(x)=1$. For this particular value of $w(x)$ the derivative in question may therefore also be found by means of the formula (24); for $w=v$, as is to be found in PINCHERLE's paper, and as we are going to verify presently, the following generalisation of (24) holds

$$a'_m \equiv T^{(m)}(v) = T(x^m v) - m_1 x T^{(m-1)} v + \dots + (-1)^m x^m T(v) \quad (45)$$

From the proof we have given of the *general development* it appears that it holds under the same conditions as the *particular*, provided that the "beginning point" $v(x)$ and "increase" $u(x)$ belong

both to the F. F. of the series P corresponding to T . Hence the general theorem of TAYLOR for the functional calculus has been proved, in the following form:

If the series P answering to a normal additive transmutation T be complete in the circular domain (α) that forms the N. F. O. of T , $T(w)$ may be developed in this domain in the functional series of TAYLOR, in the point $w = v$, if both point of origin v and increase u ($w = vu$) belong to the circle (β) corresponding to (α) .¹⁾

20. We may consider both members of (42) as an operation on the function u , and thus read this formula as a development of the transmutation $T_1 \equiv Tv$, applied to the function u in a "series of MAC-LAURIN". Since the result we arrived at in the preceding number states that this series (which we shall indicate by P_1 , since it answers to the transmutation T_1) converges in the domain (α) for any function belonging to (β) , provided this is also the case with the fixed function v , the series P_1 is likewise complete in the domain (α) , such that the corresponding domain is at most equal to (β) . This may also be derived directly from the inequality (41), which a fortiori holds for $|a'_m|$. For it is evident that, instead of the statement of which that inequality is the expression, we may as well say: Corresponding to any arbitrarily small chosen number ε there is an integer n , such that

$$|a'_m| < (\beta - \alpha + \varepsilon)^m, \quad \text{for } m > n, \quad \dots \quad (41a)$$

and from it follows, if the second part of the proof in N^o. 4 (1st communication) is consulted, the completeness of the series P_1 in (α) , with a corresponding domain that at most is equal to (β) .

We may therefore interpret the result, arrived at in N^o. 18 in this way: *If the series P answering to a normal additive transmutation T be complete in the circular domain (α) forming the N. F. O. of T , with corresponding domain (β) , we have 1^o that the series P_1 answering to the transmutation $T_1 \equiv T(v)$, in which v is a given, fixed function belonging to the circle (β) , is also complete in (α) with a corresponding domain that at most is equal to (β) , 2^o we have in the domain (α)*

$$T_1(u) = P_1(u)$$

for such functions of the F. F. of T , as belong to (β) .

We further add the following remark: Since the last equality

¹⁾ We have not expressly stated again that u, v, w , form part of the F. F. of T , since this is a matter of course now that these functions belong to (β) , according to our agreement in the beginning of this number.

according to "the theorem of MAC-LAURIN" would c.p. just hold if $T_1 \equiv Tv$ were a *normal* transmutation, the question arises whether this is the case. This question must be answered in the affirmative. For, if a function u of the functional field $F(T)$ of T belongs to (β) , this is also the case with the product vu , so that $T(vu)$ and consequently also $T_1 u \equiv T(vu)$ exists, according to our agreement in the beginning of N^o. 19, in the domain (α) . From this it follows that there is for the transmutation T_1 a pair of fields to be indicated, the *numerical* field of which is the circle (α) , and the *functional* field consists of the functions that belong to the circle (β) . Since the rational integral functions are also among these, T_1 satisfies already the conditions, sub 1^o and 2^o, which we indicated in N^o. 15 (3rd communication) for a normal additive transmutation. But T_1 is also *continuous* in the pair of fields mentioned, for, if u in the domain (β) tends towards zero, this is also the case with the product vu of u and the fixed function v belonging to (β) . But in that case $T(vu)$ tends to zero in the domain (α) according to the property of continuity of T , and since $T(vu)$ is identical with $T_1 u$ the property of continuity of T_1 has been proved.

If the expression Tvu is considered as the result of the transmutation $T_1 \equiv (Tv)$, applied to the function u , the following establishment of the expression (45) for the coefficients $a'_m \equiv T^{(m)}(v)$ of the series P corresponding to T_1 , is at once obvious. If the function in which x^m is transformed by T_1 be denoted by ξ'_m , we have

$$\xi'_m = (Tv) x^m = T(vx^m),$$

and the application of the symbolic formula (24) according to which we have

$$a'_m = (\xi' - x)^m,$$

leads at once to (45). From this the other representation (39) of a'_m may be found then, by first deriving from (45) that we have for $m = 1$

$$T'(v) = T(xv) - x T(v) \dots \dots \dots (46)$$

and further the recurrent relation

$$T^{(m)}(v) = T^{(m-1)}(xv) - x T^{(m)}(v)^{-1} \dots \dots \dots (47)$$

According to the "theorem of MAC LAURIN" we have further in the domain (α)

$$T(v) = \sum_0^{\infty} a_n \frac{v^{(n)}}{n!} \dots \dots \dots (48)$$

¹⁾ The relations (46) and (47) occur in PINCHERLE'S paper as *definition* of the respective derived transmutations of T .

$$T(xv) = xa_0v + \sum_1^{\infty} a_n \left(x \frac{v^{(n)}}{n!} + \frac{v^{(n-1)}}{(n-1)!} \right) \dots \quad (49)$$

The latter sum may be divided into

$$\sum_1^{\infty} \left(xa_n \frac{v^{(n)}}{n!} \right) + \sum_1^{\infty} \left(a_n \frac{v^{(n-1)}}{(n-1)!} \right) \dots \quad (50)$$

For the first of these two series, with the restriction that the term with $n=0$ does not occur, is equal to the series (48) multiplied by x , and therefore it converges, as well as the latter, in the domain (α) and produces there, together with the term xa_0v , the result xTv . The second series is now equally convergent in (α) , since the undivided series in (49) converged there; if further $k+1$ be substituted for n in the second series, the result will be

$$T(xv) = xT(v) + \sum_0^{\infty} a_{k+1} \frac{v^{(k)}}{k!},$$

so that, in connection with (46),

$$T'(v) = \sum_0^{\infty} a_{k+1} \frac{v^{(k)}}{k!} \dots \quad (51)$$

This series differs only, in so far from (48) that all a 's have moved up *one* place to the left; from this remark and the fact expressed by (47), that any following derived operation is obtained *in the same way* from the preceding one¹⁾, the correctness of the representation (39) for $T_m(v)$ in the domain (α) follows at once.

Let now $v(x)$ have the radius of convergence r , and let r_1 be the α -value to which, for the series P , r corresponds as a β -value. The series P_1 answering to the transmutation $T_1 \equiv (Tv)$ is then at all events complete in any domain $(\alpha) < (r_1)$, with corresponding domain $(\beta) < (r)$. But the series P_1 will often be still complete in a domain *greater* than (r_1) , as may be derived from formula (45). For according to the latter the quantities a'_m are regular in a domain, if this is the case with the transmuted of $x^m v$, for arbitrary integral positive values of m , and we amply explained in N^o. 7 and 8 (second communication) that the transmuted Tw of a function w with radius of convergence r may very well be regular in a circle *greater* than

¹⁾ We have also to take into account that the formula (51) holds if v is replaced by xv , which is caused by the fact that it holds for an *arbitrary* function belonging to (6).

the circle (r_1) , to which (r) corresponds for the series P belonging to T .

As a rule $T(x^mv)$ will further, together with Tv , be regular in a domain. For let T be *normal*, such that the N.F.O. is a circle $(\alpha) > (r_1)$, and the N.F.F. a circle $(\alpha) < (r)$. If we know that *all* functions belonging to (α) form part of the F.F., nothing is to be demonstrated as in it is included that both v and x^mv have a transmutated in (α) . But if it is provisionally only given that v forms part of the F.F. we may explain in the following way that this as a rule includes that x^mv as well forms part of it ¹⁾. If

$$v = c_0 + c_1 y + \dots + c_n y^n + \dots \quad (y = x - x_0),$$

be the power series in which v may be developed in the vicinity of $x = x_0$, we have according to the proposition of N^o. 18, in the domain (α)

$$Tv = c_0 \xi'_0 + c_1 \xi'_1 + \dots + c_n \xi'_n + \dots,$$

if ξ'_n be the transmutated of $(x - x_0)^n$. If now T is applied term by term to the development of the series of yv , we arrive at

$$c_0 \xi'_1 + c_1 \xi'_2 + \dots + c_n \xi'_{n-1} + \dots$$

From the convergence of the first series that of the second follows if the quotient of ξ'_{n+1} by ξ'_n remains within *finite* limits for all integral n values. This now is often the case, (for instance with S_ω and D^{-1}) and if so, it is clear that the series, emanating when y^mv is substituted for v , converges as well. If, for a moment, we write the result as $T_0(y^mv)$, this *need* not be equal to $T(y^mv)$ for other values than $m = 0$, but in any case a *normal* transmutation *does* exist, namely T_0 , which, with preservation of the N.F. $(\alpha) > (r_1)$, contains both v and y^mv , and consequently x^mv in its F.F., and it is evident that T in *common* cases will be defined in such a way as to be exactly *that* transmutation.

If now Tv and $T(x^mv)$ be regular in a domain (α) greater than (r_1) , this is necessarily the case for $a'_m = T^{(m)}(v)$, and there is every reason to expect that $a'_x = \lim |a'_m|^{\frac{1}{m}}$ will be *limited* in such a greater circle, consequently that the series P is *complete* in it. Hence we arrive definitely at the statement:

The series P_1 belonging to the transmutation $T_1 \equiv (Tv)$ is not

¹⁾ It is not inconsistent with our agreement made in the beginning of N^o. 19 that we speak of the case in which $T(x^mv)$ is *not* at the same time regular with Tv in domains *greater* than (r_1) . It only follows from that agreement that we only take notice of a T that for *all* functions with the radius of convergence r produces a transmutated regular in a domain smaller than (r_1) , because to the latter a domain *smaller* than (r) corresponds for the series P .

only complete in any domain smaller than (r_1) but in most cases in any domain smaller than (r) if r is the radius of convergence of Tv .

If now the radius of convergence of the function u be greater than r , the series will converge in a domain greater than (r_1) . We have in this case been able to find for the transmuted Tv of w , by developing in the point $w = v$ according to powers of $D\left(\frac{w}{v}\right)$, an expression representing this transmuted in a greater numerical field than would have been the case if we had developed in the point $w = 1$. Or we may also consider the thing in this manner that, with the preservation of the numerical field $\alpha > (r_1)$, the functional field that at first consisted of functions belonging to a circle $(\beta) > (r)$, has now been extended to some functions not belonging to (β) , namely such as show the same kind of singularity in the domain (β) as a fixed function $v(x)$, their quotient by $v(x)$ being regular in (β) ; functions of which we might say that they lie in a geometrical vicinity of the functional point $v(x)$. Taken thus we observe an analogy in the present phenomenon with the one called analytical continuation in the theory of functions (Cf. N^o. 8).

21. We shall now elucidate the more general theorem of TAYLOR by two examples. As transmutation we take in the first place, in a vicinity of the origin, the substitution S_ω , in which ω is a function of x , which has $x = 0$ as ordinary point, the radius of convergence for that point being denoted by A . We fully explained in N^o. 17, (3^d communication) that S is a normal transmutation, the numerical field being a circle with radius $\alpha < A$, and the functional field consisting of the functions belonging to the circle (σ) concentric with (α) , the radius of which σ is equal to the greatest modulus of ω in the domain (α) . We further saw that to this transmutation belongs a series P , which is complete in (α) , with a corresponding domain (β) , which is determined by the equation

$$\beta = \alpha + |\omega(x_m) - x_m|,$$

where x_m is the point on the circumference of (α) , where $|\omega - x|$ attains its maximum; we pointed out that β is at least equal to σ .

We can therefore apply the functional theorem of TAYLOR to a function $w = vu$, provided we suppose the radius of convergence r of the fixed initial function v to be greater than $|\omega(0)|$. The circle (r_1) to which, for the series P , (r) corresponds is determined here by the condition that in it the maximum modulus of $\omega - x$ is equal to $r - r_1$, while the circle of convergence (r') of $S_\omega(v)$ satisfies the condition that in it the maximum modulus of ω is equal to r . The

development in the series $P_1 u$ will in the domain (α) , for a function u belonging to (β) , *certainly* hold, if $\alpha < r_1$, but *probably* also, if $r_1 < \alpha < r'$. We shall see how this is and calculate to that purpose the coefficients a'_m by means of (45). We arrive at

$$a'_m = (\omega - x)^m v [\omega(x)] \equiv (\omega - x)^m S_\omega(v).$$

According to (42) the series $P_1 u$ becomes therefore

$$S_\omega(vu) = \sum_0^{\infty} S_\omega(v) (\omega - x)^m \frac{u^{(m)}}{m!}.$$

If in it the factor $S_\omega(v)$ is brought outside the symbol of summation the remaining series is precisely the series Pu , which answers to the transmutation $S_\omega(u)$. Apart from the factor mentioned the series therefore converges in *any* domain $(\alpha) < (A)$, provided u belongs to the domain (β) . With the factor $S_\omega(v)$ added to it the series converges consequently for such a function in any case, if α is smaller than the radius of convergence r' of $S_\omega(v)$. Thus our presumption has been affirmed.

If for instance $\omega(x) = \frac{1}{2}x$, we have $a_m = (\frac{1}{2}x)^m$, consequently $\alpha(\alpha) = \frac{1}{2}\alpha$ and $\beta = \frac{2}{3}\alpha$, so that

$$r_1 = \frac{2}{3}r$$

But the circle of convergence (r') of $S_{1/2}(v)$ has a radius

$$r' = 2r$$

so that the series P_1 is complete here in a greater domain than (r_1) .

22. As another example we take the transmutation D^{-1} , also in a vicinity of $x=0$. In N^0 . 16 we saw that D^{-1} is a normal transmutation such that the numerical field is an arbitrary circle (α) , and the functional one consists of the functions belonging to the same circle. The series P belonging to D^{-1} was further complete in (α) with corresponding domain (2α) . Thus if we keep with respect to the fixed function v the same notations as before, we have in this case,

$$r_1 = \frac{1}{2}r$$

while the circle of convergence (r') of $D^{-1}(v)$ is the same as the one of (v) , so that

$$r' = r.$$

We expect consequently that the series P_1 , which belongs to the transmutation $D^{-1}(v)$, will not only be complete in (α) for $\alpha < \frac{1}{2}r$, which is necessary according to the theorem, but also if $\frac{1}{2}r < \alpha < r$. The result confirms this. Formula (45) gives

$$\begin{aligned}
 a'_m &= \int_0^x t^m v(t) dt - m_1 \alpha \int_0^x t^{m-1} v(t) dt + \dots + (-1)^m \alpha^m \int_0^x v(t) dt \\
 &= \int_0^x (t-\alpha)^m v(t) dt,
 \end{aligned}$$

which result, to begin with, is regular within the circle of convergence (r) of $D^{-1}v$. In order to find a majorant value of $|a'_m|$ we reduce as follows

$$|a'_m| \leq \int_0^x |t-\alpha|^m \cdot |v(t)| \cdot |dt| \leq \alpha^m M(\alpha) \int_0^x |dt|$$

or

$$|a'_m| \leq \alpha^{m+1} M(\alpha),$$

if $\alpha = |x|$ and $M(\alpha)$ be the maximum modulus of v on the circumference of the circle (α).

From this it follows for values of $\alpha < r$

$$a'_x \equiv \lim_{m \rightarrow \infty} |a'_m| \frac{1}{m} < \alpha$$

consequently

$$a'(\alpha) < \alpha,$$

according to the general result (41a) in N^o. 20, but here extended to domains *greater* than ($\frac{1}{2}r$), provided they are smaller than (r). Thus, in fact, the series P_i is complete in any domain ($\alpha < r$) the corresponding domain (β') being at most equal to (2α). The series $P_1 u$, determined by (42), converges therefore within the circle ($\frac{1}{2}s$), if the radius of convergence s of u is smaller than $2r$, and otherwise within the circle (r).

Physiology. — "*Concerning Vestibular Eye-reflexes.*" By Mr. A. DE KLEYN and Mr. W. STORM VAN LEEUWEN. I. "*On the Origin of Caloric Nystagmus.*" (Communicated by Prof. H. ZWAARDEMAKER).

(Communicated in the meeting of June 30, 1917)

Although it has long been a matter of common knowledge that a nystagmus is induced by allowing cold or warm water to flow into one ear, and this has been the subject of a considerable amount of experiments with men as well as with animals, the origin of this caloric nystagmus is still a moot point.

Among the various views taken of the subject those of BARANY and BARTELS stand prominent.

BARANY holds that streams in the endolymph evolved by a change of temperature excite the caloric nystagmus, whereas BARTELS inclines to believe that by applying cold water the function of the labyrinth is eliminated entirely or in part and that by applying warm water the labyrinth is stimulated.

It being our purpose to endeavour to clarify our ideas concerning the cause of the caloric nystagmus, we first of all made a series of experiments to ascertain whether the caloric nystagmus may perhaps be provoked by arresting the function of the labyrinth through cold water. The results of this inquiry will be discussed in this paper.

In our investigation we started from the following considerations:

If the caloric nystagmus is brought about by eliminating the labyrinth on the irrigated side, the caloric nystagmus must present the phenomena resulting from an extirpation of the labyrinth.

These phenomena are:

a. The caloric nystagmus would correspond in direction, frequency and nature, exactly with the spontaneous nystagmus occurring after extirpation of the labyrinth.

b. It would be possible to arrest the nystagmus, occurring directly after extirpation of a labyrinth by ejecting cold water into the other labyrinth.

c. When in an animal one labyrinth has been extirpated, a spontaneous nystagmus will ensue, which will disappear again after some time; the nystagmus is then what is termed "compensated".

In this phase of compensation extirpation, or a squirt of cold water into the other ear may excite nystagmus. If a squirt of cold water into the ear is equivalent to elimination of the labyrinth on the same side, then both labyrinths will have been eliminated in case, in the compensatory stage. the unimpaired ear is irrigated. It follows then that the nature, the direction or the frequency of the forthcoming nystagmus can no more be modified by altering the animal's position in space.

d. A concomitant flow of water into the two ears, generally brings forth a condition in which no nystagmus manifests itself. If therefore, squirting cold water into the labyrinth is identical with elimination, a concomitant flow into the two ears cannot provoke a rotatory movement or a deviation of the eyes in case the animal's position in space is altered.

These phenomena have been examined in the following way:
Ad. a. In order to ascertain whether the caloric nystagmus (which term here always indicates the nystagmus occurring after squirting water, of from 11°—12°, into the animal's ear from a height of 1,5 m.) corresponds completely to the spontaneous nystagmus occurring after unilateral extirpation of the labyrinth, a number of experiments were undertaken. In these experiments the animals (in this series only cats) were tied to an operation board and subsequently the caloric nystagmus was examined in 6 different positions of the animal:

- 1 ventral position.
- 2 dorsal position.
- 3 vertical position, head up.
- 4 vertical position, head down.
- 5 lateral position, the irrigated ear up.
6. lateral position, the irrigated ear down.

After this the labyrinth on the side of the irrigated ear was extirpated. The technique of this operation has been described by one of us in another paper.¹⁾ After the animal recovered from the narcosis, the nystagmus was again examined in the six positions just mentioned. With some animals the examination was repeated the next day. We noted the frequency, the direction and the nature of the nystagmus. The frequency of the nystagmus cannot be accurately demonstrated in these experiments, it being apt to change every moment as well in the spontaneous nystagmus as in the caloric nystagmus. We are entirely ignorant of the cause of it.

¹⁾ Pflügers Archiv. Bd. 145 p. 549.

Spontaneous eye-movements may come into play here. Sometimes we fancied to note an increased frequency when the animal got restless.

We feel assured, however, that a change of the animal's position can exert an influence upon the nystagmus, so that e. g. the frequency is always less with ventral position than with a dorsal position, and this holds good for the caloric as well as for the spontaneous nystagmus showing itself after a unilateral extirpation of the labyrinth.

Similarly it is often very difficult to accurately determine the nature of the nystagmus. It happens again and again that the caloric nystagmus in a certain position is perfectly horizontal for some time and suddenly turns rotatory, without any assignable cause. After a change of the animal's position we invariably delayed noting down the nature of the nystagmus for some moments, in order to preclude the chance that the nystagmus brought forth by the change of the animal's position should interfere with the caloric phenomenon. The terms: nystagmus to the left or to the right always mean a nystagmus with the fast component to the left or to the right. From this inquiry it became evident that the direction of the spontaneous nystagmus is not in all positions identical with that of the caloric nystagmus, as it appeared that the spontaneous nystagmus occurring after unilateral extirpation of the labyrinth, has in all positions the fast component turned towards the unimpaired labyrinth, whereas the caloric nystagmus is, with ventral position and with vertical position (head up), turned towards the non-irrigated ear; with dorsal position and with vertical position (head down) it is turned towards the irrigated ear; with lateral position (5 and 6) the caloric nystagmus is mostly towards the same side as with ventral position.

Ad b. Directly after extirpation of a labyrinth a nystagmus reveals itself spontaneously towards the side of the unimpaired labyrinth. As appeared sub *a*, this nystagmus does not vary its direction with a change of the animal's position in space. When both labyrinths are removed during the operation with only a very short interval, no nystagmus will occur. If, therefore, caloric nystagmus should be identical with elimination of the labyrinth, it must be possible to arrest in all positions the nystagmus occurring after unilateral extirpation of the labyrinth, by allowing water to flow into the unimpaired ear. This, in fact, is not the case, as was evidenced by four experiments upon cats, which all yielded similar results. This may be instanced by the following abridged protocol:

31-5-1917. Cat. A flow of cold water 11—12° into the right meatus auditorius from 1,5 m.

Animal in ventral position; horizontal nystagmus to the left side.

Animal: vertical, head down, horizontal and rotatory nystagmus to the right side.

Extirpation of left labyrinth under narcosis of ether; operation finished at 11.15.

11.45. Spontaneous nystagmus to the right side in all positions.

Ventral position, frequency per 10 seconds $\left. \begin{array}{l} 11 \\ 11 \\ 11 \\ 11 \\ 12 \end{array} \right\}$.

Head down, frequency per 10 seconds $\left. \begin{array}{l} 14 \\ 15 \\ 15 \\ 18 \\ 16 \end{array} \right\}$.

12.10. A flow into the right meatus.

In *ventral position*, nystagmus to the right side lessens considerably; we did not succeed, however, in removing it altogether.

Eud. *head down*: nystagmus to the right side (horizontal + rotatory) grows much stronger and rapid. Now the frequency per

10 sec. is $\left. \begin{array}{l} 24 \\ 23 \\ 25 \\ 23 \\ 24 \end{array} \right\}$.

5.15. Spontaneous nystagmus to the right side in all positions.

Ventral position: horizontal nystagmus, frequency per 10 sec. $\left. \begin{array}{l} 12 \\ 12 \\ 11 \\ 13 \\ 12 \end{array} \right\}$.

Head down: horizontal + rotatory nyst.; frequency per 10 sec. $\left. \begin{array}{l} 16 \\ 14 \\ 16 \\ 14 \\ 15 \end{array} \right\}$.

A flow into right meatus.

Ventral position: eyes perfectly quiet. O.S. distinct downwards deviation.

Head down: strong horizontal rotatory nystagmus to the right side, frequency per 10 sec. $\left. \begin{array}{l} 24 \\ 23 \\ 22 \\ 20 \\ 22 \end{array} \right\}$.

Again in *ventral position* eyes perfectly quiet.

5.30 extirpation of labyrinth on the right with ether-spray.

8.30 not the slightest indication of nystagmus.

It then appeared from this experiment (and the other experiments were conducted in the same way) that after bilateral extirpation of the labyrinth there was no nystagmus, after a unilateral extirpation there was a spontaneous nystagmus which could not in all directions be arrested by a flow into the meatus of the untouched ear. From

this we may safely conclude that the phenomena, associated with the irrigation, cannot be caused by an elimination of the labyrinth. The objection that in these cases the unsatisfactory outcome of the irrigation depended on mere chance, is refuted by the fact that

1. irrigation was very effective before the extirpation of the labyrinth
2. irrigation after unilateral extirpation of the labyrinth in ventral position actually arrested the spontaneous nystagmus and
3. with head down the spontaneous nystagmus was not unaltered, but was considerably stronger.

Ad c. When, in one experiment, both labyrinths are removed, violent movements are observable, but not nystagmus. If, however, we first remove one labyrinth, the spontaneous nystagmus will be seen to vanish after a short interval. When subsequently the second labyrinth is removed, nystagmus returns and that to the side of the labyrinth that was first extirpated. We shall not enter into a discussion here about the question how this nystagmus, first described by BECHTEREW¹⁾, is originated, and which parts of the central nervous system come into play here for a nystagmus to manifest itself. This is being further investigated at our institute.

The time that has to elapse after the first extirpation of a labyrinth before a nystagmus can reveal itself after the second extirpation, is varying, but after a few days it is sure to appear.

If directly after the unilateral extirpation of the labyrinth water is sent through the meatus on the unimpaired side, the spontaneous nystagmus resulting from the unilateral extirpation of the labyrinth can be arrested in the ventral position by the irrigation as described above. A repetition of this procedure at different intervals after the extirpation of the labyrinth will prove that the spontaneous nystagmus cannot only be arrested in a ventral position, but also that after some time a nystagmus toward the opposite side is evolved by a flow of water i. e. towards the side of the first extirpation of the labyrinth. In this phase we may look for the spontaneous nystagmus detected by BECHTEREW, as quoted above, when the second labyrinth has been removed. If, therefore, irrigation is identical with elimination of the labyrinth, then the latter compensation-nystagmus must correspond entirely to the nystagmus obtained when some days after the unilateral extirpation of the labyrinth, the meatus of the unimpaired ear is irrigated. It appears, however, that

¹⁾ Pflüger's Archiv Bd. 30 p. 312.

there is not such marked concordance, as can be evidenced in the following way:

Of a cat the *right* labyrinth is extirpated; a nystagmus occurs to the *left* side. This nystagmus disappears after a few days. A flow through the meatus of the unimpaired *left* side yields nystagmus to the *right* side in *ventral position*; but on changing the position of the animal a change of the direction of the nystagmus is produced; in a dorsal position e. g. it is always to the left. If on the same day the left labyrinth is extirpated, the BECHTEREW-nystagmus to the right side appears, whose direction cannot be changed by changing the position of the animal (nor indeed can its nature or frequency).

This, then, also proves that a flow of cold water cannot completely arrest the function of the labyrinth.

Ad d. If the function of the labyrinth were arrested by ejecting cold water into the meatus, there could not be any vestibular reflexes after ejecting it into the two meatus simultaneously. Rabbits are highly serviceable for an inquiry into this matter, these animals making hardly any spontaneous eye-movements, besides having very strong eye-reflexes. We, therefore, experimented upon rabbits to see whether after ejecting water into both ears rotatory movement or deviation could be provoked through changing the animal's position in space. From an investigation made by V. D. HOEVE and DE KLEYN it appeared that in normal rabbits the greatest difference in rotatory movement of the eyes may be observed, when first the animal is examined with its head down and then with its head up.

We subjected five rabbits to the following experimentation.

First of all we ascertained whether no nystagmus at all was discernible after water had been ejected into both ears. This was necessary, as it was evident that with some animals the effect of the irrigation is not quite the same on both sides, so that a slight nystagmus still remains. Such animals were of course not suitable for an investigation. When this inquiry had been made, a photograph was taken of the head of the animal in two positions, without irrigation, viz.

animal vertical, head down

animal vertical, head up.

In order to determine the intensity of the rotatory movement a cross was burned into the cornea after cocainization. This, according to VAN DER HOEVE and DE KLEYN's experience, somewhat slackened the rotatory movement, so that it is somewhat less marked in our experiments than is usually the case with normal rabbits. Consid-

ering, however, that we only endeavoured to ascertain whether or no with bilateral irrigation a rotatory movement occurred, this did not matter at all. So when the two photographs had been taken prior to the irrigation, a simultaneous flow of cold water into both meatus of the animal was performed, and when no nystagmus was distinguishable any more, again two photographs were taken of the head, in two positions. A measurement of the rotatory movement, caused by the change of position could now be made on the photographs. The difference between the movements in the two positions (head down and head up) amounted to

Exp.	Without irrigation	after bilateral irrigation
1	66,5°	57°
2	70°	65°
3	59°	61°
4	88°	98°
5	63°	78°

From this table it is obvious, then, that after a flow of cold water into the two meatus of rabbits a strong rotatory movement is still effected by a change of the animal's position in space, perhaps as strong as with normal animals.

For the present we refrain from theoretical speculations on the basis of these experiments. Our object in publishing our experience was only to prove that the caloric nystagmus cannot possibly be provoked by a complete elimination of the labyrinth by cold water.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

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Physiology. — “*On the Effect of Lobelin*¹⁾ *on the Rise of Blood pressure by Nicotin*”. By W. STORM VAN LEEUWEN and C. DE LIND VAN WIJNGAARDEN. (Communicated by Prof. H. ZWAARDEMAKER).

(Communicated in the meeting of September 29, 1917).

When one of us was carrying out an inquiry into the effect of various lobelia preparations, the results of which will be published in the “*Nederlandsch Tijdschrift voor Geneeskunde*”, we found that the rise of bloodpressure, evoked in a cat by nicotin, was greatly influenced by a previous injection of lobelin. We decided to look more closely at this phenomenon, as we presumed this to be an instance of BÜRGI’s “potentiation” (Potenzierung) i.e. the effect of a mixture of two poisons is stronger than is expressed by the algebraic sum of the action of the component parts. The facts revealed in this inquiry are chiefly the following:

When a cat, which — to eliminate central influences — had been previously decapitated after SHERRINGTON, was given intravenously a small dosis of nicotin, e.g. 0.1 mgr., a fall of the bloodpressure generally ensued, which was succeeded by an increase of bloodpressure. The first phenomenon probably results from an inhibiting influence of nicotin upon the heart, the second from a stimulation of sympathetic ganglia, causing a constriction of the bloodvessels. The course of such a nicotin-curve is irregular. When, however, from 1 to 2 mgr. of atropin has been previously injected, the fall of the nicotin-curve disappears completely or partly and only the rise remains. The current opinion is that the first fall in the nicotin-curve is effected by a stimulation of the vagus by nicotin, which is again inhibited by atropin. Why, in some cases, the atropin does not prevent the primary fall, has not yet been explained.

¹⁾ When our supply of lobelin was exhausted and none could be procured in Holland, Prof. SCHOORL had a fresh supply prepared in his laboratory, for which we acknowledge our indebtedness.

When, after an injection of atropin, a decapitated cat is subjected to a series of injections every time of the same amount of nicotin, the subsequent increases of the bloodpressure are relatively equal, as one of the present writers has pointed out.¹⁾ The amount of nicotin, injected every time, must be small: from 0.1 to 0.2 mgr.; larger doses bring about before long a paralysis of the sympathetic ganglia, while no rise of the blood pressure is evolved. The same occurs when more than 8 or 10 small injections have been administered. When, after the 2nd or 3rd nicotin injection a similar quantum of lobelin is injected, a rise of bloodpressure reveals itself, as high as the rise after the nicotin, as shown in Table I.

TABLE I.
The effect of 0.1 mgr. of nicotin compared with that of 0.1 mgr. of lobelin, after the injection of atropin.

Exper.	rise of the blood pressure after 0.1 nicotin	rise of the blood pressure after 0.1 lobelin
18	66 mM Hg.	54 mM Hg
30	46	56
44	13	19
57	30	31
	average 38,75	average 37,5

The concordance between nicotin and lobelin need not surprise us as DRESER²⁾ and EDMUNDS³⁾ have shown before that lobelin and nicotin act similarly on many organs. The quantitative concordance between the two substances could not be surmised, especially also because the structural formula of lobelin is not known. The empiric formula was given as $C_{44}H_{24}ON(?)$.

If, however, nicotin is injected before lobelin; and after this another similar quantity of nicotin, the rise of bloodpressure after the latter amount of nicotin is much higher than that occasioned by the former (Cf. Table II).

1) W. STORM VAN LEEUWEN, Geneeskundige bladen 19e reeks N^o. 5.

2) DRESER. Arch. für exp. Path. u. Pharm. Bd, 26, page 237, 1890.

3) CH EDMUNDS. Americ. Journ. of physiol. vol. XI, page 79, 1904.

CH EDMUNDS. Journ. of pharmacol. and exp. therap. Vol. I, page 27, 1909.

TABLE II.

Cat; decapitated; subsequent injection of atropin;
Rise of blood pressure by 0.1 mgr. of nic. prior to and
after the injection of lobelin.

a. injection of 0.05 mgr. of lobelin

Exp.	Rise of blood pressure by 0.1 mgr. nicotin	Rise of blood pressure by 0.05 mgr. of lobelin	Rise of blood pressure by 0.1 mgr. of nicotin
35	45 mm Hg	12 mm Hg	69 mm Hg
38	24 "	12 "	31 "
49	11 "	0 "	10 "
54	28 "	16 "	44 "

b. injection of 0.1 mgr. of lobelin

Exp.	Blood pressure by 0.1 of nicotin	Blood pressure by 0.1 mgr. of lobelin	Blood pressure by 0.1 mgr. of nicotin
18	66 mm Hg	54 mm Hg	76 mm Hg
30	46 "	56 "	59 "
44	13 "	19 "	31 "
57	30 "	31 "	70 "

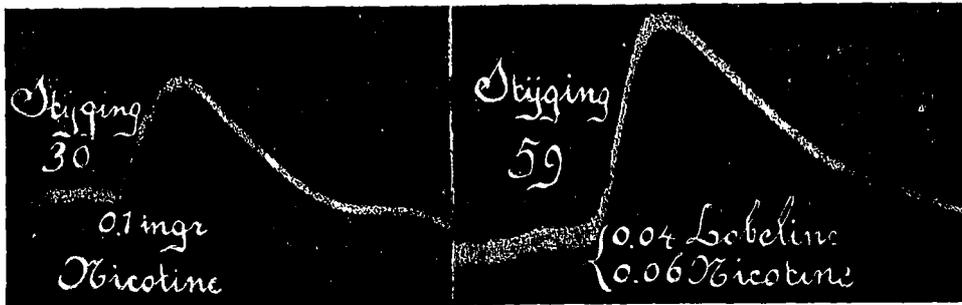
c. injection of 0.5 mgr. of lobelin

Exp.	Blood pressure by 0.1 mgr. of nicotin	Blood pressure by 0.5 mgr. of lobelin	Blood pressure by 0.1 mgr. of nicotin
46	5 mm Hg	30 mm Hg	18 mm Hg
47	24 "	90 "	90 "
48	23.5 "	28 "	42 "
53	56 "	76 "	88 "

d. injection of 1.— mgr. of lobelin

Exp.	Blood pressure by 0.1 mgr. of nicotin	Blood pressure by 1. mgr. of lobelin	Blood pressure by 0.1 mgr. of nicotin
50	20 mm Hg	122 mm Hg	79 mm Hg
51	6 "	82 "	108 "
52	22.5 "	—	163 "

It appeared, moreover, that 0.06 mgr. of nicotin + 0.04 mgr. of lobelin acted more forcibly upon the rise than 0.1 mgr. of nicotin or lobelin alone. This, then, is a case of true "Bücker-potential". This is illustrated by Fig. 1.



Stijging = Rise. — Lobeline = Lobelin. — Nicotine = Nicotin.

Fig. 1.

Bloodpressure, decapitated cat after atropin injection. *a.* 0,1 mgr. of nicotin yields a rise of bloodpressure of 30 mm. Hg.; *b.* 0,04 mgr. of lobelin + 0,06 mgr. of nicotin yields a rise 59 mm. Hg.

When we endeavour to find an explanation for this phenomenon, it would seem as if, after the lobelin injection still some portion of this substance is left behind in the cat's body, and that this, of itself incapable of any action on the blood pressure, adds its effect to that of the nicotin subsequently infused, so that this would seem to be a case of "addition" and not of "potentiation". However, the matter is not so simple, for if this were so, we might look for a higher rise of the blood pressure after a second lobelin injection. This is not the case. On the contrary the action of successive lobelin injections upon the blood pressure is most often progressively diminishing. Besides, the hypothesis alluded to is disqualified by the fact that a simultaneous injection of lobelin and nicotin is also attended by a "potentiation", as stated above. Lastly we have ascertained whether other substances affording a rise of blood pressure are "potentiated" by lobelin. This appeared not to be the case; adrenalin e.g. yields perfectly similar effects before and after lobelin.

Ultimately we have tried to make out whether, conversely, the nicotin could potentiate the lobelin. The result negated the supposition. With regard to the rise of blood pressure the effect of lobelin after nicotin is not increased, even diminished.

So far as we are able to judge the potentiating effect of lobelin for nicotin is specific. It is analogous to the re-inforcing effect exerted

by thyroïdin upon the action of adrenalin on the rise of blood pressure.

We wished to know whether larger doses of lobelin had a stronger potentiating effect than smaller ones. With a view to this several injections of 0.1 mgr. of nicotin were administered, subsequent to an atropin injection, to a number of decapitated cats, and then again varying amounts of lobelin and finally again 0.1 mgr. of nicotin. The results are given in Table II, in which we have expressed the rise of the blood pressure in m.m. Hg after the several injections.

In Table III we have tabulated for different doses of lobelin the difference in blood pressure afforded by 0.1 mgr. of nicotin before and after the lobelin.

TABLE III.
Mean values of the rise of blood pressure by 0.1 mgr. of nicotin before and after lobelin.

a	b	c	d
dosis of lobelin	mean rise of blood pr. by 0.1 mgr. of nicotin before lobelin	mean rise of blood pr. by 0.1 mgr. of nicotin after lobelin	difference
0.05 mm Hg	25 mm Hg	38 mm Hg	13 mm Hg
0.1 "	25 "	59 "	34 "
0.5 "	25 "	59.5 "	34.5 "
1.— "	25 "	117 "	92 "

Lastly the curve in Fig. 2 represents graphically the ratio between the amount of lobelin and the change in the nicotin action, brought about by those amounts, so this curve shows the relation between the values in columns *a* and *d* of Table III.

From the table and still more so from the curve it is evident that the effect of the amount of lobelin is very considerable. In our opinion the shape of the curve in Fig. 2 cannot be a basis for further speculation, for which we need the mean values of a larger number of experiments.

Since the publication in 1909 of BÜRGI's investigations other researchers and himself have detected a number of combinations of potentiating drugs. As expatiated upon by one of us in another paper, only in a very few cases has the presence of such a "potentiation" been proved.

Since "potentiation" is doubtless one of the most remarkable phenomena in modern pharmacology, we thought fit to communicate this new, striking instance of true potentiation. Further research

will have to furnish an explanation for the phenomenon in this and in other cases. It is remarkable though, that in the case under

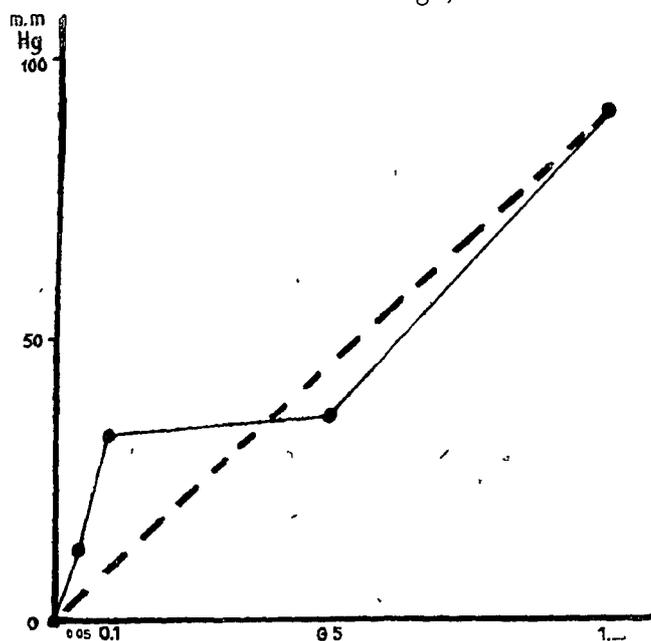


Fig. 2.

Relation of the amount of lobelin to the influence exerted by lobelin upon the rise of blood pressure after 0,1 mgr. of nicotin;

abscissa: amount of lobelin in milligrammes.

ordinate: difference in nicotin action before and after the lobelin injection, expressed in mgr. Hg.

discussion a potentiation has been found in a mixture of two substances, no doubt pharmacologically closely allied, and on that account should, according to BÜRGI's preconceived idea, *not* display the phenomenon.

In conclusion we wish to say that we do not ignore that the tinctura lobelin is seldom prescribed in Holland, but it is used rather largely in other countries, so that this potentiating effect upon nicotin (and maybe also upon other drugs, not investigated by us) has also its practical side.

Chemistry. — “*Contributions to the theory of dyeing*” (First communication) by Prof. H. R. KRUYT and Miss J. E. M. VAN DER MADE. (Communicated by Prof. ERNST COHEN).

(Communicated in the meeting of June 30, 1917).

1. Three different explanations have been suggested for the way in which dyes are taken up by fibres and other solids. First a merely chemical combination of dye and fibre was suggested; but a chemical theory gave rise to so many contradictions, that, as soon as the theory of solid solutions was developed, it was tried to explain dyeing in agreement with the new theory. But in this way it was just as impossible to bring experiments and theory into harmony, and the new knowledge in the chemistry of colloids, especially that of the phenomena of adsorption and of the electricity of contact, gave a better starting-point for the explanation of the way in which wool, silk, cotton etc. take dyes from their solutions in water, both when electrolytes are added and when this is not the case. FREUNDLICH, in collaboration with several pupils (LOSEV¹), NEUMANN²), stated the fact, that amorph. carbon takes the dye from its solution in quite the same way as textile-fibres do; PELET³) has made numerous investigations with his pupils on this subject⁴). It may be stated that nowadays the interpretation of the process of dyeing as a phenomenon of electro-adsorption is generally accepted.

This point of view may be summarized as follows: the faculty of the fibre to take up the dye depends on the electric potential at the confines of fibre and solution, in connection with the sign of the electric charge of the dye-ions. The fibres and charcoal are charged negatively with regard to water, therefore they generally adsorb the basic dyes better than acid dyes. Every influence increasing the negative charge of the adsorbentia, will increase the adsorption

¹) Zeitschr. f. physik. Chem. 59, 284 (1907).

²) Zeitschr. f. physik. Chem. 67, 538 (1909).

³) The results of these investigations are brought together in the interesting monograph PELET-JOLIVET, Die Theorie des Färbeprozesses (Dresden 1910).

⁴) BANCROFT and his pupils too have paid much attention to the process of dyeing of late years. A summary of the theory of dyeing can be found: W. D. BANCROFT, Journ. of physical chemistry 18, 1, 118 and 385 (1914).

of basic dyes. All inorganic compounds and their ions are adsorbed in nearly equal amounts from solutions of equal molecular concentration, excepted the ions of H, OH and of the heavy metals, which show an abnormally high adsorption. So the hydroxides of the alkali-metals will add to the negative charge, for the OH ion is adsorbed more fully than the metal-ion. The same will be caused by alkali salts of polybasic acids, as the negative ion has a greater electric charge than the kation; and again the same will be the case by adding salts of organic acids, because organic ions are more fully adsorbed than anorganic ones. When dyeing with acid dyes, we shall meet with an exactly opposite effect of electrolytes, dyeing being increased by acids, by salts of bi- and trivalent kations and of organic ones. Influences, diminishing the process of dyeing, may easily be inferred to the same line of thought.

PELET's investigations are in perfect accord with the above theory, both for the adsorption of the dyes itself and for the influence of dyes and electrolytes on capillary electric phenomena.

2. W. REINDERS¹⁾ lately published a paper in which he drew the conclusion that there remained much doubt about the connection between dyeing and the phenomena of adsorption. He had made investigations on the ratio in which a solution in water gave the dye to another phase, which was not a solid with great development of surface, but which was a liquid; the dyesolution was shaken with isobutylic alcohol. First the distribution of the dye in the two layers showed to be not in harmony with the distribution-law. In the second place he remarked in those cases, that whether acid or alkali increased the process of dyeing, the transition of the dye into the alcohol layer was also favoured. He came to the conclusion that these facts pointed clearly to a solution theory, and that it was of no use to refer to the theory of adsorption.

The interesting question, that was brought forward again by that paper, induced us to make the following investigation. First of all we are of opinion that for a good solution of this intricate problem it is of the greatest importance to avoid all unnecessary complication; therefore we shrink from drawing conclusions from experiments, when alkali or acid is present together with the dye. For these bodies often cause a chemical change in the molecule of the dye, in which case we have to deal with a chemical phenomenon and the process of dyeing simultaneously. So we have studied the

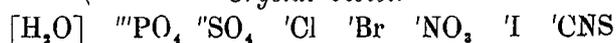
¹⁾ Koll. Zeitschr. 13, 96 (1913).

distribution of the dyes between water and isobutylic alcohol when only the sodium salts¹⁾ of different acids were present.

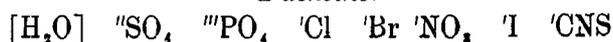
1 ccm. of the solution of the electrolyte (12 millimol p. L.) was added to 2 ccm. of a 0.5% solution of the dye (the first experiment was made, of course, with 1 ccm. of pure water). Then 2 ccm. of isobutylic alcohol were added and the whole was shaken in a tube with a glass stopper.

As the result we give the series in which the salts favour the transition from the waterlayer to the alcohol. From the left to the right the ions are written in the same series as they cause the alcohol to take a darker colour, resp. the waterlayer to take a brighter tinge. When two ions are united with a brace, we wish to express that the difference of colour was too small to decide about their sequence.

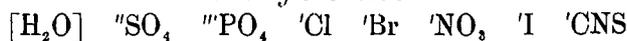
Crystal violet.



Fuchsine.

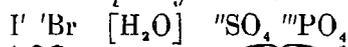


Methylene blue.

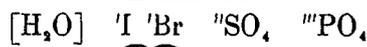


The first thing that strikes us is the fact that the ions are placed in the sequence of the so called *lyotropic series of anions*. The sequence of the ions is the same as regards their influence on the solubility of other bodies; the salting out of proteids; the influence on surface tension; enlargement of swelling; the kinetics of many reactions etc. These three dyes were basic, but when acid ones are taken we can expect the anions to have either no influence at all or an opposite one. Indeed we found such an influence though very weak.

Naphtolyellow S.



Alcaliblu.



3. PELET's theory of dyeing suggests an increasing adsorption of basic dyes when NaCl, still more when Na₂SO₄ and even much more when Na₂HPO₄ is added to the dyeing tub; we found however that the adsorption by the alcohol was not increased according to the

¹⁾ We only used NH₄CNS in staed of NaCNS.

basicity of the anions but according to their lyotropic strength. Lyotropically SO_4 and PO_4 are nearly equal, but Cl has a sharply different position, contrary to the sequence of basicity. Operating with neutral salts we therefore seem to have missed the parallelism REINDERS found with acids and alkalies.

One is inclined to consider the transition of the dye from the water to the alcohol layer as the process of salting out, so common to the emulsoids. Indeed the CNS ion, the extreme term of the series, caused precipitation after 24 hours,¹⁾ when brought to the dye solution in water to an amount of 4 millimol p. L., (the same concentration as the electrolytes had in the water-layer before the alcohol was added). It is evident that dyes, showing in many respects the properties of lyophobic colloids, are salted out by electrolytes in the sequence of the lyotropic series; and it is therefore easy to understand that lyotropic influences (it would be preferable to say *hydrotropic* here) cause a distribution of the dye in such a way, that the most active ion causes the greatest transition of the dye to the alcoholic layer.

4. Our knowledge about the influence of neutral salts on dyeing is however small. The dissertation of BACCIO BECCARI²⁾, a pupil of PELET, is the only systematical investigation we know, and even in this methylene blue is the only basic dye, and Na_2SO_4 and Na_2HPO_4 are the only neutral salts considered. The sequence in which that dye is taken up is this: solution in water — solution containing Na_2SO_4 — solution with Na_2HPO_4 , all according to PELET's theory³⁾.

As we thought it interesting to know whether lyotropic phenomena had any influence on the process of dyeing, we have made investigations about the quantity of dye adsorbed in the presence of the sodium salts of PO_4 , SO_4 , Cl , Br or NO_3 .

For dyes we took methylene blue, crystal violet and auramine; bloodcoal was the adsorbens. In each series the initial concentration and the amount of coal were exactly equal. The concentration at the end of the process was estimated by PELET and GARUTI's volume-

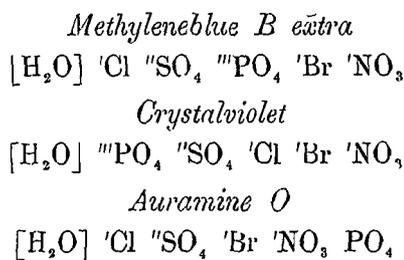
¹⁾ When in contact with isobutylic alcohol, a precipitate could only be seen after some weeks at the boundary of the layers.

²⁾ Diss. Lausanne: Etude des relations des phénomènes de teinture et d'adsorption. (Florence 1908).

³⁾ Investigations of A. WILD, mentioned in PELET JOLIVET's book p. 98, show the following sequence in the case of methyleneblue: $\text{H}_2\text{O}—\text{Cl}—\text{SO}_4—\text{PO}_4$.

metric method¹⁾; methylene blue was measured by naphtholyellow S, crystalviolet by picrate of sodium and auramine by alcaliblu.

The adsorption showed to have been increased by the salts in this sequence:



In these series the ion which effects the adsorption is mostly placed at the right.

5. These results of our first series of measurements indicate that the interpretation must be more complicated than one should think from PELET's theory. When only the ions of 'Cl, "SO₄ and "'PO₄ are taken into consideration our results are in harmony with this theory with regard to methyleneblue and auramine, the increasing influence is added to with the basicity of the anions.

But the 'Br and 'NO₃ ion already show the importance of lyotropic influence. So we may draw the conclusion that dyeing is affected by the two sorts of phenomena; — when two ions are of nearly equal lyotropic strength, it will be possible for their electro-adsorptive character to preponderate and therefore to fix the sequence; when, however, there is great lyotropic difference between two ions, this fact will be decisive. With crystal violet the lyotropy of the salts is so predominant that no other influence can be noticed in the sequence.

An exact interpretation of lyotropic phenomena is always difficult because lyotropy can have so many different effects. Even the supposition that the cause of lyotropy is to be found in the power to combine with watermolecules, the so called "solvation", — though acceptable in many respects — leads to so many consequences, that the explanation remains totally arbitrary, as long as we cannot verify our theoretical conclusions with many series of experiments. We intend therefore to extend our researches to several dyes, electrolytes and adsorbentia. But we may call attention now already to the fact that the importance of lyotropy is not in contradiction with a theory regarding the process of dyeing as a phenomenon of adsorption, though this complication has remained un-

¹⁾ Bull. de la Soc. Vaudoise des Sc. nat. 43, 1 (1907).

considered till now¹⁾. For without sufficient reason it is only *electro-adsorbative-phenomena* that have been compared with the process of dyeing; the investigation of FREUNDLICH and POSER²⁾ showed however that such a way of interpretation is quite insufficient. Adsorption is not determined by electrical causes only, besides there is certainly a non electrical adsorption, determined by the surface tension according to GIBBS' law. As the lyotropic series shows the sequence in which the ions influence surface tension, it will be clear that the principle of adsorption explains both the importance of valency and lyotropic strength.

Attention must all the same be directed to the possibility, that the electrolytes do not leave the dyesolutions itself³⁾ unaltered. The peculiar condition of dyesolutions, often polydispers with the character of a pseudo-binary system⁴⁾, make the problem all the more complicated; only a wide investigation of each sort of influence by itself can make it clear. Hence we already made a beginning with such experiments.

Utrecht, June 1917.

VAN 'T HOFF-laboratory.

¹⁾ The only investigation showing the lyotropic influence on dyeing is to be found Biochemical Journal 1 175 (1906). BAYLISS made some researches on the dyeing of filtering paper by congo-red in presence of salt; the influence of these salts proved to be as according to the lyotropic series. BANCROFT (loc. cit.) does not mention this paper, PELET-JOLIVET does, but only in connection with other questions. So BAYLISS' paper came to our knowledge only when this investigation was closed.

²⁾ Koll. Beih. 6, 297 (1914).

³⁾ See I. TRAUBE, Koll. Beih. 3, 237 (1912).

⁴⁾ The remarkable observation DROOGLEEVER FORTUYN published [These Proceedings 23 1380 (1915)] have convinced us again on this point. It is obvious that in a solution of new fuchsine in water there are two kinds of molecules, a coloured and a non coloured one, which are in equilibrium with one another. And in water this equilibrium is reached only after a long time and as by absorption only the coloured modification is taken away, some days are wanted to colour the water again after it has been decoloured by coal (acetic acid seems to catalyse). It is a wellknown phenomenon that a solution of fuchsine is decoloured by alcali as the dye is changed into the pseudo base; still such a solution will dye silk [JACQUEMIN, C.R. 82, 261, (1876)] and wool. But the red colour returns too when the solution is shaken with isoamylic- or isobutylic alcohol [WITT, Farber Zeitung 1, 1 (1891)]. The same thing occurs when we shake a solution decoloured in the same way as followed by DROOGLEEVER FORTUYN, with isobutylic alcohol; this suggests that water is a solution of a pseudo base, which was present already in the primary solution. Perhaps this is also the reason, why the adsorption of dyes seems to take much more time than that of other bodies. The regeneration of dye, the only component which has really been adsorbed, from the carbinol base, which is even not in real solution (as an ultramicroscopic investigation shows), makes it appear as if the process of adsorption should be slow in this case.

Physics. — “*On the Theory of the BROWNIAN Movement and the Experiments of BRILLOUIN*”. By H. C. BURGER. (Communicated by Prof. W. H. JULIUS.)

(Communicated in the meeting of April 27, 1917).

The purpose of this inquiry is of two kinds viz:

1st. to give a rigorous proof of some well known formulae of the Brownian movement, with and without external force.

2nd. to trace the boundary-condition at a fixed wall and to interpret some experimental results concerning this.

§ 1. When a material particle is suspended in a liquid, one may inquire after the probability that, in consequence of the Brownian movement, it will in the time t in the direction of X cover a distance between x and $x + dx$. This probability is determined by v. SMOLUCHOWSKI¹⁾ by using the following image. Suppose that this particle regularly after a time τ covers a distance σ , with equal probability to the right or to the left. Now, when one makes σ and τ zero, but keeps $\frac{\sigma^2}{2\tau} = D$ finite, one finds for the required probability:

$$f(x, t) dx = \frac{1}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} dx. \quad \dots \dots (I^a)$$

From this formula we find for the mean square of the displacement,

$$\overline{x^2} = 2Dt.$$

By entering closer into the mechanism of the phenomena, we may find the last equation, in which D then proves to be:

$$D = \frac{RT}{N} \frac{1}{6\pi\mu a}, \quad \dots \dots (I^b)$$

where R , T and N have the usual meaning, μ is the coefficient of viscosity of the liquid and a the radius of the particle.

Now we may deduce (I^a) however in a perfectly rigorous manner, without making use of any image, whereby however the constant D remains entirely undefined; and at the same time we may prove,

¹⁾ Vorträge über die Kin. Theorie der Materie p. 101, 1914 and Bull. Acad. Cracovie p. 419, 1913.

that an infinite number of images lead to the same final-equation. We may viz., as has already been shown by v. SMOLUCHOWSKI¹⁾ come to an integral-equation for $f(x, t)$ in the following manner:

When the particle in the time t has covered a distance between a and $a + da$, this may have taken place in such a way that:

in the time t_1 a distance is covered between x_1 and $x_1 + dx_1$
 " " " t_2 " " " " " " " " x_2 " " $x_2 + dx_2$

 " " " t_n " " " " " " " " x_n " " $x_n + dx_n$

in which $\sum t_i = t$ and $\sum x_i$ lies between a and $a + da$. When we suppose that the times t_i are not too small so that the number of shocks in t , is great enough to allow the use of probability-calculus, the probability of this occurring is given by

$$f(x_1, t_1) f(x_2, t_2) \dots f(x_n, t_n) dx_1 dx_2 \dots dx_n,$$

in which f is the required function. Now this product, integrated for all values of $x_1 \dots x_n$ for which $\sum x_i$ lies between a and $a + da$, must give the probability, that the particle in the time t has covered a distance between a and $a + da$, so $f(a, t) da$, in which this f will be the same as the "elementary" f from the above product, when only t_i is not too small.

So we get:

$$\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} f(x_1, t_1) \dots f(x_n, t_n) dx_1 \dots dx_n \cdot A = f(a, t) da. \dots (II^a)$$

Here A is a factor of discontinuity that satisfies the conditions

$$A = 0 \text{ when } \sum x_i < a \text{ or } \sum x_i > a + da$$

$$A = 1 \text{ ,, } a < \sum x_i < a + da.$$

When $n = 2$ (II^a) becomes:

$$\int_{-\infty}^{\infty} f(x, t_1) f(a - x, t_2) dx = f(a, t_1 + t_2) \dots (II^b)$$

One easily sees that inversely (II^a) follows from (II^b) so that each of these equations may be used as a basis for the following surveys.

We will now show in different ways how we may deduce the formula (I^a) from the equations (II).

I. Take in (II^a) the times $t_1 \dots t_n$ small then n is great²⁾.

¹⁾ Comp. M. v. SMOLUCHOWSKI. Ueber Browns'sche Molecularbewegung etc. Ann. der Physik. 48 p 1103, 1915.

²⁾ When we want, that in the first member of (II^a) $f(x, t)$ is the required function, then t_i must be larger than a certain very small time, which EINSTEIN has estimated at 10^{-7} sec. for particles of a radius of 1μ . (Ann. d. Phys. 19.371, 1906).

In connection with the physical meaning of $f(x, t)$ we know that the function f is even in x , and for a small t differs only from zero for small values of x . From the proof of the law of errors as given by BESSEL ¹⁾, we know that under these conditions a product that is built as the first member of (II^a), becomes for great values of n :

$$f(a, t) da = \varphi e^{-\psi a^2} da, \dots (III)$$

in which φ and ψ are functions of t still unknown. To determine these, we substitute (III) in (II^b). This gives after integration

$$\frac{\varphi(t_1)\varphi(t_2)\sqrt{\pi}}{\sqrt{\{\psi(t_1)+\psi(t_2)\}}} e^{-a^2 \frac{\psi(t_1)\psi(t_2)}{\psi(t_1)+\psi(t_2)}} = \varphi(t_1+t_2) e^{-a^2\psi(t_1+t_2)}$$

From this follows

$$\psi(t_1+t_2) = \frac{\psi(t_1)\psi(t_2)}{\psi(t_1)+\psi(t_2)} \text{ and } \varphi(t_1+t_2) = \frac{\varphi(t_1)\varphi(t_2)\sqrt{\pi}}{\sqrt{\{\psi(t_1)+\psi(t_2)\}}}$$

The solution of the first equation is: $\psi(t) = \frac{c}{t}$ ²⁾.

This, substituted in the equation for φ , gives:

$$\varphi(t_1+t_2) = \frac{\varphi(t_1)\varphi(t_2)\sqrt{\pi t_1 t_2}}{\sqrt{c(t_1+t_2)}}$$

This functional equation is solved by

$$\varphi(t) = \sqrt{\frac{c}{\pi t}} e^{c't} \text{ ³⁾}$$

When we substitute this in (III) and consider moreover that:

$$\int_{-\infty}^{\infty} f(a, t) da = 1,$$

then it is proved that $c' = 0$ and we find

$$f(a, t) = \sqrt{\frac{c}{\pi t}} e^{-\frac{a^2 c}{t}}$$

¹⁾ Astr. Nachr. 15 (1838) p 369 = Ges. Abh. 2. p. 372.

²⁾ Put:

$$\psi(t) = \frac{k(t)}{t}, \text{ so } \frac{k(t_1+t_2)}{t_1+t_2} = \frac{k(t_1)+k(t_2)}{t_2 k(t_1)+t_1 k(t_2)}.$$

When we put herein successively: $t_2 = t_1, 2t_1, 3t_1, \dots$, then appears: $k(t_1) = k(2t_1) = \dots$ so $k(t)$ is a constant

³⁾ Put viz. $\varphi(t)\sqrt{t} = \sqrt{\frac{c}{\pi}} L(t)$, than $L(t_1+t_2) = L(t_1)L(t_2)$ or $L(t) = e^{c't}$ in which $c' = \text{constant}$.

When moreover we put herein $c = \frac{1}{4D}$, in which D is a new constant, we get exactly (I_a)¹).

II. From (II^o) we can deduce a differential equation for $f(a, t)$. When viz. we expand in the first member $f(a-x, t_2)$ in a series of powers of t_2 , we find:

$$f(a, t_2) + \frac{\partial^2 f(a, t_2)}{2! \partial a^2} \int_{-\infty}^{\infty} x^2 f(x, t_1) dx + \dots = f(a, t_2) + t_1 \frac{\partial f(a, t_2)}{\partial t_2} + \dots,$$

¹) We may give this proof in a slightly different way yet, viz. by using only (II_a). Take in (II_a) $t_1 = t_2 = \dots = t_n = \tau$, and make n great. As is known from the quoted proof of BESSEL (l. c.):

$$f(a, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \{\chi(\lambda)\}^n \cos a\lambda dt,$$

in which

$$\chi(\lambda) = \int_{-\infty}^{\infty} f(x, \tau) \cos x\lambda dx.$$

By expanding $\cos x\lambda$, we get:

$$\chi(\lambda) = 1 - \frac{\lambda^2}{2!} \int_{-\infty}^{\infty} x^2 f(x, \tau) dx + \dots$$

When τ is small, the coefficients of the powers of λ diminish rapidly and are small, so:

$$\chi(\lambda) = 1 - \frac{\lambda^2}{2!} \int_{-\infty}^{\infty} x^2 f(x, \tau) dx = 1 - p_2 \lambda^2$$

and:

$$\{\chi(\lambda)\}^n = (1 - p_2 \lambda^2)^n = e^{-p_2 n \lambda^2},$$

while p_2 is small and n great. Finally:

$$f(a, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \cos a\lambda e^{-p_2 n \lambda^2} = \frac{1}{2\sqrt{\pi p_2 n}} e^{-\frac{a^2}{4p_2 n}}$$

Now $n\tau = t$. Further take $\frac{p_2}{\tau} = D$, then we find again the formula (I_a). Herein D is independent of τ , while from the found form of f follows that p_2 is proportional to τ .

This proof shows that always the same $f(a, t)$ is found, independent of the choice of the "elementary" f in the first member of (II_a). The value of D however in this case depends on the form of this function.

When we consider that

$$\int_{-\infty}^{\infty} f(x,t) dx = 1 \quad \text{and} \quad \int_{-\infty}^{\infty} x^{2n+1} f(x,t) dx = 0.$$

When in this we take t_1 small enough to allow the neglecting of following terms and further

$$\frac{1}{2t_1} \int_{-\infty}^{\infty} x^2 f(x,t_1) dx = D, \dots \dots \dots (IV^a)$$

we get the equation,

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial a^2} \dots \dots \dots (IV^b)$$

As here $\frac{\partial f}{\partial t}$ and $\frac{\partial^2 f}{\partial a^2}$ are functions of a and t , D will not contain t_1 and therefore will be a constant.¹⁾

It is remarkable that we find here the diffusion-equation as a direct consequence of the integral-equation (II^b), while (IV^a) immediately connects the diffusion-coefficient with the mean displacement.

This equation (IV^b) has to be solved without boundary-conditions and with the beginningconditions:

$$1^\circ \int_{-\infty}^{\infty} f da = 1 \quad , \quad 2^\circ f(a, 0) = 0 \quad \text{except for } a = 0.$$

This is a well-known problem of diffusion or conduction of heat, the solution of which is given by (I^a).

The exponential function of (I^a) satisfies the integralequation (II^a) for arbitrary n and t . When we take however for the "elementary" function $f(x_0)$ in the first member an arbitrary function, that only answers to the conditions

- 1 $f(x_0)$ is even,
- 2 $f(x_0)$ differs perceptibly from zero only when x_0 has a small value,

the integral in the first member of (II^a) will, for great n always give the same $f(a, t)$.²⁾ Therefore we understand that the simple image of the Brownian movement, that is given by v. SMOLUCHOWSKI yields a right result, in spite of the fact that it approximates the true movement very badly.

¹⁾ When we introduce the solution of (IV^b) i. e. (Ia) in (IV^a), D becomes actually a constant, as is supposed in the solution of (IV^b).

²⁾ See note 1, p. 645.

When one chooses however another image, i.e. another form for the "elementary" function $f(x)$, one gets the same formula (I^a), but then D depends on the choice of $f(x)$ in another way.¹⁾ Only when the "elementary" function is the required $f(x, t)$, D will be an indefinite constant, which is determined by the nature of the Brownian movement.

§ 2. In the preceding paragraph we have always supposed that the Brownian movement is not influenced by an external force. In consequence of this, we might, for reasons of symmetry, accept $f(x, t)$ to be even in x . When however a force acts upon the particles, the probability of a certain displacement will be no longer an even function of this displacement. Nor will this probability only depend on the displacement, but also on the starting-point. First we will consider displacements in the direction of X only. When we call the abscissa of the particle at the time $t = 0$ x , we may represent the probability that this abscissa at the time t lies between p and $p + dp$, by $f(x, p, t) dp$. One easily understands, that this function f also satisfies an integral-equation viz.:

$$\int_{-\infty}^{\infty} f(x, p, t_1) f(p, a, t_2) dp = f(x, a, t_1 + t_2)^2. \quad (V)$$

From this integral-equation v. SMOLUCHOWSKI²⁾ for the case of a quasi-elastic force, has determined f by repeated integration, but hereby he remarks, that this way is only serviceable when we make a simple supposition about the force ψ , and that, in general it is preferable to determine f from a generalised equation of diffusion. This equation is deduced by v. S. on a somewhat phenomenological manner, without making use of (V). We will now show how this equation may be deduced from (V), when we use suppositions that are also put forward by v. S., determining f by repeated integration.

When namely in (V) we give t_2 a very small value, $f(p, a, t_2)$

¹⁾ Suppose e.g. that regularly after the time τ the displacement δ may occur to the right or to the left, each with the probability $\frac{1-\kappa}{2}$, so that the chance of remaining at rest is κ . By this the form of $f(x, t)$ is defined and we find for D :

$$D = \frac{p_2}{\tau} = \frac{1}{2\tau} \int_{-\infty}^{\infty} x^2 f(x, \tau) dx = \frac{\delta^2 (1-\kappa)}{2\tau}.$$

²⁾ See also M. SMOLUCHOWSKI Ann. d. Phys. 48 p. 1103, 1915.

³⁾ Ann. d. Phys. 48 p. 1104, 1915

is in first approximation an even function φ of the displacement $p-a$ ¹⁾, because the influence of the external force for small times is small with regard to that of the Brownian movement. To take into consideration the influence of the force, we determine the displacement σ , that the particle, starting from p , would undergo, when there was no Brownian movement. So, the displacement in consequence of the Brownian movement in the time t_2 is $p + \sigma - a$, when we suppose that the two displacements are simply superposed, t_2 being small.

So for small t_2 we may substitute $\varphi(p + \sigma - a, t_2)$ for $f(p, a, t_2)$ whereby φ is a function that is even in its first argument. As the influence of the force is entirely included by the quantity σ , φ , which relates to the undisturbed Brownian movement, has the following properties:

$$\int_{-\infty}^{\infty} \varphi(\xi, t) d\xi = 1 \quad \text{and} \quad \int_{-\infty}^{\infty} \xi^2 \varphi(\xi, t) d\xi = 2Dt. \quad \dots \quad (VI)$$

To compute σ , we make use of the fact that small particles, under the influence of a constant force, cover a distance that is proportional to the time, when we leave the influence of the Brownian movement out of account. As however the force $\psi(x)$ is a function of x , the distance σ , which has been covered, is a function of t_2 that will also contain the higher powers of t_2 , being expanded into a series of ascending powers of this quantity. As t_2 is chosen small, so that in every instance we keep only the first power, we may take for σ :

$$\sigma = \beta t_2 \psi(p) \dots \dots \dots (VII)$$

So (V) becomes:

$$\int_{-\infty}^{\infty} f(x, p, t_1) \varphi\{p-a + \beta t_2 \psi(p), t_2\} dp = f(x, a, t_1 + t_2).$$

By taking $p = a + \xi$ we may expand f and φ as follows:

$$f(x, a + \xi, t_1) = f(x, a, t_1) + \xi \frac{\partial f}{\partial a} + \frac{1}{2} \xi^2 \frac{\partial^2 f}{\partial a^2} + \dots$$

$$\varphi\{p-a + \beta t_2 \psi(a + \xi), t_2\} = \varphi(\xi, t_2) + \left\{ \beta \psi(a) + \beta \xi \frac{\partial \psi(a)}{\partial a} \right\} \frac{\partial \varphi(\xi, t_2)}{\partial \xi} t_2 + \dots$$

¹⁾ Though we do not want the form of this function, we may remark that this will be:

$$\varphi(p-a, t_2) = \frac{1}{2\sqrt{\pi Dt_2}} e^{-\frac{(p-a)^2}{4Dt_2}}$$

We also expand the second member of (V):

$$f(x, a, t_1 + t_2) = f(x, a, t_1) + t_2 \frac{\partial f(x, a, t_1)}{\partial t_1} + \dots$$

After having multiplied and performed the integrations, we find, making use of (VI), when we keep only the terms with t_2 and drop those with higher powers:

$$\frac{\partial f(x, a, t_1)}{\partial t_1} = D \frac{\partial^2 f}{\partial a^2} - \beta \psi(a) \frac{\partial f}{\partial a} - \beta f \frac{\partial \psi}{\partial a}$$

or

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial a^2} - \beta \frac{\partial}{\partial a} (\psi f) \dots \dots \dots (VIII)$$

This is the generalised equation of diffusion that v. SMOLUCHOWSKI uses, however, deduced from the integral-equation (V).

When one does not restrict oneself to the problem of one dimension, but investigates the case of three dimensions, the probability that a particle with the coordinates x, y, z will have after the time t coordinates between p, q, r and $p + dp, q + dq, r + dr$ may be represented by $f(x, y, z, p, q, r, t) dp dq dr$.

We easily understand, that this function satisfies the following integral-equation:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y, z, p, q, r, t_1) f(p, q, r, a, b, c, t_2) dp dq dr = f(x, y, z, a, b, c, t_1 + t_2) \dots (IX)$$

When we call again the force, that is now a vector, ψ , we find for f in an analogous manner as in the preceding, the equation of diffusion:

$$\frac{\partial f}{\partial t} = D \Delta f - \beta \operatorname{div} (\psi f) \dots \dots \dots (X)$$

The operations Δ and div . here refer to the second three independent variables in f , on which ψ also depends.

The truth of (X) is also easily proved in another way.

With the help of (VIII) we can solve the following problem:

The plane $x=0$ is formed by a fixed wall, which, on a particle in the liquid by positive x , exercises a repelling force, which becomes perceptible in a point A at a small distance of the wall, increases by approaching the wall, and becomes infinite when $x=0$, remaining so for negative x ¹⁾. What is the probability that a particle for which

¹⁾ A wall with the described properties will reflect the particles colliding against it, without ever one of them adhering.

$x = x_0$ when $t = 0$, has at the time t an abscissa between x and $x + dx$?

For this case (VIII) becomes:

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2} - \beta \frac{\partial}{\partial x} (\psi f),$$

in which $f(x_0, x, t) dx$ is the required probability.

This equation, integrated with respect to x from a point B with negative x to A , gives:

$$\frac{\partial}{\partial t} \int_B^A f dx = D \left\{ \left(\frac{\partial f}{\partial x} \right)_A - \left(\frac{\partial f}{\partial x} \right)_B \right\} - \beta \{ (f\psi)_A - (f\psi)_B \}.$$

As in A $\psi = 0$ and in B f and $\frac{\partial f}{\partial x}$ will be very strongly zero by the immense repelling force, we get:

$$\frac{\partial}{\partial t} \int_B^A f dx = D \left(\frac{\partial f}{\partial x} \right)_A.$$

When we now make the thickness of the layer in which perceptible forces act, very small, $\int_B^A f dx$ disappears for every time, because f is in this layer certainly not infinite. So we get at the wall:

$$\left(\frac{\partial f}{\partial x} \right)_A = 0.^1)$$

How f may be determined from this equation, needs not be explained here.

§ 3. The boundary-condition at a reflecting wall may be easily deduced from (VIII), and this is perhaps also possible for an adsorbing wall in the latter case, however, it seems simpler to take another way. We suppose that the adsorbing wall may detain a particle that collides against it, and that such a detained particle never gets free again. This property may be observed under several circumstances.

Suppose that a particle at the time t has a distance x from the wall that is situated at $x = 0$. After a time t the particle may be adsorbed by the wall or may still be free. So it naturally suggests itself to introduce in this case the two following functions:

¹⁾ Comp. M. v. SMOLUCHOWSKI, Phys. Zeitschr. 17 p. 587, 1916.

1st. The probability that the particle mentioned has at the time t a distance from the wall between p and $d + dp$. $f(x, p, t) dp$.

2nd. The probability that, at the time t , it has been adsorbed by the wall: $\chi(x, t)$.

Since a particle, that is not adsorbed at the time $t_1 + t_2$, is also free at the time t_1 , f will satisfy the integral-equation:

$$\int_0^\infty f(x, p, t_1) f(p, a, t_2) dp = f(x, a, t_1 + t_2) \dots (XI)$$

We can further obtain a simultaneous integral-equation for f and χ by remarking that the probability $\chi(x, t_1 + t_2)$ consists of two parts viz. the probability that the particle was already adsorbed at the time t_1 and the probability, that at the time t_1 it was somewhere in the liquid and is adsorbed by the wall during the time t_2 . This leads to the equation:

$$\chi(x, t_1 + t_2) = \chi(x, t_1) + \int_0^\infty f(x, p, t_1) \chi(p, t_2) dp \dots (XII)$$

As, after the time t the particle must be somewhere, we finally have as third equation for f and χ :

$$\int_0^\infty f(x, p, t) dp + \chi(x, t) = 1. \dots (XIII)$$

Just as in § 2 we are able to derive from (XI) a differential-equation for f , with this difference however, that now in the liquid the external force $\psi = 0$.¹⁾

So in the liquid $f(x, p, t)$ satisfies the equation:

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial p^2} \dots (XIV)$$

However to determine f we need a boundary-condition. This may be found from (XII), (XIII) and (XIV).

When viz. we write for (XII):

$$\frac{\chi(x, t_1 + t_2) - \chi(x, t_1)}{t_2} = \frac{1}{t_2} \int_0^\infty f(x, p, t_1) \chi(p, t_2) dp, \dots (XII^a)$$

and make t_2 very small, then the second member of (XII^a) becomes

¹⁾ The forces, that the wall exercises on the particle, are accounted for by the function χ .

$$x(x, 0, t_1) \cdot \frac{1}{t_2} \int_0^\infty \chi(p, t_2) dp,$$

because, in consequence of the meaning of $\chi(p, t)$, this function for small t only differs from zero when p is small too. Now, while the limit in the first member exists and is finite, this will also be the case with the limit of the second member and is therefore:

$$\lim_{t_2 \rightarrow 0} \frac{1}{t_2} \int_0^\infty \chi(p, t_2) dp = \lim_{t_2 \rightarrow 0} \int_0^\infty \left\{ \frac{\chi(p, t_2) - \chi(p, 0)}{t_2 - 0} \right\} dp = \int_0^\infty \left\{ \frac{\partial \chi(p, t_2)}{\partial t_2} \right\}_{t_2=0} dp = \kappa,$$

where x is a constant.

So it follows from (XII^a):

$$\frac{\partial \chi(x, t_1)}{\partial t_1} = \kappa f(x, 0, t_1) \dots \dots \dots (XV)$$

Now, when we integrate (XIV) with respect to p from zero to infinite, we find:

$$\frac{\partial}{\partial t_1} \int_0^\infty f(x, p, t) dp = - D \left(\frac{\partial f}{\partial p} \right)_{p=0}.$$

In reference to (XIII) and (XV) this gives the boundary-condition:

$$D \left(\frac{\partial f}{\partial p} \right)_{p=0} = \kappa f_{p=0} \dots \dots \dots (XVI)$$

From (XIV), with the help of this boundary-condition and the beginning-condition, we may determine f . f being found, χ follows from (XIII).

While the functions f and χ , used above, are probabilities, we can test the obtained results only by making a very great number of observations. This is easily done by bringing not *one* but many particles in the liquid. Though we cannot say then how many particles after the time t will be adsorbed by the wall, we may calculate the most probable number from which the true number will differ the less, as there are more particles.

Imagine a cylindric volume, limited only at one side by the wall that lies at $x = 0$. In this volume are, at the time $t = 0$ a great number of particles homogeneously dispersed, so that the number of those particles being at a distance from the wall between x and $x + dx$, is $n_0 dx$. Now we ask after the most probable number of particles, that at the time t will be adsorbed by the wall.

Of the $n_0 dx$ particles at a distance from the wall between x and $x + dx$ there will probably, after the time t , $n_0 \chi(x, t) dx$ adhere

to the wall, so after the time t there will be adsorbed in total

$$n = n_0 \int_0^{\infty} \chi(x, t) dx \text{ particles.}$$

To compute this number it is not necessary to know f . As namely the beginning-condition for f is less simple, we introduce a new function:

$$F(p, t) = n_0 \int_0^{\infty} f(x, p, t) dx \quad (XVII)$$

Integrating (XIV) and (XVI) with respect to x from zero to infinity, it is easily seen that $F(p, t)$ satisfies the same differential-equation and boundary-condition as $f(x, p, t)$, considered as a function of p and t . Further it follows from (XIII) and (XVII) that the beginning condition is $F(p, 0) = n_0$.

The solution of the differential-equation for F , regarding the beginning and boundary-conditions, is:

$$F(p, t) = n_0 \Theta\left(\frac{p}{2\sqrt{Dt}}\right) + n_0 e^{\frac{p^2}{2D}} \left\{ 1 - \Theta\left(\frac{p}{2\sqrt{Dt}} + \sqrt{\frac{t}{D}}\right) \right\} \quad (XVIII)$$

in which

$$\Theta(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-u^2} du$$

The number of particles, adsorbed in the time t follows from (XV):

$$n_t = n_0 \int_0^{\infty} \chi(x, t) dx = n_0 z \int_0^t dt \int_0^{\infty} f(x, 0, t) dx = z \int_0^t F(0, t) dt,$$

which, after integration, gives:

$$n_t = -\frac{D}{z} e^{\frac{z^2 t}{D}} \Theta\left(\sqrt{\frac{z^2 t}{D}}\right) + 2\sqrt{\frac{Dt}{\pi}} + \frac{D}{z} \left(e^{\frac{z^2 t}{D}} - 1\right) \quad (XIX)$$

With this the problem is solved that is mentioned by v. SMOLUCHOWSKI²⁾ with respect to the fact that this theory was not in accordance with the experimental results of BRILLOUIN³⁾. The

¹⁾ $F(p, t)$ is the concentration of the particles at the time t at a distance p from the wall.

²⁾ H. WEBER, Die Part. Diff. Gl. der Math. Phys. 11, p. 95.

³⁾ M. v. SMOLUCHOWSKI, Phys. Zeitschr. 17, p. 570, 1916

⁴⁾ L. BRILLOUIN, Ann. Chim. Phys. 27, p. 412, 1912.

latter has experimented with particles of gamboge in a mixture of glycerine and water. The number of the particles that was adsorbed by the wall could be determined by counting them on a microphotograph.

Now, while BRILLOUIN has concluded, that his observations agree with theory, v. SMOLUCHOWSKI has pointed out the incorrectness of this method of reckoning and has substituted this by a better one. Thereby he supposes however that every particle that collides against the wall, sticks to it, and he further solves the problem by using the very schematic image of the Brownian movement that is mentioned in § 1. The result of this computation agrees very badly with the observations and v. SMOLUCHOWSKI thinks that this is a consequence of the fact, that a particle, colliding against the wall, does not adhere at once, but on the average has to collide several times before being adsorbed. So this would mean, that the boundary-condition has to be altered.

As now is demonstrated by v. SMOLUCHOWSKI ¹⁾, we find the solution of the problem as given by him, from the diffusion equation, when we use $F(0, t) = 0$ as boundary condition, while (XIX) is deduced with the general limiting-condition:

$$D \left(\frac{\partial F}{\partial p} \right)_{p=0} = \kappa F_{p=0}.$$

So we may expect that by a suitable choice of κ we get a result that is more in accordance with the experiments of BRILLOUIN.

To be able to decide in how far this is the case we compute from the data furnished by BRILLOUIN, n_0 and D the latter with the help of (Ib). When we now choose a certain value of κ , we can represent n_t graphically as a function of t . This is to be seen in fig. 1, in which the abscissa represents the number n_t of the adsorbed particles, and the ordinate, in accordance with BRILLOUIN, the square root of the time, expressed in hours. Further, for practical reasons, not the values of κ but those of $\alpha = \frac{\kappa}{\sqrt{D}}$ have been written at the curves.

For $\kappa = \infty$ ($\alpha = \infty$) we get a straight line, agreeing with the theory of v. SMOLUCHOWSKI. One sees that the observations of BRILLOUIN, indicated by crosses, do not at all correspond with them.

Smaller values of κ or α give curves that agree better with the observations, though none of the curves gives an entirely satisfying result. Probably $\alpha = 0.003$ ($\kappa = 1.5 \times 10^{-8}$) comes nearest to the truth, when we bear in mind, that the observations made after short times

¹⁾ M. v. SMOLUCHOWSKI Phys. Zeitschr. 17, p. 585, 1916.

are least to be trusted. Then the influence of small differences of temperature may viz. still be observed; this influence disappears after a long time. Also, because we can only determine theoretically

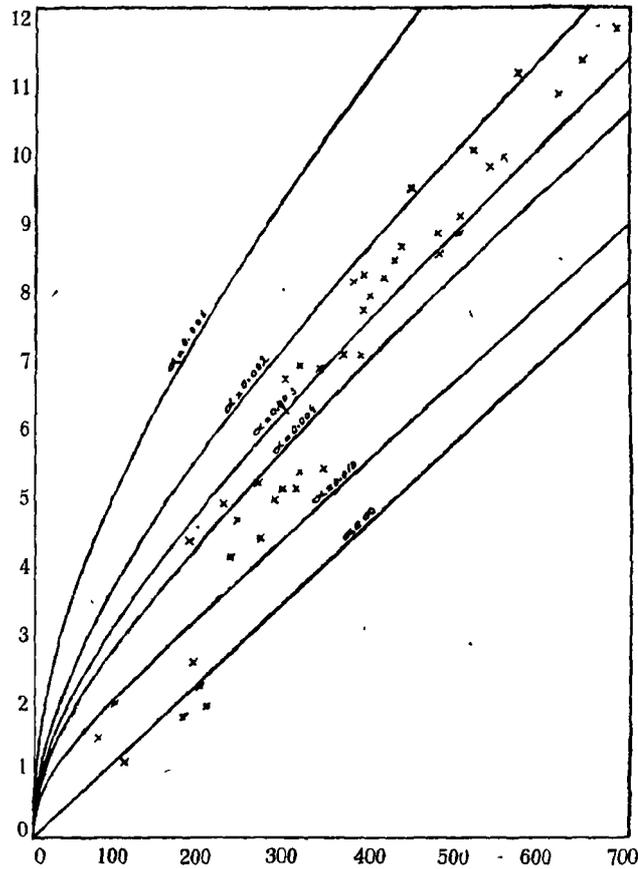


Fig. 1.

the most probable number, the observations after a long time, which deliver larger numbers, have more importance.

It is not to be denied however, that there seems to be a systematic error. Perhaps this may be sought in the fact of the particles not being exactly equal, or in a slow change of the electrical double-layers at the particles and the wall, in consequence of the numerous collisions. Further observations of the behaviour of colloidal particles with respect to a fixed wall, will have to decide whether this explanation is tenable.

A remarkable circumstance is, that the curves practically coincide

with the straight line for $\alpha = \infty$ ($\alpha = \infty$), when α or α are above a certain small value. With regard to the precision of the measurements all cases in which $\alpha > 5 \times 10^{-7}$ ($\alpha > 0.01$) may be treated as if $\alpha = \infty$ ($\alpha = \infty$). If the observations agree with the theory for $\alpha = \infty$, we may consequently only conclude from this that α is larger than this small value.

The quantity α occurring above has the dimension of a velocity and to know what the values of α mentioned before mean, we have to find out with what velocity α has to be compared. So we have to enter into a closer investigation of the physical meaning of α , also to decide whether α may assume all values between zero and infinity as has been tacitly supposed up till now.

From the way in which (XIX) is deduced, follows:

$$\frac{dn_t}{dt} = \alpha F(o, t) \dots \dots \dots (XX)$$

Now bearing in mind, that $\frac{dn_t}{dt}$ represents the number of the particles that sticks to the wall in a unit of time, it naturally suggests itself to compare this with the number of the particles that collides against the wall. This number, as is known from the kinetic theory of gases and liquids, amounts to:

$$\frac{v}{\sqrt{6\pi}} F(o, t) = \alpha_1 F(o, t)^1), \dots \dots \dots (XXI)$$

where v is the mean velocity of the particles that is given by the known formula:

$$v = \sqrt{\frac{3RT}{Nm}} \dots \dots \dots (XXII)$$

Here R , T and N have the known meaning and m is the mass of the particle. With the help of the values given by BRILLOUIN we find for the number of the collisions in a second:

$$\alpha_1 F(o, t) = 0.1 F(o, t)$$

From this follows, that of the particles, colliding against the wall only a very small fraction ε sticks. This ε , that consequently represents the probability that a colliding particle adheres, is to be found from:

¹⁾ When we want to take the change of the concentration with the distance from the wall into account, we have to substitute $F_{\rho=0} + \lambda \left(\frac{\partial F}{\partial \rho}\right)_{\rho=0} = 0$ for $F_{\rho=0} = 0$, where λ is a length of the order of magnitude of the mean free path of a particle. As $D \left(\frac{\partial F}{\partial \rho}\right)_{\rho=0} = \alpha F_{\rho=0}$, the ratio of the correction to the used value is $\frac{\lambda}{D}$, i.e. always very small.

$$\varepsilon = \frac{\varkappa F(0, t)}{\varkappa_1 F(0, t)} = \frac{\varkappa}{\varkappa_1} \dots \dots \dots (XXIII)$$

So it follows from the observations of BRILLOUIN that $\varepsilon = 1.5 \times 10^{-7}$. As the maximum value of the probability is 1, \varkappa can never be larger than \varkappa_1 i.e. for the particles used by BRILLOUIN $\varkappa < 0.1$. But \varkappa_1 will never be so small that, when $\varepsilon = 1$ or a not too small fraction, we cannot take $\varkappa = \infty$, without appreciably changing the result, so that for these cases the boundary condition $F(0, t) = 0$ gives a serviceable result. Strictly speaking the boundary-condition can however never be $F(0, t) = 0$, because then \varkappa must be infinite, which is impossible.

The probability ε will be connected with the mechanism of the collision of a particle against the wall and to get any insight into this, it is desirable to know ε as a function of different circumstances. Except the experiments of BRILLOUIN, no other experimental data to determine ε , are known to me.

§ 4. Though the boundary-condition in § 3 is deduced only for a plane wall, we may undoubtedly also apply it to a curved wall in the form:

$$D \frac{\partial \bar{F}}{\partial r} = \varkappa \bar{F} \dots \dots \dots (XXIV)$$

where the horizontal line denotes values at the wall and v is the normal directed towards the liquid.

This we may apply to the case of a fixed sphere with a radius R , surrounded by a liquid in which at the time $t = 0$ many particles are dispersed homogeneously (n_0 per unit of volume). The solution of this problem is namely used by v. SMOLUCHOWSKI¹⁾ in his theory of the coagulation. Where he however uses as boundary-condition $\bar{F} = 0$, we will here take (XXIV) as limiting-condition. The number of particles that sticks in a unit of time after some computations proves to be:

$$\frac{dn_t}{dt} = 4\pi RD n_0 \frac{\varkappa R}{\varkappa R + D} = 4\pi RD n_0 \frac{\varepsilon \varkappa_1 R}{\varepsilon \varkappa_1 R + D}, \quad (XXV)$$

when we, like v. SMOLUCHOWSKI, only consider times that are large with respect to $\frac{R^2}{D}$.

¹⁾ M. v. SMOLUCHOWSKI, Phys. Zeitschr. 17, p. 594, 1916.

When $\epsilon = 1$ or is at least not too small, we get very approximately $\frac{\epsilon \kappa_1 R}{\epsilon \kappa_1 R + D} = 1$ and (XXV) becomes :

$$\frac{dn_t}{dt} = 4\pi RD n_0, \dots \dots \dots (XXV^a)$$

as is also found by v. SMOLUCHOWSKI. If ϵ is however very small, then the same formulae remain valid as is also remarked by v. S., when we only multiply t with a constant factor. This factor however is not, as v. S. assumes ϵ , but $\frac{\epsilon \kappa_1 R}{\epsilon \kappa_1 R + D}$. So, as long as ϵ does not become very small, the formula (XXV^a) of v. SMOLUCHOWSKI holds good. When however ϵ becomes a very small fraction, then the number of particles that sticks per unit of time also becomes smaller, so that in this way the slow coagulation may be explained.

Finally I wish to express my sincere thanks to Prof. Dr. L. S. ORNSTEIN for his kind help and advice at the composition of this communication.

Utrecht, April 1917.

Institution for Theoretical Physics.



Chemistry. — “*In-, mono- and divariant equilibria*”. XVIII.

By Prof. SCHREINEMAKERS.

(Communicated in the meeting of October 27, 1917).

Equilibria of n components in n phases at constant temperature.

In the considerations of the previous communication XVII we have changed the temperature under constant pressure, now we shall change the pressure, while the temperature remains constant. Then we find similar properties as in the previous communication, e.g.

“In an equilibrium of n components in n phases at constant T the pressure is maximum or minimum, when a phase-reaction may occur between the phases”.

“When at constant T the pressure on the turning-line is a maximum (minimum), then from this turning-line two leaves of the region go towards lower (higher) pressures and no leaf towards higher (lower) pressures”.

We see that the figs. 2 [XVI], 4 [XVI] and 7 [XVI] are in accordance with this.

We call the equilibrium E , which occurs under the maximum- or minimumpressure P_R again E_R and the equilibria which occur under $P_R + \Delta P$ [$\Delta P > 0$ when P_R is a minimum, $\Delta P < 0$ when P_R is a maximum] again E' and E'' . The rules a , b , and c , which have been deduced in the previous communication now apply again to the position of those three equilibria with respect to one another.

In order to examine whether the pressure is a maximum or minimum, we can use again formula 15 [XVII]; this now becomes

$$\Sigma(\lambda V) \cdot \Delta P = \frac{1}{2} \Sigma(\lambda d^2 Z) \dots \dots \dots (1)$$

Herein is:

$$\Sigma(\lambda V) = \lambda_1 V_1 + \lambda_2 V_2 + \dots + \lambda_n V_n$$

consequently the change in volume, which occurs at the reaction:

$$\lambda_1 F_1 + \lambda_2 F_2 + \dots + \lambda_n F_n = 0$$

Just as in the previous communication also now we may apply this formula (1) to special cases.

Equilibria of n components in n phases, between which a phase-reaction may occur, at variable T and P. The turning-line E_R.

For the equilibrium $E = F_1 + F_2 \dots + F_n$ the equations (2) [XVII] and (3) [XVII] are true. When the equilibrium E passes into an equilibrium E_R , then $x_1 y_1 \dots x_2 y_2 \dots$ etc. have also to satisfy (13) [XVII]. From those latter equations which we once more mention here sub (2).

$$\left. \begin{aligned} \lambda_1 + \lambda_2 + \dots + \lambda_n &= 0 \\ \lambda_1 x_1 + \lambda_2 x_2 + \dots + \lambda_n x_n &= 0 \\ \lambda_1 y_1 + \lambda_2 y_2 + \dots + \lambda_n y_n &= 0 \end{aligned} \right\} \dots \dots \dots (2)$$

follows one single relation between the variables $x_1 y_1 \dots x_2 y_2 \dots$; we are able to find this relation by eliminating from (2) $\lambda_1 \dots \lambda_n$. We shall call this relation, resulting from (2), which we may write also in the form of a determinant, equation' (2).

Now we have $n^2 + 1$ equations and $n^2 + 2$ variables; consequently the equilibrium E_R is monovariant; it is represented, therefore, in the P, T -diagram by a curve, e.g. curve ef in fig. 2 (XVI) and fig. 4 (XVI).

From (2) [XVII] now follow the n equations (7) [XVII], they are of the form:

$$\left. \begin{aligned} -V_1 \Delta P + H_1 \Delta T + x_1 [d(x)_1 + \dots] + y_1 [d(y)_1 + \dots] + \dots \\ \dots + \frac{1}{2} d^2 Z_1 + \frac{1}{3} d^3 Z_1 + \dots = -\Delta K \end{aligned} \right\} (3)$$

From (3) [XVII] follow the $n(n-1)$ equations (8) [XVII]; they are of the form:

$$\left. \begin{aligned} d(x)_1 + \frac{1}{2} d^2(x)_1 + \dots = d(x)_2 + \frac{1}{2} d^2(x)_2 + \dots = \dots = \Delta K_x \\ d(y)_1 + \frac{1}{2} d^2(y)_1 + \dots = d(y)_2 + \frac{1}{2} d^2(y)_2 + \dots = \dots = \Delta K_y \end{aligned} \right\} (4)$$

etc. When we differentiate the equation resulting from (2), then we obtain another relation between $\Delta x_1 \Delta y_1 \dots \Delta x_2 \Delta y_2 \dots$. For our purpose we may find this in the following way. It follows viz. from (2)

$$\left. \begin{aligned} \Delta \lambda_1 + \Delta \lambda_2 + \dots + \Delta \lambda_n &= 0 \\ x_1 \Delta \lambda_1 + x_2 \Delta \lambda_2 + \dots + x_n \Delta \lambda_n + \lambda_1 \Delta x_1 + \dots + \lambda_n \Delta x_n &= 0 \\ y_1 \Delta \lambda_1 + y_2 \Delta \lambda_2 + \dots + y_n \Delta \lambda_n + \lambda_1 \Delta y_1 + \dots + \lambda_n \Delta y_n &= 0 \end{aligned} \right\} (5)$$

etc. As relation (2) exists between $x_1 y_1 \dots$, we may eliminate $\Delta \lambda_1 \dots \Delta \lambda_n$ from (5). For this we add the n equations (5) after having multiplied the 1st by μ_1 , the 2nd by μ_2 , etc. Now we may put:

$$\left. \begin{aligned} \mu_1 + \mu_2 x_1 + \mu_3 y_1 + \dots &= 0 \\ \mu_1 + \mu_2 x_2 + \mu_3 y_2 + \dots &= 0 \end{aligned} \right\} \dots \dots \dots (16)$$

etc. Then we have n relations between the $n-1$ ratio's $\mu_1 \dots \mu_n$;

it is apparent from (2) that we may also satisfy (6). Now follows from (5) in connection with (6):

$$\lambda_1 [\mu_1 \Delta x_1 + \mu_1 \Delta y_1 + \dots] + \lambda_2 [\mu_2 \Delta x_2 + \mu_2 \Delta y_2 + \dots] + \dots + \lambda_n [\mu_n \Delta x_n + \mu_n \Delta y_n + \dots] = 0 \quad (7)$$

Now we have in (7) the equation sought for; for the ratios between $\lambda_1 \dots \lambda_n$ we have yet to substitute their values from (2) and for the ratios between μ_1, \dots, μ_n still their values from (6).

In order to calculate $\frac{dP}{dT}$ we add the n equations (3) after having multiplied the 1st by λ_1 , the 2nd by λ_2 , etc. By using (2) and (4) we find:

$$-\Sigma(\lambda V) \cdot \Delta P + \Sigma(\lambda H) \cdot \Delta T + \frac{1}{2} \Sigma(\lambda d^2 Z) + \frac{1}{3} \Sigma(\lambda d^3 Z) + \dots = 0 \quad (8)$$

or:

$$\frac{dP}{dT} = \frac{\Sigma(\lambda H)}{\Sigma(\lambda V)} \quad (9)$$

Herein is:

$$\Sigma(\lambda H) = \lambda_1 H_1 + \lambda_2 H_2 + \dots + \lambda_n H_n$$

the increase of entropy, and

$$\Sigma(\lambda V) = \lambda_1 V_1 + \lambda_2 V_2 + \dots + \lambda_n V_n$$

the increase of volume, which occur at the phase-reaction

$$\lambda_1 F_1 + \lambda_2 F_2 + \dots + \lambda_n F_n = 0$$

The direction of the tangent to a turning-line E_R is, therefore, defined in each point by (9) consequently by the same conditions as a system of n components in $n + 1$ phases. It appears from (9) that this curve has a point of maximum or minimum-temperature when the phase-reaction proceed without change of volume [$\Sigma(\lambda V) = 0$]; it has a point of maximum-pressure, when $\Sigma(\lambda H) = 0$, consequently when no heat is taken up or given out with the phase-reaction.

Now we shall examine whether a singular point may occur on the turning-line; then ΔP and ΔT have to be of higher order. For this purpose it is necessary that we are able to give the value zero to ΔP and ΔT in (3) and (4) without all other increments $\Delta x_1, \Delta y_1, \dots$ becoming zero also.

Consequently we must be able to solve from:

$$\left. \begin{aligned} x_1 d(x)_1 + y_1 d(y)_1 + \dots &= -\Delta K \\ x_2 d(x)_2 + y_2 d(y)_2 + \dots &= -\Delta K \end{aligned} \right\} \quad (10)$$

etc. and from:

$$\left. \begin{aligned} d(x)_1 = d(x)_2 = \dots = d(x)_n &= \Delta K_x \\ d(y)_1 = d(y)_2 = \dots = d(y)_n &= \Delta K_y \end{aligned} \right\} \quad (11)$$

etc. and from (7) the ratios between the increments. In (10) and (11) the sign d indicates now that we have to differentiate with respect to all variables, except to P and T . We now have $n^2 + 1$ equations between $n^2 - 1$ ratios of the n^2 increments; consequently relations must exist between the coefficients. It follows again from (10) and (11) that x_1, y_1, \dots have to satisfy (2), which is also the case here. (7), however, must also be satisfied. When we compare (6) with (10), then we see in connection with (11) that we may put

$$\begin{aligned}\mu_2 &= ad(x)_1 = ad(x)_2 = \dots \\ \mu_3 &= ad(y)_1 = ad(y)_2 = \dots\end{aligned}$$

When we substitute those values in (7) then we find:

$$\lambda_1 d^2 Z_1 + \lambda_2 d^2 Z_2 + \dots = \sum \lambda d^2 Z = 0 \quad (12)$$

[Prof. W. VAN DER WOUDE has drawn my attention to the fact that we are able to express generally in a determinant the conditions in order that (7), (10), and (11) may be satisfied. We then obtain the same determinant as that one to which attention is drawn in the previous communication. We have, however, to add to this determinant still a series, which follows from (7). The conditions sought for are then, that all determinants which may be formed from this, are zero].

The turning-line E_R has, therefore, a singular point when (12) is satisfied, then it follows from (8):

$$-\sum (\lambda V) \cdot \Delta P + \sum (\lambda H) \cdot \Delta T + \frac{1}{3} \sum (\lambda d^3 Z) + \dots = 0$$

Consequently for $\frac{dP}{dT}$ the same values as in (9). ΔP and ΔT itself are values of the second order; when we express them in one of the others, e. g. in Δx_1 , then we may write

$$\begin{aligned}\Delta P &= a \Delta x_1^2 + b \Delta x_1^3 + \dots \\ \Delta T &= a_1 \Delta x_1^2 + b_1 \Delta x_1^3 + \dots\end{aligned}$$

It is apparent from (9) that $a : a_1$ must be $= \sum (\lambda H) : \sum (\lambda V)$. We now give to Δx_1 the two opposite values $+S$ and $-S$; in the one case we go along curve E_R starting from the singular point towards the one side, in the other case towards the other side of the curve. It follows for $\Delta x_1 = +S$ that:

$$\Delta P = aS^2 + bS^3 + \dots \quad \text{and} \quad \Delta T = a_1 S^2 + b_1 S^3 + \dots \quad (13)$$

for $\Delta x_1 = -S$ that:

$$\Delta P = aS^2 - bS^3 + \dots \quad \text{and} \quad \Delta T = a_1 S^2 - b_1 S^3 + \dots \quad (14)$$

Consequently ΔP and ΔT have the same sign in (13) and (14), curve E_R consists, therefore, in the vicinity of the singular point S of two branches Su and Sv with the common tangent Sw ; the

direction of this tangent is defined by $a : a_1$ or by (9). Consequently curve E_R has a form as uSv in figs. 1 or 2. In fig. 1 it forms a turning-point in S , in fig. 2 a cusp. It follows, however, from (13)

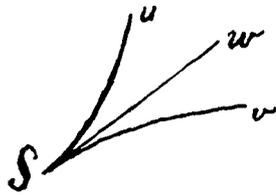


Fig. 1.

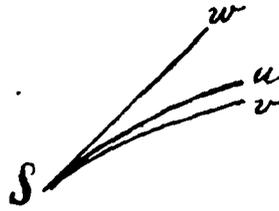


Fig. 2.

and (14) that $\Delta P : \Delta T$ is larger in the one case and smaller in the other case than $dP/dT = a : a_1$; consequently curve E_R has a turning-point as in fig. 1.

In our considerations on the region E in fig. 7 [XVI] we have already used this result; we have viz. drawn there the turning-line MSm in the point S with a turningpoint.

In the previous communication we have deduced for an equilibrium of n components in n phases under constant pressure:

When $\Sigma(\lambda H)$ and $\Sigma(\lambda d^2 Z)$ have the same sign, then T is maximum;

When $\Sigma(\lambda H)$ „ $\Sigma(\lambda d^2 Z)$ have opposite sign, then T is minimum;

When $\Sigma(\lambda d^2 Z) = 0$ then T is neither maximum nor minimum.

Similar properties are valid for equilibria of n components in n phases at constant temperature.

Let us assume now, for fixing the ideas, that $\Sigma(\lambda H)$ is positive on the turning-line MSm in fig. 7 [XVI]. Then it follows from the rules mentioned above, that $\Sigma(\lambda d^2 Z)$ must be positive in each point of the branch mS and negative in each point of branch MS . In accordance with (12), however, $\Sigma(\lambda d^2 Z) = 0$ in the point S . When we draw in the figure a horizontal or vertical line through the point S , then we see that this line does not trace the three-leaved-region; under the pressure P_S , therefore, the temperature is neither maximum nor minimum and at the temperature T_S the pressure is neither maximum nor minimum.

Equilibria of n components in n phases in the concentration-diagram.

Until now we have considered the equilibria E in the P, T -diagram; now we shall briefly discuss their representation in the concentration-diagram. The composition of a phase, which contains n components,

may be represented by $n-1$ variables; in order to represent it graphically, we want, therefore, a space with $n-1$ dimensions.

We now take an equilibrium $E = F_1 + \dots + F_n$ under the pressure P_0 ; we call this the equilibrium $E(P = P_0)$. Besides the $n(n-1)$ variables $x_1y_1 \dots x_2y_2 \dots$, etc. we then have also the $n+1$ variables $T, K, K_x \dots$, consequently in total n^2+1 variables. They are connected to one another by the n^2 equations (2) [XVII] and (3) [XVII]. We imagine now all variables to be eliminated, except those, which relate to a phase F_i [consequently except $x_iy_i \dots$]. Then we keep $n-2$ equations between the $n-1$ variables $x_iy_i \dots$. Consequently the phase F_i follows in the concentration-diagram on change of T an $(n-1)$ dimensional curve; we call this "curve $F_i(P = P_0)$ ". Of course the position of this curve depends on the assumed pressure P_0 and it changes with this pressure.

Consequently the pressure is P_0 in each point of this curve $F_i(P = P_0)$. T changes however from point to point; it is maximum or minimum when a phase-reaction can occur, consequently when the equilibrium E passes into an equilibrium E_R .

As the equilibrium $E(P = P_0)$ contains n phases, it is represented, therefore, by n curves $F_i(P = P_0)$ in a space with $n-1$ dimensions.

Now we take an equilibrium E at constant temperature T_0 ; we call this $E(T = T_0)$. A phase F_i of this equilibrium now follows on change of P a curve $F_i(T = T_0)$. Of course the position of this curve depends on the assumed temperature T_0 , and changes with this. Consequently the temperature is T_0 in each point of this curve; the pressure changes, however from point to point and is maximum or minimum when the equilibrium E passes into an equilibrium E_R .

Finally we still take an equilibrium of n components in n phases, between which a phase-reaction may occur, consequently the equilibrium E_R . Each phase F_i of this equilibrium follows a curve $F_i(R)$ in the concentration-diagram. The P and T change along this curve from point to point.

Consequently we have the following. Each of the equilibria $E(P = P_0)$, $E(T = T_0)$ and E_R is represented in the concentration-diagram by n curves F_i ; these are situated in a space with $n-1$ dimensions. When one or more phases have a constant composition, then the corresponding curves disappear of course. As we may change P_0 and T_0 , an infinite number of curves $F_i(P = P)$ and $F_i(T = T_0)$ exist therefore; one single curve $F_i(R)$ exists however.

We now take a point X on curve $F_i(R)$; through this point goes a curve $F_i(P = P_X)$ and $F_i(T = T_X)$, which touch one another in the point X . Curve $F_i(P = P_X)$ has viz. a maximum- or minimum

temperature in the point X ; the increments $\Delta x_i, \Delta y_i, \dots$ have, therefore, to satisfy (9) [XVII] and (10) [XVII]. This is, however, also true for the increments $\Delta x_i, \Delta y_i, \dots$ in the point X of curve $F_i(T = T_X)$, as this curve has a maximum- or minimum pressure in the point X .

In the same way the following appears yet also. When the curve $F_i(R)$ has a turning-point S , in the P, T -diagram, then in the concentration-diagram the three curves $F_i(R), F_i(P = P_0)$ and $F_i(T = T_0)$ touch one another in the point S .

Corresponding points on the $n-1$ other curves belong to each point X (or S) of a curve $F_i(R)$; consequently the properties deduced above are valid also for each of those curves.

We shall apply now those general considerations to the ternary equilibrium $E = B + L + G$, which we have discussed in communication XVI in connection with the figs. 6 and 7. As this equilibrium is a ternary one, it may be represented in a plane viz. in triangle ABC of fig. 6. As B is a phase of invariable composition, each of the equilibria is represented by two curves, viz.:

$$\begin{array}{llll} E(R) & \text{by the curve} & L(R) & \text{and } G(R), \\ E(P = P_0) & \text{,, ,, ,,} & L(P = P_0) & \text{and } G(P = P_0), \\ E(T = T_0) & \text{,, ,, ,,} & L(T = T_0) & \text{and } G(T = T_0). \end{array}$$

Curve $L(R)$ is indicated in fig. 6 by curve mSM (in fig. 7 this curve mSM has a turning-point in S); curve $G(R)$ is not drawn in fig. 6. Further in fig. 6 we find several curves $L(T = T_0)$; $abcd$ represents viz. a curve $L(T = T_a)$ (we have to bear in mind that $T_a = T_b = T_c = T_d$); $efgh$ represents a curve $L(T = T_e)$, iSk a curve $L(T = T_i)$ and ln a curve $L(T = T_l)$. The little arrows indicate the direction in which the pressure increases along these curves; this is a maximum on branch MS , a minimum on branch mS of the turning-line. The reader may imagine the curves $L(P = P_0), G(T = T_0)$ and $G(P = P_0)$ which have not been drawn to be also indicated in fig. 6.

Let us now imagine in fig. 6 to be drawn through a point x of curve mSM the curves $L(T = T_x)$ and $L(P = P_x)$; in accordance with our general considerations, those curves must, therefore, come in contact with one another in the point x . When we take the point b on mSM , then curve $L(T = T_b)$, which is represented by $abcd$ and the curve $L(P = P_b)$, which is not drawn, touch one another in b , therefore. In the point c curve $L(T = T_c) = abcd$

and the curve $L(P = P_c)$ which is not drawn, touch one another, etc. Consequently curve $a b c d$ touches two curves $L(P = P_a)$ viz. in b curve $L(P = P_b)$ and in c curve $L(P = P_c)$.

In the point S three curves touch one another viz. curve $L(R) = mSM$, curve $L(T = T_S) = iSk$, and the curve $L(P = P_S)$, which is not drawn.

Some special cases.

Before we have already drawn the attention to the fact, what changes have to be made in the conditions (2) and (3) [XVII], when one or more of the phases have a constant composition. When, however, all phases have a constant composition, then the considerations must be somewhat altered. Let us take a phases-complex

$$E = F_1 + \dots + F_n$$

in which all the phases have a constant composition. We now may distinguish two cases, according to the fact whether in this complex a phase-reaction may occur either never or always. In the latter case E passes into an equilibrium E_R and the phase-reaction is

$$\lambda_1 F_1 + \dots + \lambda_2 F_2 + \dots + \lambda_n F_n = 0$$

in which $\lambda_1 \dots$ are independent of P and T .

The condition for equilibrium becomes now:

$$\lambda_1 Z_1 + \lambda_2 Z_2 + \dots + \lambda_n Z_n = 0.$$

As $Z_1 \dots$ depend only upon P and T , the equilibrium is represented therefore, in the P, T -diagram by a curve. The direction of this curve is defined by (9).

We may also imagine the case that phases occur with limited changeable composition viz. phases in which one or more components have a constant composition and the other components a variable composition. This is e.g. the case when two hydrates $A \cdot nH_2O$ and $B \cdot nH_2O$ form mixed-crystals; then they have the composition $PA \cdot (1-P)B \cdot nH_2O$, in which P may change from 0 to 1. We may also represent the composition of this mixed-crystal by: $aH_2O + yA + (1-a-y)B$, in which $a = n : (n + 1)$ and $y = P : (n + 1)$.

When F_1 represents a similar phase, in which x_1 and y_1 are constant, $z_1, u_1 \dots$ variable, then we have to omit in (3) [XVII] $\frac{\partial z_1}{\partial x_1}$

and $\frac{\partial z_1}{\partial y_1}$, and we must replace them in the first equation (2) [XVII]

by the corresponding quantities of another phase F_r .

We have assumed in our previous considerations that at least one of the variable phases contains all components, we may imagine also, however, that this is not the case. Let us take e.g. the ternary system: $A + \text{water} + \text{alcohol}$, in which A is a salt, which is not volatile and which forms a hydrate $A \cdot n H_2O$. The equilibrium $E = A + A \cdot n H_2O + G$ is then ternary, but the variable phase, viz. the gas G , contains only the two components water and alcohol.

For the contemplation of similar equilibria it is in general easier when we do not use the general formulas (2) [XVII] and (3) [(XVII)] but the conditions of equilibrium, which are true for the special case. In the communication "Equilibria in ternary systems" XVII I have treated a similar case. I shall refer to this in a following communication.

(To be continued)

Leiden, Inorg. Chem. Lab.

Physiology. — “*Experimental researches on the permeability of the kidneys to glucose.*” By Prof. H. J. HAMBURGER and R. BRINKMAN.

(Communicated in the meeting of Sept. 29, 1917).

III. THE NaHCO_3 PERCENTAGE IN THE TRANSMISSION-FLUID ¹⁾.

In a former paper ²⁾ on this subject we discussed the reason which induced us to enter upon a systematical investigation of the effect which the composition of the RINGER-fluid had upon the retention-power of the frog's kidney with respect to glucose. This investigation

T A B L E I.

Effect of the Ca-concentration in the RINGER-fluid on the retention of glucose.

% NaCl	% NaHCO_3	% KCl	% CaCl_2 6 aq.	Reduction of transmission-fluid.	Reduction of urine		Retention of glucose.
					Left	Right	
0.6	0.020	0.010	0.000	0.098	0.095	0.096	0
0.6	0.020	0.010	0.001	0.10	0.095	0.094	0
0.6	0.020	0.010	0.002	0.090	0.092	0.088	0
0.6	0.020	0.010	0.004	0.090	0.090	0.090	0
0.6	0.020	0.010	0.006	0.098	0.10	0.096	0
In like manner rising with 0.002 % CaCl_2 6 aq. to 0.012 % no retention of sugar.							
0.6	0.020	0.010	0.012	0.098	0.080	0.082	0.017
0.6	0.020	0.010	0.014	0.098	0.076	0.075	0.022
0.6	0.020	0.010	0.015	0.09	0.060	0.061	0.030
0.6	0.020	0.010	0.016	0.096	0.066	0.068	0.030
0.6	0.020	0.010	0.018	0.102	0.102	0.096	0
0.6	0.020	0.010	0.020	0.098	0.10	0.10	0

¹⁾ A more detailed account will be given in the *Biochemische Zeitschrift*.

²⁾ HAMBURGER and BRINKMAN: *Verslagen van de Koninklijke Akademie v. Wetenschappen van Jan 27, 1917, p. 944.*

³⁾ Obviously the results relate to the glomerulusproduct. Cf the above-mentioned paper p. 946,

brought to light that, apart from other factors, the permeability of the glomerulus membrane is, to a high degree, dependent on the CaCl_2 percentage of the transmission-fluid and further that this permeability is also affected by the KCl and NaCl concentrations.

We subjoin a series of experiments which demonstrates the effect of *calcium* and which was not published in our first paper. (See Table I, preceding page).

This series of experiments was carried out in February—March 1917.¹⁾

Evidently -glucose-retention took place only when the CaCl_2 -concentration varied between 0.012% and 0.016%, that is to say the Ca -concentration has its strict limits, and admits of but little variation. Of the $\pm 0.1\%$ of glucose in the transmission fluid at most 0.03% of glucose was retained.

To determine the effect of *Potassium* in the transmission-fluid the KCl concentration was modified while the NaCl , NaHCO_3 and CaCl_2 remained the same. Increasing quantities of KCl were therefore added to the fluid composed of NaCl 0.6%, NaHCO_3 0.02%, CaCl_2 .6 aq.

TABLE II.

Effect of the KCl concentration in the RINGER fluid. Experiments of March 1917.

% NaCl	% NaHCO_3	% KCl	% CaCl_2 6 aq.	Reduction of transmission fluid.	Reduction urine		glucose retention
					Left	Right	
0.6	0.020	0.000	0.015	0.095	0.070	0.072	0.025 %
0.6	0.020	0.000	0.015	0.090	0.068	0.069	0.021
0.6	0.020	0.002	0.015	0.095	0.070	0.070	0.025
0.6	0.020	0.004	0.015	0.115	0.092	0.088	0.025
0.6	0.020	0.006	0.015	0.10	0.098	0.10	0
0.6	0.020	0.006	0.015	0.085	0.080	0.084	0
0.6	0.020	0.008	0.015	0.10	0.070	0.070	0.03
0.6	0.020	0.010	0.015	0.098	0.070	0.070	0.03
0.6	0.020	0.014	0.015	0.10	0.065	0.070	0.03
0.6	0.020	0.016	0.015	0.10	0.070	0.075	0.028
0.6	0.020	0.018	0.015	0.092	0.094	0.092	0
0.6	0.020	0.020	0.015	0.080	0.070		0.010
0.6	0.020	0.022	0.015	0.098	0.095	0.098	0

¹⁾ It is desirable to know whether summer- or winter frogs are used for the experiments. Cf. Verslagen van Jan. 27, 1917 p. 949.

0.15% and glucose 0.1%. Some of the results are given in Table II.

It becomes evident that if from the RINGER-fluid *containing the right* $\text{CaCl}_2 \cdot 6 \text{ aq. concentration}$ viz. 0.015% (see Table I) all the potassium is omitted, glucose is still retained viz. $\pm 0.02\%$; if the KCl is increased to 0.005—0.006%, all the glucose passes through; at a further increase to KCl 0.008—0.017% the maximum amount of glucose is retained (0.03%); at higher KCl concentrations the retention decreases again.

Hence we see that the potassium is not absolutely necessary¹⁾; the chief function of the K in the transmission-fluid is probably to balance an excess of Ca.

It appeared from our last paper that the NaCl concentration also affects the results.

The composition of the transmission-fluid thus found could, however, be hardly looked upon as the optimum one *since from a transmission-fluid with 0.1% of glucose at most only 0.03% was retained*. And this value decreased even when the glucose-concentration in the transmission-fluid was lowered. The reason why also experiments with glucose-concentrations below 0.1% were made was due to the fact that the normal glucose-concentration of frog's blood varies between 0.03 and 0.06%. If we used a glucose-concentration of 0.03—0.04% not 0.03% was retained but at most 0.015%. The glucose retention was, consequently, dependent on the glucose-concentration of the transmission-fluid; a decrease in the glucose-concentration causes a corresponding decrease in the retention. In spite of a great number of experiments, we did not succeed in obtaining a glomerulus-filtrate which contained no glucose. But even if the transmission-fluid contained 0.1% of glucose and moreover the abovementioned favourable Ca- and K-concentrations were used, it not unfrequently occurred, more especially in summer when the frog's have less vitality, that little or no glucose was retained. Probably the most effective composition of the Ringer-fluid had, therefore, not been arrived at.

Increase of the usual NaHCO_3 -concentration.

We, therefore, attempted to improve upon our transmission-fluid.

¹⁾ The fact that it is necessary in the transmission-fluid for the heart need not surprise us, because the heart uses potassium in its muscular labour; things are different for the kidney, which is mainly a passive though complicated and sensitive living filter. Besides, the same arterial blood must supply all organs and provide every one with what it needs. Thus it may be understood that the most effective artificial transmission fluid need not have the same composition for every separate organ.

The effect of CaCl_2 , KCl and NaCl had already been determined; *it only remained to examine the effect of the NaHCO_3 concentration.*

Since RINGER it has been generally assumed that in artificial transmission fluids NaHCO_3 is indispensable. The present researches have likewise shown that it cannot be dispensed with in the transmission-fluid. One of the functions of NaHCO_3 consists as we know in maintaining a very slight actual alkalinity of the body-fluids which would otherwise, owing to the continual formation of acids, pass into an acid reaction. Like serum protein it acts as a buffer; hence we also speak of a tampon or moderator. Besides a specific HCO_3^- -action may have to be assumed (E. LAQUEUR).

It appears already theoretically that a concentration of NaHCO_3 , 0.01 % is too low to act as a sufficient buffer. We shall revert to this later on, in connection with other more theoretical considerations.

RINGER himself added 5 cc. of a 1 % NaHCO_3 -sol. to 100 cc. of fluid. TYRODE even used 0.1 % of NaHCO_3 . But 0.02 % of NaHCO_3 is the rule in RINGER's fluid. ¹⁾ That the usual concentration of 0.02 % of NaHCO_3 is too slight for frogs' kidneys could be determined experimentally in the following manner.

If namely to a transmission-fluid composed: NaCl 0.6 %, NaHCO_3 0.02 %, CaCl_2 6 aq 0.015 % some neutral red ²⁾ is added, the colour of the indicator is orange yellow (slightly alkaline), which corresponds with $[\text{H}^+] = 1.10^{-8}$. It is necessary to use boiled out aq. dest. and to prevent the absorption of CO_2 . Now we need only shake this fluid for a moment with air or lead it through an india rubber tube and the colour turns to pink, which points to an acid reaction of $[\text{H}^+] > 1.10^{-7}$. If, however, one is careful in preparing this fluid then one succeeds in keeping it slightly alkaline. Now if this fluid is transmitted through the kidney, the latter becomes evidently acid, which is manifested by the red colour it assumes and also the metabolism products which have passed into the urine, colour the indicator red after some time. We have made the oxygenation in the experiment as intense as we could to eliminate metabolism products of greater acidity as much as possible, without succeeding, however, in keeping the reaction of the urine neutral.

What is the reaction of the normal urine of the frog?

It is not difficult to obtain it by squeezing out the bladder of

¹⁾ Cf. e.g. BAYLISS: Principles of General Physiology, 1916, p 211.

ZWAARDEMAKER and his collaborators also use this concentration of 0.02 %.

(See e.g. Proceedings 1916, April 28, May 27, Sept. 30).

²⁾ The reader will be aware that the colour of this vital indicator is at $[\text{H}^+] = 1.10^{-7}$ pink, at $[\text{H}^+] = 1.10^{-8}$ orange yellow and at $[\text{H}^+] = 1.10^{-9}$ yellow.

the animal. It appears then that the liquid is slightly alkaline.

The same can be demonstrated in the following way. If 1 cc of a saturated watery neutralred solution is injected into the back lymph sac, an investigation, half an hour after, brings to light the following facts: skin, muscles, brain and spinal cord are pink, intestine yellow and pink, depending on place and degree of peristalsis, but the urine is yellow, and is, therefore, though only slightly, alkaline. When we followed the practice hitherto adopted and transmitted a RINGER fluid containing 0.02% of NaHCO_3 , the quantity generally used for the heart, then the urine after some time became permanently pink, that is to say, acid. *Hence we see that the protective value of NaHCO_3 , 0.02% is not great enough.*

At the same time it appeared that the acidity of the urine and the diminution or loss of the kidney's retention-power to glucose went hand in hand. As an example we add the following experiment.

Transmission from the aorta with a sol. of NaCl 0.6%, NaHCO_3 0.02%, KCl 0.01%, $\text{CaCl}_2 \cdot 6 \text{ aq.}$ 0.016%, and glucose 0.098%, saturated with O_2 ; no india rubber tube was used; the colour of the solution is orange owing to neutralred. The first urine is yellow and has a reduction of 0.06%; the latter red, its reduction being 0.090%, in other words: *now that the urine has become acid, the kidney is found to have lost the power of retaining glucose.*

The obvious course was now to increase gradually the NaHCO_3 -conc. of the transmission-fluid. It was raised to 0.090%. Now we had therefore a transmission-fluid of the following composition: NaCl 0.6%, NaHCO_3 0.90%, KCl 0.010%, glucose $\pm 0.1\%$ and had to discover the suitable $\text{CaCl}_2 \cdot 6 \text{ aq.}$ concentration, Table III contains the results of these experiments.

In the first place it is observed that a much greater quantity of glucose is retained than before. It amounts to no less than 0.079%. But this requires a concentration of $\text{CaCl}_2 \cdot 6 \text{ aq.}$ of 0.024–0.030%.

Below this concentration and above it little is retained. The $\text{CaCl}_2 \cdot 6 \text{ aq.}$ conc. necessary for a maximum glucose retention has, therefore, risen from 0.015% (Cf. tables I and II) to 0.024%–0.030%. This need not surprise us for the concentration of ions of Ca is repressed by NaHCO_3 , and the ions of Ca are an important factor. It may, therefore, be said that *an increased NaHCO_3 conc. in a transmission-fluid with $\pm 0.10\%$ of glucose raises the maximum retention from 0.03% to an average of 0.06%.*

Further increase of the NaHCO_3 concentration.

We did not stop short, however, at this increase of the NaHCO_3 .

concentration. We have namely made the titration-alkalinity of our transmission fluid equal to that of frog's serum.

TABLE III.

Effect of an increased NaHCO₃-concentration.

Transmission from the aorta of NaCl 0,6 ‰, NaHCO₃ 0,090 ‰, KCl 0,010 ‰ and CaCl₂ · 6 aq. 0,020 ‰—0,050 ‰; colour of transmission-fluid orange-yellow caused by neutral red.

(Experiments of June—July 1917).

CaCl ₂ · 6 aq.	Reduction transmission fluid.	Reduction urine.	Retention glucose	Colour urine ¹⁾
0.020	0.100	0.098	0.020 ‰	colourless
0.020	0.105	0.080	0.025	colourless
0.022	0.105	0.080	0.025	colourless
0.024	0.115	0.062	0.053	light-yellow
0.025	0.100	0.040	0.060	light-yellow
0.025	0.10	0.041	0.059	yellow
0.026	0.115	0.058	0.057	yellow
0.028	0.115	0.064	0.051	greenish yellow
0.028	0.111	0.052	0.059	yellow
0.030	0.105	0.042	0.063	light yellow
0.030	0.105	0.026	0.079	light yellow
0.030	0.105	0.031	0.074	light yellow
0.031	0.115	0.102	0.013	colourless
0.032	0.115	0.10	0.005	very light yellow
0.032	0.115	0.091	0.024	colourless
0.035	0.10	0.089	0.011	colourless
0.040	0.102	0.090	0.022	first light yellow afterwards colourless
0.045	0.098	0.075	0.023	colourless
0.050	0.098	0.080	0.018	colourless

For this purpose frog's serum was titrated with $\frac{1}{25}$ normal tartaric acid with neutralred paper as an indicator, according to the method of SNAPPER ²⁾. 1 cc. of defibrinated only slightly haemolytic

¹⁾ For the meaning of this column see p. 677.

²⁾ J. SNAPPER: Biochemische Zeitschrift 51, (1913), 88.

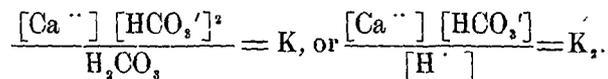
frog's serum required 0.85 cc. of $\frac{1}{25}$ normal tartaric acid. The titration alkalinity of frog's serum is, therefore equal to that of a 0.034-normal or a 0.285 % NaHCO_3 -sol. We have, therefore, given a NaHCO_3 conc. of 0.285 % to our transmission-fluid; to prevent a resulting increase of osmotic pressure the NaCl conc. was lowered to 0.5 %. Now again it was obvious that the suitable CaCl_2 6 aq. conc. would have to be raised again, as the conc. of the free ions of Ca would again be repressed.

The result will be found in Table IV.

The maximum quantity of glucose begins to be retained at CaCl_2 6 aq. 0.030 %; so this concentration is still somewhat higher than if NaHCO_3 0.9 % is used (then the conc. of CaCl_2 6 aq. was, as appears from Table III 0.024 %).

Table III shows that if the CaCl_2 6 aq. rose to above 0.030 %, the retention of glucose began to decrease. In Table IV, however, when a higher conc. of NaHCO_3 was used, this was not the case; even if the CaCl_2 6 aq. conc. rises to 0.080 %, the glucose-retention remains pretty well invariably high viz. an average of 0.07 %. One will be inclined to assume that this is due to the fact that in the latter case the most favourable conc. of ions of Ca is brought about automatically.

Indeed when through the RINGER fluid containing 0.285 % of NaHCO_3 and 0.080 % of CaCl_2 6 aq., oxygen is led for some time, a precipitate is formed of CaCO_3 ¹⁾. The following physico-chemical exposition will make matters clearer.



The latter formula teaches that the concentration of the free ions of Ca is only dependent on the conc. of the ions of H and those of HCO_3 , or also that the amount of Ca salt makes no difference, when $[\text{H}']$ and $[\text{HCO}_3']$ are present in a certain suitable proportion. Hence we see that there must be a buffer-system for ions of Ca in this fluid.

To sum up: in order to maintain a proper concentration of ions of Ca it appears that not only the conc. of ions of HCO_3 , but also that of ions of H' is of importance. A satisfactory regulation of the conc. of ions of H is not so easy to arrive at in our circumstances, where, if the kidney is to function well, the fluid must be saturated

¹⁾ We have invariably observed at the ultrafiltration of bloodserum that the clear filtrate becomes troubled when shaken with air, owing to the formation of CaCO_3 , which was kept in solution by CO_2 .

with O_2 ; this regulation will have to be further investigated.
An experimental confirmation of our view was obtained by deter-

TABLE IV.

Effect of a still greater increase of the $NaHCO_3$ -Concentration.

Transmission of $NaCl$ 0.5 ‰, KCl 0.010 ‰, $NaHCO_3$ 0.285 ‰,
 $CaCl_2 \cdot 6 aq.$ 0.028–0.080 ‰, glucose \pm 0.1 ‰.

All solutions have been made again in boiled out water and saturated
with oxygen.

(Experiments of July 1917.)

$\%CaCl_2 \cdot 6 aq.$	Reduction transmission fluid.	Reduction urine.	Difference (Retention of glucose).
0.028	0.145	0.130	0.015
0.028	0.091	0.076	0.015
0.030	0.091	0.038	0.055
0.030	0.092	0.027	0.065
0.032	0.088	0.066	0.022
0.032	0.091	0.056	0.035
0.034	0.098	0.042	0.056
0.034	0.091	0.040	0.051
0.036	0.098	0.052	0.046
0.036	0.125	0.040	0.085
0.036	0.125	0.035	0.090
0.040	0.106	0.031	0.075
0.042	0.105	0.029	0.076
0.044	0.105	0.045	0.060
0.048	0.105	0.035	0.070
0.050	0.105	0.031	0.074
0.052	0.105	0.063	0.052
0.056	0.105	0.050	0.055
0.060	0.115	0.062	0.053
0.064	0.115	0.058	0.057
0.080	0.115	0.041	0.074

minations of the electric conductivity of the system $NaHCO_3$ and
 $CaCl_2$. This will be discussed in a subsequent paper.

But the state of things in the RINGER fluid is still more complicated than in the system CaCl_2 and NaHCO_3 , especially because the fluid contains a rather considerable quantity of NaCl . This renders the determination of the conc. of free ions of Ca rather difficult.

It seems that the equilibrium of the system CaCl_2 , NaHCO_3 and NaCl , so important to life, has hitherto not been studied. We intend to revert to this subject later on. *At any rate we have now obtained a transmission fluid of which, of the 0.1 % of glucose, on an average 0.07 % is retained, and in which automatically that conc. of ions of Ca^{++} sets in which causes ± 0.07 % of the 0.1 % of glucose to be retained.*

It is this transmission-fluid which has enabled us to obtain a *urine free from sugar*, which had hitherto been found impossible. According to BANG¹⁾ frogs' blood gives a reduction which corresponds to 0.03—0.05 % of glucose. We accordingly found in September a reduction value of 0.04—0.06 %. Now the question was: will the kidney be able to keep back all the sugar from a RINGER-fluid of the above composition and containing 0.05 % of glucose. The unanimous result of our experiments proved that this was indeed the case,

All glucose was likewise retained, even when the RINGER-fluid contained 0.06 % of glucose.

Now it will be of importance to determine to what pitch hyperglycaemia can be raised before glycosuria sets in, in other words *how much sugar the kidney can bear*. This question will be treated in a subsequent paper.

CONCLUSIONS.

The fact that by modifying the composition of the RINGER-fluid the colloid state of the glomerulus-epithelium can be regulated in such a manner that it either admits or does not admit sugar, seems to us of great importance, for now it has become superfluous to assume as an explanation of physiological glucose-retention, that substances are found in the serum which keep back the glucose in colloid compounds and that the glucose cannot pass through the glomerulus-membrane in that form. That this supposition is no longer necessary will afford satisfaction, after MICHAELIS and RONA and also ABEL by dialysis-experiments and we by ultra-filtration have found that parchmentpaper and ultra-filters of celloidin allow all glucose in the

¹⁾ J BANG, *Der Blutzucker* 1913. J. F. BERGMANN, Wiesbaden.

serum to pass, which as we observed before¹⁾ is not a strict proof that sugar cannot be present in a composition with a serum-compound which can pass through these two membranes, but not through the glomerulus-epithelium. Now, however, it has been demonstrated that the glomerulus epithelium can keep back the glucose as such.

We have evidently to deal here with *a new form of permeability*: cells, here the glomerulus-epithelium, allow salts to pass, but not the likewise crystalloid sugar, which under the circumstances is highly useful; for thus a substance necessary for our nutrition is kept in circulation. As far as we can see we find ourselves confronted here by a phenomenon not observed before. The intestinal epithelium and likewise the pleura and the peritoneum are permeable to salts as well as to glucose, the red blood-corpuscles of most animals are *impermeable* to salts and to sugar both²⁾.

Finally we wish to point out another fact. An examination of table III makes it evident that although the transmission-fluid contained neutral red, mostly a colourless urine was obtained in these cases, therefore, the neutral red had been kept back by the glomerulus-epithelium. That the urine was free from neutral red appeared from the fact that neither the addition of acid nor that of alkali to the urine caused colouring.

Hence we may assume that *if the NaHCO₃ concentration is high enough*, the glomerulus-membrane is impermeable to the colloid neutral red. If the NaHCO₃ conc. amounts to only 0.02 %, then the glomerulus-filtrate becomes red, because the RINGER-fluid, on being transmitted, grows too acid. That this is really only a glomerulus-product appears when for instance the porta renalis is ligatured, for then the urine-secretion through the tubulus epithelium is prevented (cf. our first publication³⁾). According to table III, however, the urine in some of these experiments was yellow, but this colouring originated from neutral red, which is excreted by the tubulus epithelium; this is confirmed by the experiments of HÖBER and KONIGSBERG, to which we shall have to refer again presently.

Our experiments also throw a light on the contradiction between the results of the experiments of GERZOWITSCH⁴⁾ and those of HÖBER⁵⁾.

¹⁾ Cf. our first paper in Verslagen Jan. 1917.

²⁾ Only some blood corpuscles viz. those of man, of the monkey and of the dog seem, to a certain extent, permeable to sugar

³⁾ Meeting of January 27, 1917.

⁴⁾ GERZOWITSCH: Zeitschr. f. Biologie, **66**, 391, (1916).

⁵⁾ HÖBER und KÖNIGSBERG: Pflügers Archiv **108**, 324. (1905).

GERZOWITSCH namely dissolved neutral red in ordinary RINGER fluid, the composition of which is not stated, and obtained at *arterial* transmission a "coloured" glomerulus filtrate; he does not say whether the colour was red or yellow orange. HÖBER on the other hand injected neutral red into the back lymph sac, and on examining the capsule microscopically he saw a "colourless" glomerulus filtrate.

Probably the contradiction may be thus explained: GERZOWITSCH uses "eine für den Frosch physiologische RINGER-lösung". This must have been one, containing 0.02% NaHCO_3 (see above p. 672) and this gives an acid i.e. a pink urine. HÖBER and KONIGSBERG, however, worked under physiological conditions, for normal blood flowed through the frogs; only some vital colouring-matter had been introduced into the back lymph sac. The glomerulus filtrate was, just as with us, colourless, but in its passage through the ducts it took up neutral red, which was secreted by the epithelium of the tubuli. This would be in conformance with the yellow colour of the urine, which we obtained when under practically physiological conditions a suitable RINGER-fluid was used.

S U M M A R Y.

1. If, the usual RINGER-solution containing 0.02% NaHCO_3 , passes through the kidney, then it is found that of the 0.1% glucose at most 0.03% is retained (table II) in however favourable a manner we may vary the Ca and K percentage.

A considerable increase of the glucose retention may be attained if the NaHCO_3 conc. of the transmission fluid is raised from 0.02% to 0.090%.

2. *Experiments with neutralred teach that the cause of this phenomenon is connected with the reaction of the transmission-fluid.*

If the alkalinity of the latter (i. e. its protective value) is so slight that on being transmitted it is easily acidified, then the urine formed gives an acid reaction (neutralred becomes pink) and little or no glucose is retained.

If, however, the NaHCO_3 conc. is raised to 0.090% then the artificial urine remains alkaline (neutral red remains yellow) and of the $\pm 0.1\%$ of glucose about 0.06% is retained.

In order to obtain this favourable result, however, the Ca-concentration, the most effective conc. of which amounted hitherto to CaCl_2 , 6 aq. 0.015% (see table I) must be raised to 0.024—0.030% (table III), but not higher. That the CaCl_2 conc. should have to be raised if the NaHCO_3 conc. is increased need not surprise us, since an increase of the NaHCO_3 conc. impedes the dissociation of the CaCl_2 , and a sufficient concentration of ions of Ca in the transmission fluid is of great importance.

3. *The kidney can retain even more than 0.06% of glucose if*

the NaHCO_3 conc. is raised to 0.285 % i.e. the conc. which corresponds to the titration-alkalinity of frogs' serum. But then again more CaCl_2 must be added, at least 0.030% (table IV).

4. It is remarkable that otherwise than in the experiments in which NaHCO_3 0.09 % was used (table III), now that the conc. is 0.285 %, an addition of more CaCl_2 , 6 aq than 0.030 %, even of much more, does not impair the retention (table IV). There are reasons to assume that the most favourable conc. of ions of Ca brings itself about automatically, when more CaCl_2 is added. The RINGER-sol. in the latter case, when of ± 0.1 % of glucose upon an average 0.07% was retained, was composed as follows: NaCl 0.5 %, NaHCO_3 0.285 %, KCl 0.01 %, CaCl_2 6 aq. 0.040 %.

5. If the transmission-fluid contained 0.05 % of glucose, the average concentration found in frogs' blood, then a sugarless urine was obtained. This was even the case when the RINGER-sol. contained 0.06 % of glucose.

6. This result seems important to us from a physiological-clinical and from a general biological point of view; from a physiological-clinical point of view, because the retention of sugar by the kidney has now been reduced to a question of permeability, so that the supposition that glucose is bound by one of the serum substances (sucre virtuel of LÉPINE) has become altogether unnecessary. Evidently the chemical composition of the transmission-fluid determines the state of the glomerulus epithelium, and consequently the permeability of the membrane to sugar. The results are important from a general biological point of view, because we have to deal here with a new form of permeability, one in which cells under physiological conditions, though easily permeable to salts, are impermeable to the likewise crystalloid glucose, a form of permeability hitherto unknown and very useful under the circumstances.

Groningen, September 1917.

Physiological Laboratory.

filled with a gas which is in molecular-statistical equilibrium. Its molecules collide both with m_1 and m_2 .

Considering a corresponding canonical ensemble, the expression

$$\text{const. } e^{-\frac{2\Phi(x_1, x_2) + m_1 u_1^2 + m_2 u_2^2}{2kT}} dx_1 dx_2 du_1 du_2 \dots \dots \dots (2)$$

(where x_1, x_2, u_1 and u_2 are the coordinates and velocities of the two particles, and $\Phi(x_1, x_2)$ is the potential energy of the force holding them together) gives the number of individuals of the ensemble for which x_1, x_2, u_1 and u_2 have their values between specified infinitely close limits. For given values of x_1, x_2 and especially also of u_1 (2) gives the same number of individuals in the ensemble for equal and opposite values of u_2 , i.e.: *equal and opposite values of u_2 are still equally probable, u_2 is "independent" of u_1 .* On the other hand the Brownian movement will in the course of time cause great displacements along the X -axis. At the same time the points will remain close together in virtue of the inequality (1). This is the paradox mentioned at the end of § 1.

§ 3. Let us first leave aside the molecular-statistic side of the problem and put the following *purely kinematical* question. During a long time Θ the two points m_1 and m_2 , may be conducted along the x -axis in an arbitrary way, only restricted to the conditions that

- a. the inequality (1) shall remain valid;
- b. the distance between the final and original positions of the pair of points may be great compared with D . This implies that m_2 „accompanies” m_1 . Now we ask: does this imply that always the mean with respect to the time

$$\overline{u_1 u_2} = \frac{1}{\Theta} \int_0^\Theta dt u_1 u_2 > 0 \dots \dots \dots (3)$$

will be positive, or is it possible that the integral can be zero or eventually even negative?

The sign of the integral (3) indicates in a natural way in how far the two points move more in the same or in opposite directions. But we can point out that for the above described motion of the pair of points m_1, m_2 the inequality (3) need not be fulfilled. This will become evident by an example of a case for which the integral becomes negative. In fig. 1 the two zigzag lines represent a possible x, t -diagram of the two points m_1, m_2 . We see that the conditions

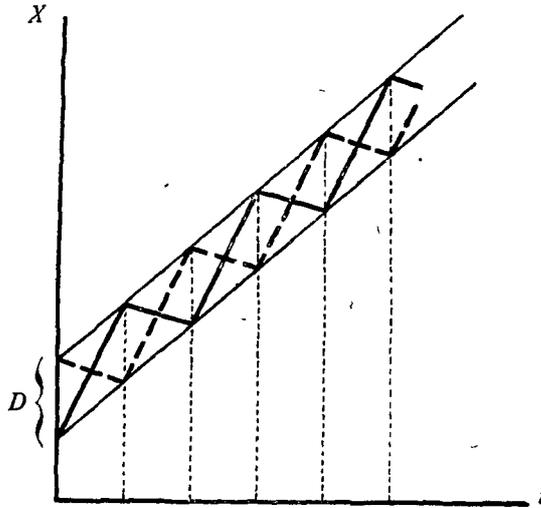


Fig. 1.

a and b are fulfilled and that still u_1 and u_2 have continually opposite signs, so that the integral (3) becomes *negative*.

§ 4. Now we have:

$$4 \overline{u_1 u_2} = \overline{(u_1 + u_2)^2} - \overline{(u_1 - u_2)^2}. \dots \dots (4)$$

The sign of $\overline{u_1 u_2}$ is determined by which term is the greater of the two.

When the motions of the pair of points obey the equipartition theorem, $\overline{u_1 u_2}$ is just equal to zero. (See the appendix).

From the above it is evident that a motion of the pair of points is possible, in which they remain close together and at the same time travel through great distances, while still at every moment the velocity u_2 is "independent" of u_1 . The paradox mentioned in §§ 1 and 2 proves thus to be apparent only. *Therefore there is no objection against EINSTEIN'S assumption that a suspended sphere during its BROWNIAN movement imparts its motion to the surrounding fluid in the same way as in the case of a systematic motion under the influence of a constant force.*

§ 5. In the *positive* proof however that EINSTEIN'S assumption follows from the fundamentals of statistical mechanics we meet with the following difficulty: Let us demand, (to stick to our example), that the inequality $u_{10} < u_1 < u_{10} + \epsilon$ exists

1st at the instant t_0 ;

2nd also during the interval from $t_0 - r$ till t_0 ; and let us ask what can be said of the occurrence of different values of u_2 . In

the first case we have to take from the canonical ensemble an easily defined sub-ensemble M_1 , in which u_2 has equally often equal and opposite values (and therefore is "independent" with respect to u_1). For the second demand a more closely limited sub-ensemble $M_{1,2}$ has to be selected from the mentioned ensemble M_1 . It is however hardly possible to determine $M_{1,2}$. Still this should be done in order to decide whether the distribution of the values of u_2 in it does or does not agree with EINSTEIN'S assumption.

APPENDIX.

Let

$$\begin{aligned} \frac{m_1 x_1 + m_2 x_2}{M} &= q_1, & \frac{m_1 x_1 - m_2 x_2}{M} &= q_2, & m_1 + m_2 &= M, \\ \frac{dx_1}{dt} &= u_1, & \frac{dx_2}{dt} &= u_2, \\ u_1 &= \frac{M}{2m_1} (\dot{q}_1 + \dot{q}_2), & u_2 &= \frac{M}{2m_2} (\dot{q}_1 - \dot{q}_2). \end{aligned} \quad (\alpha)$$

Then:

$$\frac{1}{2} (m_1 u_1^2 + m_2 u_2^2) = \frac{M^2}{8m_1 m_2} \{ \dot{q}_1^2 M + \dot{q}_2^2 M + 2 \dot{q}_1 \dot{q}_2 (m_2 - m_1) \}.$$

Let p_1, p_2 be the momentum corresponding to the coordinates q_1, q_2 , then we have

$$\dot{q}_1 p_1 = \frac{M^2}{4m_1 m_2} \{ M \dot{q}_1^2 + (m_2 - m_1) \dot{q}_1 \dot{q}_2 \}, \quad (\beta)$$

$$\dot{q}_2 p_2 = \frac{M^2}{4m_1 m_2} \{ M \dot{q}_2^2 + (m_2 - m_1) \dot{q}_1 \dot{q}_2 \}, \quad (\gamma)$$

and because of the equipartition theorem the mean values with respect to time of (β) and (γ) are both equal to kT , so that their difference

$$\frac{M^3}{4m_1 m_2} \overline{\{ \dot{q}_1^2 - \dot{q}_2^2 \}} = 0 \quad (\delta)$$

On the other hand (α) gives:

$$\overline{u_1 u_2} = \frac{M^2}{4m_1 m_2} \overline{(\dot{q}_1^2 - \dot{q}_2^2)} \quad (\epsilon)$$

From (δ) and (ϵ) combined we find: $\overline{u_1 u_2} = 0$ (q.e.d.).

Physics. — “A new Electrometer, specially arranged for radio-active Investigations”. Part II. By Miss H. J. FOLMER. (Communicated by Prof. H. HAGA).

(Communicated in the meeting of September 29, 1917.)

In Part I, communicated by Prof. H. HAGA in the meeting of May 30, 1914, the following brief description was given of the electrometer which is represented in figure 1 and reproduced here once more:

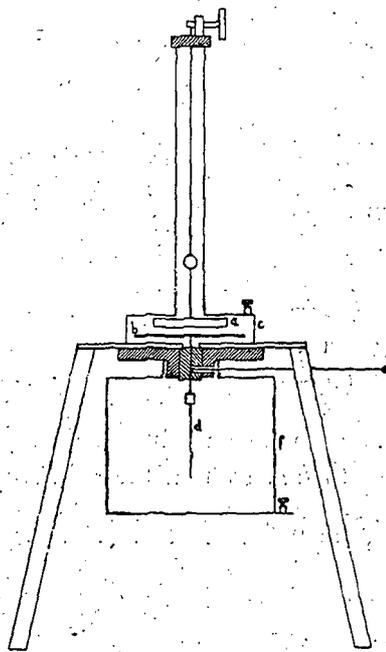


Fig. 1.

The apparatus consists of two separate spaces, viz: the measuring space *c*; a brass cylinder of small height, and the ionisation space proper *f*; a brass cylinder of volume 1 litre; the two cylinders are insulated from each other by ebonite.

In the measuring space *c* is the metal needle *b*, supported in the middle by a second needle *d*, insulated by amber; *b + d* together form the conductor, which is charged by the ionisation current.

In *c* is also found the very thin aluminium strip *a*, which a few mm. above *b* is fastened to a thin metal rod with mirror, suspended on a Wollaston wire,

which is fastened to a torsion head insulated by means of ebonite. Through a perforation in the amber and in the ebonite a rod *l* can be brought in contact with the needle *d*.

In this way, *a*, *b + d*, *c* and *f* can therefore be separately brought in a conductive connection with a storage battery or with the earth; *c* rests on a brass bottom plate to which legs are fastened which

Miss H. J. FOLMER. "A new Electrometer, specially arranged for radio-active Investigations." (II).

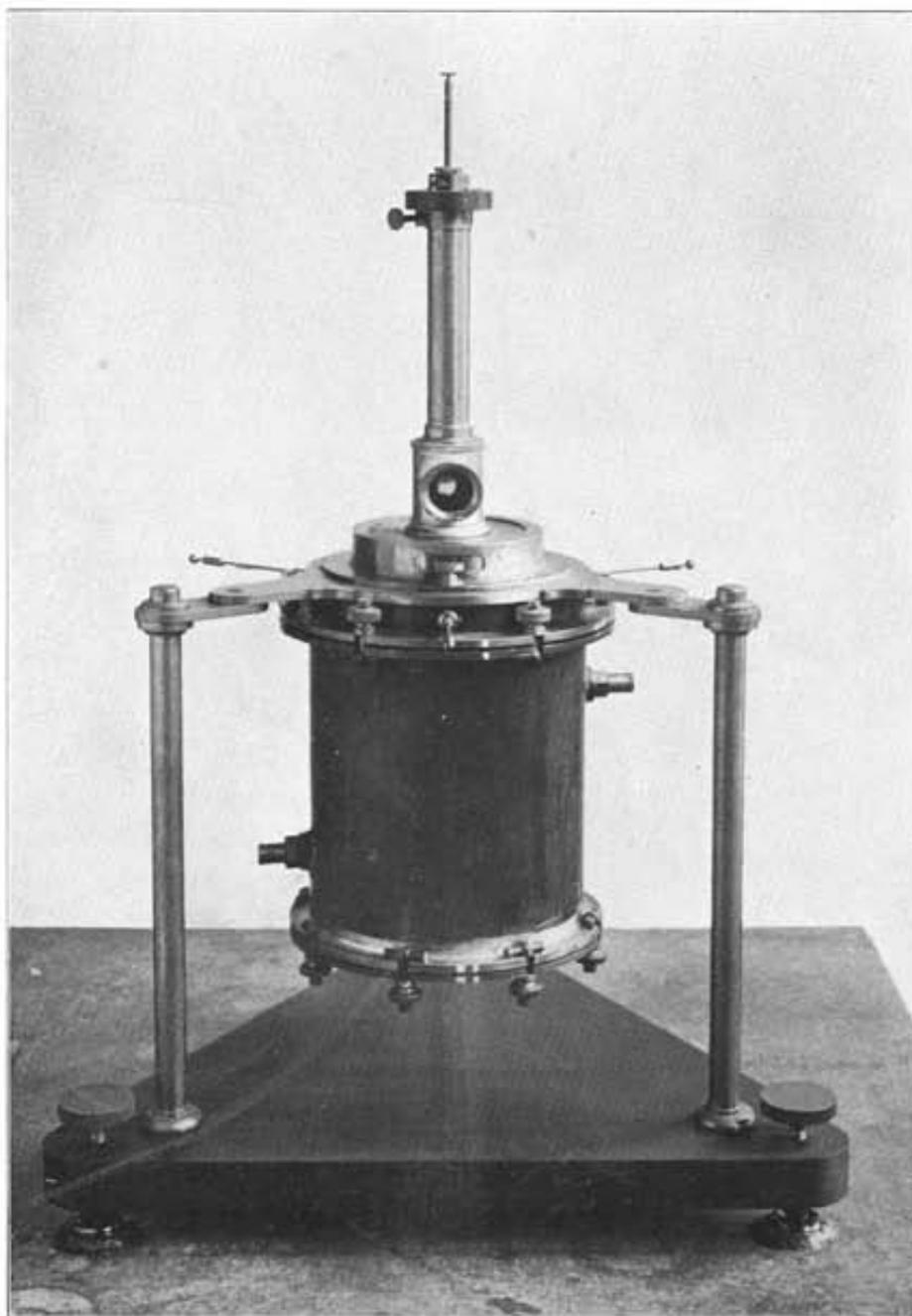


Fig. 2.

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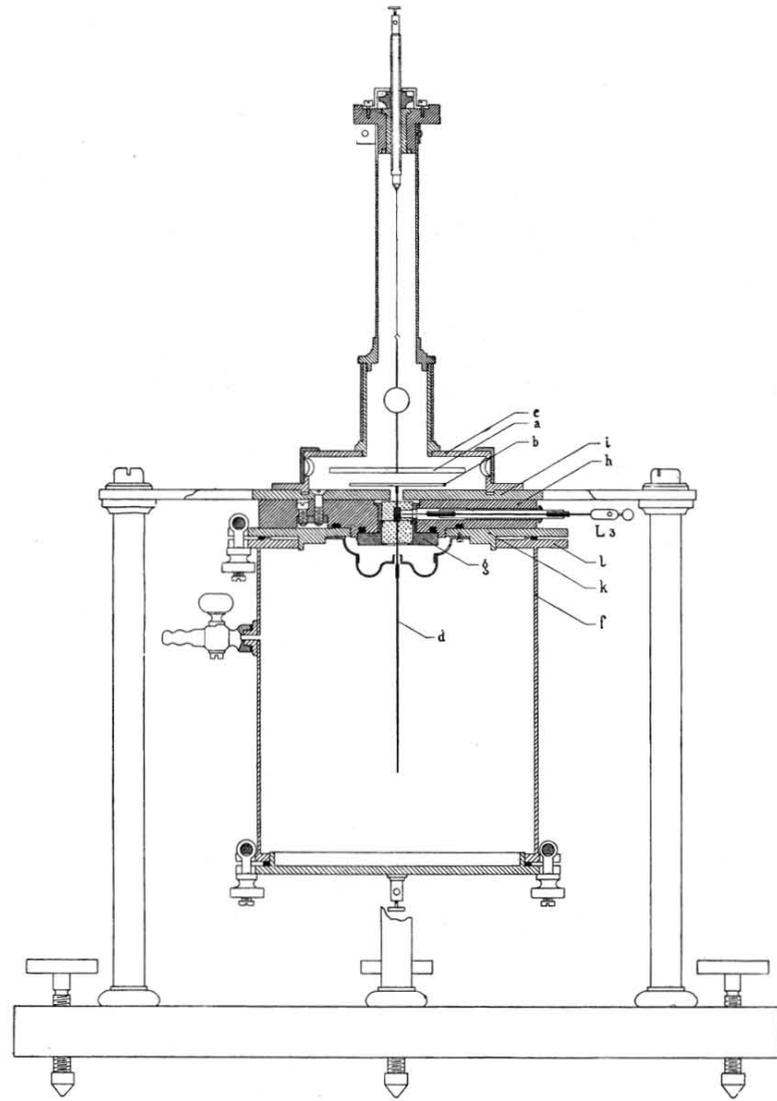


Fig. 3.

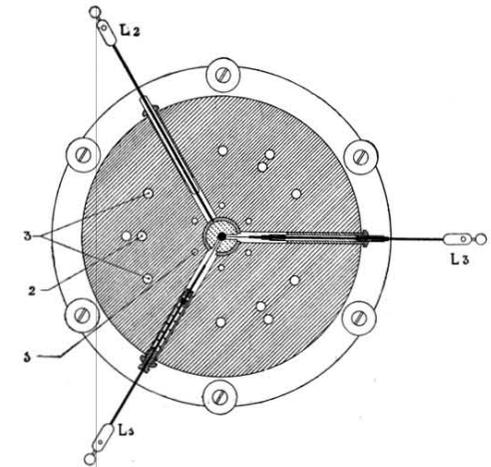


Fig. 4.

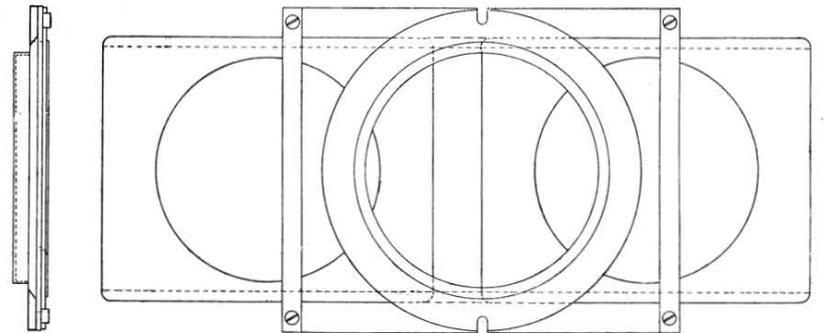


Fig. 5.

" (II).

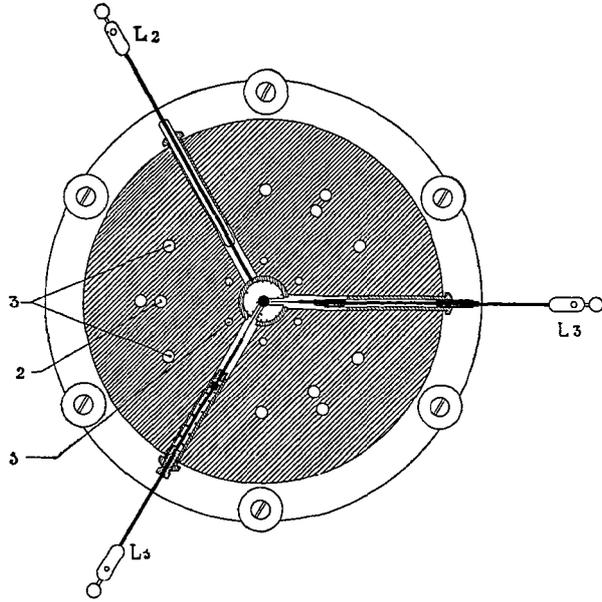


Fig. 4.

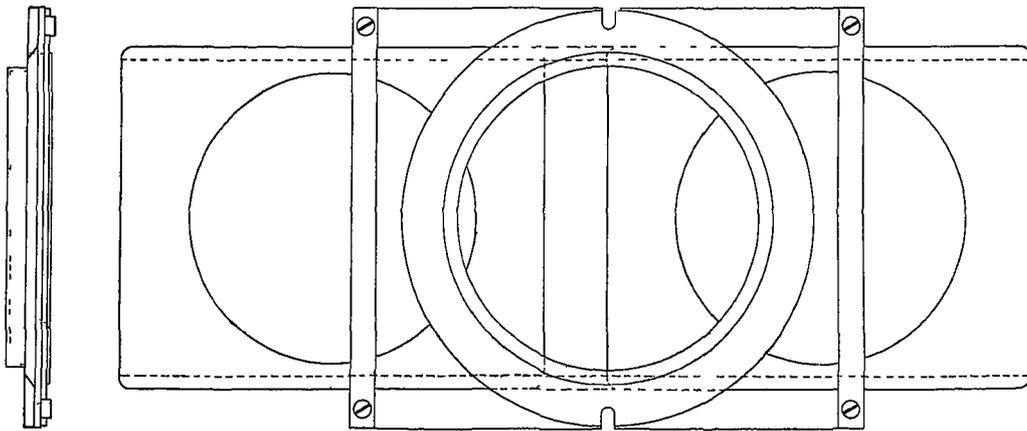


Fig. 5.

support the apparatus. Here follows a more detailed description of the arrangement ^{1) 2)}.

Description of the apparatus:

It is illustrated by the following reproductions:

Fig. 2 has been taken from a photo representing the apparatus as if seen somewhat from the top.

Fig. 3 is a vertical section through the plane of one of the rods, viz: the capacity rod l_3 , while Fig. 4 shows the ebonite disc in horizontal section, the two last being at a third of their real size.

Starting from the central part of the apparatus we shall find that the needle d is exactly in the middle; it is made of platinum and consists of two parts, the lower part of which slides tightly into the upper; in the middle this upper part is surrounded by a very small cylinder, which contains two small cavities in order to promote the good contact of the needle with the two rods which touch it on two sides; viz. the charging rod l_1 and the capacity rod l_2 . (Cf. Figures 3 and 4). The needle d is insulated by ambroid (dotted in Fig. 3) which consists of two cylindrical pieces, to the lower of which the needle is fastened, while the upper part, provided with two wide perforations for the rods, enclose the needle loosely. The ambroid is entirely surrounded by a brass tube serving as guardring, in order to prevent loss of charge of the needle as well as electrostatic disturbances upon it. This tube also consists of two parts: of a small lower cylinder with a thick outer rim at the bottom containing screw-perforations (in Fig. 4: 1) by means of which the guardring with the ambroid and the needle can be fastened to the surrounding ebonite plate. The lower cylinder fits loosely in the excavation of the ebonite and slides tightly in the upper part of the guardring, which, besides two wide perforations for the rods l_1 and l_2 , is yet provided with a screw-perforation for the third rod l_3 , which brings the guardring to the potential value desired. (Cf. Fig. 4). The ebonite plate itself is fastened to the lower side of the brass bottom plate i of the measuring space c by means of three brass screws and nuts (Fig. 4: 2; Fig. 3: the screws to the left of

¹⁾ The electrometer was constructed in the workshop of the Physical Laboratory at Groningen by Mr. H. J. Sres, who, with great devotion, surmounted in such a masterly way the many difficulties which arose when he performed his task.

Mr. D. A. Vonk, as chief of the workshop, in many respects gave also valuable indications.

²⁾ The Instrument-Manufacture and Trade late of P. J. KIPP and Sons, (lim.) Delft (Holland) is willing to construct the apparatus described here on sufficient demand.

the middle); the nuts are pressed against the ebonite by screws. Besides, the lid *k* of the ionisation cylinder *f* is attached to the ebonite plate; for this purpose the ebonite plate is perforated in six places, so that from the top countersunk screws can be driven into the lid; they will penetrate the lid only half way (Fig. 4:3). Six clamping screws cause the upper edge *l* of the ionisation cylinder to press closely against the lid. At the top the brass ionisation cylinder is partly shut off by the lid, partly by a small brass basin consisting of two parts, with an opening in the centre for the needle; bayonet closure unites these two parts, as well as the outer part with the lid. The basin is to hold CaCl_2 , which has to protect the ambroid from moisture; at the same time the needle in the ionisation cylinder, except for the small space of air mentioned above, is thus quite surrounded by metal, which is desirable for the measurement of ionisation. The bottom of the cylinder consists of a separate brass plate, pressed against the rim of the cylinder by clamping screws. As to the upper part of the apparatus, the chief part certainly is the brass measuring cylinder *c*, the dimensions of which are chosen in such a way as to cause the upper needle to undergo a thorough damping during its motion. This cylinder fits into a ring-shaped groove of the bottom plate and is provided with a broad rim with two circular slits through which two screws with notched heads fasten the measuring cylinder to the bottom plate. This enables the measuring cylinder to move over a rather large angle. (Cf. Fig. 2). In order to be able to check the state of things inside the cylinder and to see whether the upper needle is in the right position, there are in the walls of *c*, diametrically opposed, two oval openings, covered with celluloid, which correspond with two openings of the same size in a second brass outer cylinder, which is revolvable, so that during the measurement the inner space can be entirely shut off by metal.

The bottom plate *i* of the measuring space *c* is fastened by screws to brass legs, which support the apparatus. These rest on a triangular wooden base with levelling screws fitted with ebonite insulating toes.

To the lower needle *b*, which slides tightly into an excavation of *d*, a definite position can be given with the help of a scale made on the bottom plate of *c*.

The upper needle consists of a small aluminium strip, 0.05 mm. thick, and is fastened to a thin aluminium rod with mirror and mirror-supporter; the suspension consists of a thin platinum Wollaston wire.

The needle-system is arranged so as to let vibrations, which act on the system from without bring about as little disturbance as possible¹⁾. In order to obtain as much symmetry of inertia as possible with respect to the suspension wire, a disc of aluminium of the same size was affixed behind the mirror by way of counterweight. Moreover particular care was bestowed on the shape of the thin connecting hooks between rod and wire; finally the planes of mirror and needle were placed perpendicularly with each other²⁾. With these precautions a fine, restful motion of the needle could be successfully obtained. The brass tube with glass window that encloses it, is fitted at the top with an ebonite torsion head and with an arrangement which makes it possible to raise or lower the upper needle without making it turn round.

The following still requires to be said about the arrangement how and the way in which the three rods (cf. especially Fig. 4) can touch the needle or guardring through the ebonite: rod l_1 is the one that, touching the lower needle $b + d$, brings it to the desired potential before measuring; at the beginning of the measurement this contact is stopped and the charge of the ionisation current can be carried to the then insulated needle. The rod is made of brass and fitted with a subtle platinum point, in order to make sure of a good contact with the platinum needle. In order to bring about the insulation of the needle from the observer's place behind the telescope the rod has been placed in a brass tube which can be pushed tightly into the ebonite; this tube has been shut off at both ends by small brass covers each with a round opening through which the rod can pass freely without much friction. Round about the rod between the outer small brass cover and a thicker part of the rod a steel spiral spring has been placed which is tightened when the rod is drawn out. Now, the arrangement is chosen in such a way as to make a weight which hangs by a cord over a pulley draw the rod out and consequently break the contact with the needle, whereas by raising the weight the spring reestablishes this contact; this raising and lowering of the weight can be brought about from a distance by means of a cord over a pulley.

Rod l_2 , which brings the guardring to potential, is fastened in an ebonite tube, which has been fixed by means of an enclosing small brass cylinder into the ebonite perforation. Rod l_3 does only duty when capacity has to be measured (Harms-method); it is made of brass with a platinum point; it is insulated from the enclosing

¹⁾ Cf. a.o. H. E. J. G. DU BOIS and H. RUBENS: Wied. Ann. 48 p. 236, 1933.

²⁾ In Fig. III these planes were put parallel to each other for clearness' sake.

brass tube by two small pieces of ambroid; round about this we have once more a brass cylinder as mentioned above.

At the ends of the rods terminals are affixed in order to fasten the required connecting wires to the storage battery; also the screw of the torsion head, the bottom plate *i* and that of the ionisation cylinder *f* possess such screws, in order to bring the upper needle *a*, the measuring space *c*, and the ionisation cylinder *f* to the potential desired.

The arrangement of the electrometer having been explained in this elaborate way, some particulars should now be added in relation to some special purpose for which the apparatus has to be employed. If, namely, one wishes to use it for measuring the radio-activity of emanations, the ionisation cylinder must be exhausted, and therefore it must be possible to close it hermetically. Without taking particular precautions this cylinder would communicate by various ways with the air outside; among others along the axle and the walls of the ambroid cylinder; to prevent this, the needle in the lower ambroid cylinder has been cemented air-tight, while between this and the upper rim of the lower cylinder of the guardring a ring-shaped cavity has been filled with piceine (cf. Fig. 3). Thereupon, in order to prevent leakage along the lower rim of the guardring and then along the screws or to the centre, a rubber ring was inserted (in Fig. 3 the first ring mentioned from the centre) which fits closely in a ring-shaped groove in the ebonite, cut a little outside screws 1, and prevents the air to enter. In the same way a second rubber ring on the inside of screws 2 (cf. Fig. 3) prevents leakage from the cylinder along these screws or to the outer rim. At the bottom the guardring *g*, besides having a wide outer rim, still possesses a narrow rim turning inside, to prevent the ambroid, in consequence of difference in pressure of air, from being pressed inward. Further the closure of the cylinder at the top (by the lid *K*) is brought about in the same way as at the bottom (by the brass bottom plate) viz: by means of rubber rings.

In the wall of the ionisation cylinder are two hermetically closing taps of glass for the filling or exhaustion of air or emanation. With all these precautions it appeared to be possible to bring the pressure inside the cylinder down to 2 mm. with the pump (GAEDE'S new single barrel air-pump), while only after three days it was raised one mm., which is quite sufficient for the purpose we have in view.

If, however, the measurement must be done with regard to solid substances (direct method), which one must be able to exchange quickly and in which renewal of air should be avoided as much

as possible, then the bottom plate must be replaced by a ring (cf. Fig. 5) which bears on the lower side in two places diametrically opposed, two flat brass rails, along which one can slide a deepened bottom plate with the sides dovetailed, which forms the bottom of the ionisation cylinder. A second plate, fashioned in the same way, can be slid along the same ways and replace the first. The ring is pressed against the cylinder by two clamping screws.

Some particulars on insulation and arrangement.

In order to make sure that the ambroid really insulates the lower needle, several experiments were still made; thus a tension of +10 Volt was given to the guardring, f brought to the same tension as b : (0 Volt) in order to avoid an ionisation current, then b insulated, so that the charging of b could only be the consequence of a transition of charge from the guardring via the amber to b . With a sensitive state of charge the needle displacement amounted to no more than 1 à 2 mm. per minute. If we take into consideration that in measuring, the difference of tension between b and the guardring is very small — the latter is kept at $V=0$ — and that the rise in potential of b amounts during the measurement only to a small fraction of a Volt, this will sufficiently prove how excellently the ambroid insulates the needle, and that the leak it causes is of no account. As to the arrangement of apparatus, storage-battery etc., it is such as to make it possible to perform all the manipulations necessary for the preparation of the measurements from the place at the telescope.

First of all we find here within the observer's reach the storage-battery from which our wires start, in order to bring a , b , c , and f to potential. The connection with a , b , and f is direct, as these conductors are always charged to a potential given by a whole number of accumulators; c on the other hand receives exactly that potential wanted to bring the needle back again to its untwisted state after having charged a . Therefore the desired potential is obtained by means of an adjustable laboratory rheostate working as a simple type of potentiometer through which a small current is carried of an accumulator, whose one pole is in connection with a storage-battery. Looking through the telescope at the position of the needle, one can at the same time regulate the tension at will by adjusting the rheostate.

If, in this way, some state of charge has been given to the apparatus, and f brought to potential, then the measurement can be started simply by insulating b from a distance with the assistance of the pulley-system described above.

Theory of the apparatus.

Of late years numberless new electrometers have been constructed which, for the greater part, possess great sensibility and are to be considered as modifications of two of the principles, known until now; viz: that of W. THOMSON'S "quadrantelectrometer" and the principle realised in the "HANKEL-BOHNENBERGER" electrometer. To the first belong among others the measuring instruments of: DOLEZALEK¹⁾, MÜLLY²⁾, HOFFMANN³⁾, PARSON⁴⁾, to the second principle those of LUTZ and EDELMANN⁵⁾, ELSTER and GEITEL⁶⁾, WULF⁷⁾.

Besides the part of the measuring system which is charged to the tension to be determined, there are also in all these electrometers two conductors, which are kept at constant potential during the measurement. The electrometer described here possesses, it is true, this latter quality, but yet cannot be reduced to any of the principles mentioned; in shape it somewhat resembles the antique measuring instrument of KOHLRAUSCH-DELLMAN⁸⁾, which also has a cylindrical measuring space with two metal needles. As these needles, however, are charged together to the tension to be determined and in consequence repel each other, so the similarity spoken of here is not mentioned with regard to the principle of measuring, but only with regard to the exterior of both instruments and the system KOHLRAUSCH-DELLMANN has to be looked upon more as a realisation of the simple gold-leaf principle, while torsion has been made use of at the same time. The electrometer which concerns us here, however, strives after the combination of the following conditions:

1. Simplicity in the arrangement of the system (Cf. I, pp. 22 and 26).
2. Great sensibility by making use of the small torsion of thin wires.
3. Utilizing as much as possible the lines of force which arise through addition of charge to the system for the motion on the movable conductor.

As to the third condition, in communication I the motives were already indicated why I thought better to abandon entirely the principle of the quadrantelectrometer⁹⁾ (cf. I p. 26); at the same

1) F. DOLEZALEK, Ann. d. Phys. 26, p. 312, 1908.

2) C. MÜLLY, Phys. Z. 14, p. 237, 1913.

3) G. HOFFMANN, Ann. d. Phys. 52, afl. 7, p. 665, 1917.

4) A. L. PARSON. Phys. Rev. N. S. Vol VI. p. 390, 1915.

5) C. W. LUTZ, Phys. Z. 9, p. 100, 1908.

6) J. ELSTER and H. GEITEL, Phys. Z. 10, p. 664, 1909.

7) THEOD. WULF, Phys. Z. 15, p. 250, 1914.

8) Pogg. Ann. Bd. 72.

9) The drawback of the horizontal wing-surface holds for the measurement of a definite quantity of charge, of course not of fixed potentials.

time light was thrown upon the fact that the advantage of the system with regard to this had been obtained by the fact that the lines of force which undergo a change by addition of charge to the system, act especially on the one vertical side of the upper needle, i. e. will especially cause a *moving couple*. Let it be added that, the arrangement once having become such as to show an asymmetrical character, there had been introduced into the system at the same time the principle called by HOFFMANN the "Labilisierungsprinzip", which, considered by itself will yield "*under certain conditions*" a decisive advantage in relation to the sensibility of the apparatus, as will become clearer yet from the following considerations.

For this it is necessary to account for the behaviour of the electrometer in the various states of charge, as these are realized before the measurement takes place. Suppose that one of the states of charge has been given to the apparatus, e.g. $a + 12$ Volt, b 0 Volt, $c - 4$ Volt, *wire untwisted*, angle of needles 30° (cf. I). The equilibrium then arising is shortly due to the following: in consequence of charging a to 12 Volt — if b and c are still supposed to be 0 Volt yet — a greater density of lines of force arises between a and b than between a and c , in consequence of a slighter distance between $a-b$ in relation to that of $a-c$; on account of this a resulting electric couple will act on a , which can be compensated, however, by a second electric couple in an opposite direction, which takes place in consequence of charging c to negative potential (-4 Volt); for b acts as a screen to the lines of force $a-c$ (cf. also I pp. 24 and 25). If it is supposed that the needle has been suspended in this condition *without* torsion, then, in theory at least, the equilibrium will continue; however, this is an unstable equilibrium, for with constant potentials at a slight turning of the upper needle into the direction that will decrease the angle with b , the density of the lines of force between a and b will increase and a resulting electric couple will arise according to the direction of the movement. The equilibrium will also be unstable in the opposite direction, because with an increase of the distance $a-b$, there will be a decrease in the influence of b , and the influence of the negative of c will be preponderating. The torsion of the suspension wire, however, can yield a couple, if sufficiently large, which brings about a stable equilibrium; the torsion, however, can have a value too, so much so that it does not counterbalance these above mentioned electric couples, in which case the equilibrium remains unstable. Given a definite height and angle of needles there will exist two conditions by which these cases are determined:

1. the value of the force of the torsion, consequently the thickness and nature of the suspension wire;

2. the state of charge in which we can distinguish high and low states of charge, meaning that the potential $a-b$ can be large or small thus e.g. the state ($a + 30$ Volt, $b 0$ Volt, $c - 8$ Volt) is a higher state of charge than ($a + 12$ Volt, $b 0$ Volt, $c - 4$ Volt).

The meaning of condition 1 is sufficiently clear in itself; as regards 2, if, with a definite wire one will always try to realise higher states of charge, in the end the equilibrium from being stable will always become unstable. For with a higher state of charge, the density of the lines of force between a and b and of course also those between a and c (for there is a greater potential difference between a and c at the same time) will always be greater; then also the electric couple that occurs will increase in consequence of a supposed slight displacement of the needle, so that the torsion couple with a sufficiently high state of charge will finally be unable to compensate this electric couple any more. Of course the stable conditions are used for measurements; yet it is practically possible to approximate the unstable equilibrium with torsion, in which case, interesting phenomena occur; if e.g. under otherwise equal conditions one increases the state of charge continually, it will in the end be impossible to give a fixed position to the needle in or near the equilibrium (untwisted); seemingly the needle is at rest, yet it gradually approaches the lower needle, at first with slight velocity, but steadily increasing so that the image of the scale will shortly disappear from the field of the telescope; the parallel position of the needles is almost reached. Such conditions are meant in communication I, when we say that the needle "turns".

As the behaviour of the electrometer has been accounted for in the various *states of charge*, there still remains to examine the behaviour in the various *states of measurement* where we shall also be able to observe the importance of the "Labilisierungsprinzip". To the conception of capacity, which is connected with it, I should like to give the meaning of what PULGAR and WULFF¹⁾ call the "total" capacity of the conductor, which conception is used by them for cases similar to those considered here and for which the conception of capacity, as MAXWELL gives it, is not sufficient; for the conductors a and c are not at 0 Volt, nor does the angle of the needles remain constant.

Further I wish to distinguish between (cf. communication I p. 29):
1: useful, and 2: injurious capacity; meaning by useful capacity that

¹⁾ J. DEL PULGAR and TH. WULFF, Ann. d. Phys. 30, p. 700, 1909.

part which influences the motion of a ; by injurious capacity that part that lacks this influence and therefore means only disadvantage here. As to the measurements, the sensibility will rise together with the increased states of charge. In order to bring this out, we have to compare e.g. the measurements of the two following states: State I: (+ 8, 0, -4) Volt and state II: (+ 14, 0, -6) Volt, and suppose b to be insulated, so that a supposed ionisation current gives a positive charge to the lower needle $b + d$ (f at + 80 Volt e.q.). What then will be the effect with in both cases a definite equal increase of charge? The potential value of b will rise, the number of lines of force between a and b decrease at the same time so that the upper-needle recedes from the lower. In consequence of the fact that a , which is positively charged, recedes from b , part of the negative charge induced on b by a in the state of equilibrium, will be set free and therefore will be spread over the now insulated system $b + d$. The influence of this will, first of all, consist in a decrease of potential of b , causing the potential value of b to increase less than would follow from the addition of charge considered by itself (ionisation current). This influence is felt strongest in the case of II, where in consequence of greater potential difference between a and b , a greater quantity of induced charge is set free, so that the potential decrease, caused by this will be greater. But from yet another point of view we shall have to look at the part played by the induced charge: as soon as the latter spreads from b over $b + d$, this *in itself* means again a *decrease* of lines of force between a and b , i.e. a cause of *motion* on the needle. The result of this consideration therefore is that the displacement of the upper needle a will only partly be the consequence of a direct addition of charge from the ionisation current, but at the same time must be partly considered as the consequence of the displacement of induced charge in the system.

Where, therefore, this displacement is greatest i.e. in case II, the motion on the needle will be strongest and consequently the sensibility of charge greatest.

In communication I the above mentioned explanation has been worded somewhat differently; it was namely said there, that the greater sensibility in II would be the consequence of the fact that the increase of the capacity of $b + d$ would especially mean increase of *useful* capacity in the system, by which the sensibility of charge will increase. In order to elucidate this more clearly, I shall return to what was communicated above; that, namely, by displacement of induced charge, owing to the motion of a , the rise in potential of b turns out smaller than might follow from the addition of charge

considered by itself. When, however, through this influence a definite addition of charge causes a smaller rise in potential than would be the case without it, this in itself means that the capacity of $b + d$ has been increased by it. It is this increase of capacity that is of great advantage to the sensibility of charge in the system, and that because this increase of capacity means increase of the useful capacity of $b + d$. Let us first imagine the phenomenon in two phases to take place the one after the other (practically they act at the same time).

I. the *positive* increased charge is distributed over $b + d$; the upper needle describes the corresponding angle.

II the *negative* induced charge which is set free by this movement near b spreads over $b + d$.

The effect of I and II together then comes to the same, as if I had only taken place, but at the same time a greater part of the added charge goes to those places of b , where the induced charge of case II was to be set free. In my opinion it is clearly shown in this way that the influence of phase II really consists in an increase of the useful capacity of b . In the state of charge $(+14,0, -6)$ that useful capacity is yet more increased by the movement than in the state of charge $(+8,0, -4)$; from which follows that in that state the sensibility of charge will also be greater, because, as was already said in Communication I, the sensibility of charge will of course be all the greater according as a greater part of the added charge causes a change in the lines of force between a and b , which is attended by motion. Ultimately there are limits to the use of an ever increasing state of charge; when e.g. the case of instability as described above, sets in. An approximation as closely as possible to this unstable equilibrium is of course the most favourable condition for the sensibility, because then (see above) the motion of the needle will chiefly be the consequence of displaced induced charge and for a small part only of the increase of charge itself.

The "Labilisierungsprinzip" also occurs in some other electrometers, a. o. in those of WULFF, WILSON (Kipsystem), whereas the electrometer of HOFFMANN aims at such a favourable variation of the binant-electrometer that the mentioned system was introduced into the system for that very reason, for which purpose the shape of the needle was chosen in a particular way. Yet the conception that the "Labilisierungsprinzip" in itself would guarantee the greatest possible sensibility in a system, is not correct according to my opinion; with the application of this principle the ratio of useful to injurious capacity will also remain of the greatest importance. If e.g. one just imagines that in the system $b + d$, d possesses a great

capacity (i.e. injurious) there will be wanted near the unstable state of charge a very slight increase of charge for the variation in the course of the lines of force between a and b considered by themselves; consequently for the motion of the needle; yet at the same time the needle d will yet require much charge for itself; or: though the useful capacity strongly increases in the unstable state, yet the injurious capacity must be seriously taken into account. This drawback makes itself felt especially when that injurious capacity in the system undergoes the influence of the instability as well as the useful capacity. If it is supposed e.g. that a consists of a horizontal disc, then part of the capacity of b will relate to lines of force going from b to the *horizontal* plane of a (i.e. injurious capacity). Also these lines of force will then undergo a change in consequence of the *movement*; that is. to say, that also this injurious capacity will constantly increase while passing to higher states of charge, which in itself is disadvantageous. From this consideration it follows that the advantage of instability is still bound up with another condition; the optimum is implied in the following rule: the greatest sensibility of charge in a system will be obtained by a maximal approximation to the unstable state; at the same time the amount of the injurious capacity will have to be as small as possible and by no means to undergo the influence of instability.

As regards further the capacity of the whole system together, peculiar relations may crop up in the case of change of the latter. We have noticed already that with a positive increase of charge the induced charge, which is displaced by the movement of the needle arrests the increase of potential in the system. Thus it may occur that the increase of potential is compensated by that very influence, i.e. the system would then possess an infinitely great capacity; this will occur among others when the injurious capacity of the system possesses a small amount of capacity. If one passes on to higher states of charge then a positive increase of charge will even bring about a decrease of potential i.e. a negative capacity for the system.

As to the electrometer described here, I think I have obtained favourable results in relation to the consideration given here. Experiments are arranged for in order to become more acquainted yet with the ratio of useful to injurious capacity in the various states of charge in this system, which cannot yet however, be considered as being put an end to; also about the influence of the thickness of the suspension wire and modification in the shape of the needle a closer investigation is still in preparation.

Physical Laboratory of the University of Groningen (Holland).

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Physiology. — "*On the ventricle-electrogram of the Frogs' heart.*" By Dr. S. DE BOER. (Communicated by Prof. G. VAN RIJNBERK.¹⁾)

(Communicated in the meeting of October 27, 1917).

It has appeared from my former investigations that we can admit the width of the R-oscillation of the ventricle-electrogram as a measure for the velocity, with which the impulse is transmitted through the ventricle.¹⁾ A decrease of the velocity of impulse-transmission is expressed by a widening of the R-oscillation, whilst a narrower R-oscillation betrays an increase of the velocity of impulse-transmission through the ventricle.

If now we want to trace the influence that the velocity of impulse-transmission has on the shape of the ventricle-electrogram, then we can consequently conclude from the width of the R-oscillation, whether the impulse is transmitted with more or less velocity through the ventricle. Now we can make the velocity of impulse-transmission decrease by exciting an extra-systole of the ventricle at an anticipated moment of the heart-period. If we wish however to compare the electrogram of such an anticipated extra-systole of the ventricle with those of the normal periodical systoles of the ventricle, then the requirement must be satisfied, that this anticipated ventricle-systole is brought about by an impulse, that reaches the ventricle along the atrio-ventricular systems of connection. The place where the impulse hits the ventricle at such an anticipated ventricle-systole must be the same as at the normal periodical ventricle-systoles. Only then we can make a comparison. Otherwise the modification of the shape of the ventricle-electrogram might be attributed to the fact, that the impulse proceeded from another place of the ventricle (e.g. at the surface of the ventricle as at extra-stimulation of this part of the heart). We apply consequently an extrastimulus to the auricle at an anticipated moment of the heart-period. After the extrasystole

¹⁾ These investigations were likewise communicated in the meeting of the Biological section of the Genootschap ter bevordering van Natuur- Genees- en Heelkunde (Physiologendag) held on the 20th of December 1917.

²⁾ Zeitschrift für Biologie Bd. 65 Seite 128 and Journal of Physiology. Vol 49 page 310.

of the auricle, obtained in this way, the impulse continues along the atrio-ventricular systems, and causes an anticipated ventricle-systole. We can compare the electrogram of this systole with those of the normal periodical ventricle-systoles. It had appeared to me already during my investigations into this subject in 1914¹⁾, that the electrograms of those anticipated ventricle-systoles showed R-oscillations, of which the width, compared with those of the normal periodical ventricle-systoles, had increased. At the same time I stated that the T-oscillations of these anticipated ventricle-systoles had changed in a negative sense.²⁾

We may expect, that after the compensatory pause during the post-compensatory systole the velocity of impulse-transmission had increased, and a decrease of the width of the R-oscillation of the electrograms belonging to it proved indeed, that this was the case. The T-oscillation of these electrograms has changed in a positive sense (a negative T-oscillation of the periodical ventricle-systoles had decreased, a positive T-oscillation had increased).

Modifications of the velocity with which the impulse was transmitted through the ventricle were consequently expressed by the width of the R-oscillation and by the dimension and the direction of the T-oscillation. During the last year I continued these investigations and systematically observed the changes that occurred in the ventricle-electrogram, when I modified the velocity of impulse-transmission. This continued investigation consists of 3 parts.

1. In the first place I caused the velocity of impulse-transmission to decrease by poisoning with digitalis or antiarine. Before the poisoning first a photogram was made, and then, whilst the poisoning continued, constantly with definite pauses a photogram was made, till the halving of the ventricle-rhythm set in. As the velocity of impulse-transmission suddenly increased again after the halving of the ventricle-rhythm, directly an other photogram was made. In this way I could compare the electrograms of the frogs' hearts before the poisoning with those that were made after the poisoning, and even before disturbances of rhythm set in,

¹⁾ Zeitschr. für Biologie, Bd. 65, Seite 428, 1915.

²⁾ By the change of the T-oscillation in a negative sense is meant, that a positive T-oscillation of the electrograms of the periodical ventricle-systoles decreases during an anticipated ventricle-systole or changes into a negative T-oscillation. If however the T-oscillation of the periodical ventricle-systoles is already negative, then an increase of it during an anticipated ventricle-systole means also a change in a negative sense.

The ventricle-electrograms produced after the halving of the ventricle-rhythm were compared in the first place with the electrograms taken immediately before the halving, and at the same time with all the previously registered ventricle-electrograms.

2. A second series of experiments was made with frogs' hearts in which, after the application of the mentioned poisons, halving of the ventricle-rhythm had set in already. This halved ventricle-rhythm was thereupon converted into the normal twice as quick one by an induction-stimulus, as was mentioned in my previous essays¹⁾. The normal ventricle-rhythm was converted again into the halved one. In this way I obtained in one photogram the ventricle-electrograms of the normal ventricle-rhythm and those of the halved one. During the normal ventricle-rhythm the impulse is transmitted much slower through the ventricle than during the halved one, because the number of ventricle pulsations in the first rhythm is twice as great as in the second. Occasionally a spontaneous modification of rhythm of the not-poisoned heart was registered.

3. In a third series of experiments anticipated ventricle-systoles were excited in the not-poisoned frog's heart by applying extra-stimula to the auricle. I caused then in the beginning of the irritable ventricle-period and at a later period anticipated ventricle-systoles. As I explained already before, the electrograms of these anticipated ventricle-systoles could be compared with those of the periodical ventricle-systoles. The electrograms of the anticipated ventricle-systoles were also mutually compared. During the ventricle-systoles that were excited in the beginning of the irritable ventricle-period the impulse was transmitted slower through the ventricle than during the ventricle-systoles that were excited at a later period of the irritable ventricle-period.

These 3 series of experiments produced me a rich material for the study of the influence of the velocity of impulse-transmission on the shape of the ventricle-electrogram. I shall first discuss these 3 series of experiments successively, guided by some photograms, and afterwards communicate my conclusions in a theoretical explanation, and add to these conclusions a few considerations concerning the signification of the views obtained for the electrophysiology of the heart.

I. *Comparison of the ventricle-electrograms of frogs' hearts before and after the poisoning with digitalis.*

The experiments were made in the following manner. The frog

¹⁾ Archives Néerlandaises de Physiologie de l'homme et des animaux Tome I, p. 271 et 502.

was extended on a cork-plate, and thereupon the heart was laid bare in the usual way and suspended at the point. The oscillations of the lever were photographed on the sensitive plate beside the electrograms that were obtained after placing one unpolisable electrode on the heart point and one on the auricle. The time was likewise indicated in all photograms in $\frac{1}{5}$ second. The experiments of the second and the third series were arranged in the same way, but for these a stimulator was moreover placed against one of the parts of the heart, and the moment at which the stimulus was applied, was indicated on the sensitive plate by a signal that was linked in the primary current-circuit of the induction-apparatus ¹⁾).

In this series of photograms as well as in the two following ones we shall trace in the first place the width (duration) of the R-oscillation, then the extent and the direction of the T-oscillation. We call a T positive, when its direction is equal to that of the R-oscillation, and negative when it is opposite to the latter. Thereupon we consider the line of connection between the R- and the T-oscillation. When this line of connection is removed in the direction of the R-oscillation, it rises, it lowers, when it is removed in a direction opposite to that of the R-oscillation. In this communication I shall consequently explain more accurately of the photograms represented only these 3 parts of the ventricle-electrograms.

In order to avoid occupying too much room for the figures, I shall restrict myself to reproduce five photograms, one taken before and four after the poisoning with digitalis dialysate (GOLAZ).

In Fig. 1 the suspension-curves of a frog's heart are reproduced before the poisoning and likewise the electrograms (deduction auricle-point). The T-oscillation is positive, the line of connection between the R- and the T-oscillation is above the line indicating the position of rest of the string. Then I inject under the skin of the thigh 12 drops of digitalis dialysatum. Another photogram is taken under equal conditions fifteen minutes after the injection (Fig. 2). If we compare the width of the R-oscillation of this photogram with that in Fig. 1, we see that it has considerably increased. This teaches us that the velocity of impulse-transmission through the ventricle has decreased. The T-oscillation is still positive, but has become very little and the line of connection between the R-oscillation and the T-oscillation coincides now almost with the position of rest of the string.

¹⁾ When the primary current-circuit was closed the signal moved downward, when opened upward. The closing induction shocks were blended off, the opening induction shocks directed towards the frog's heart.

Fig. 3 has been taken 15 minutes after Fig. 2. The width of the R-oscillation has still increased very much¹⁾. The T-oscillation has now become strongly negative and the line of connection between

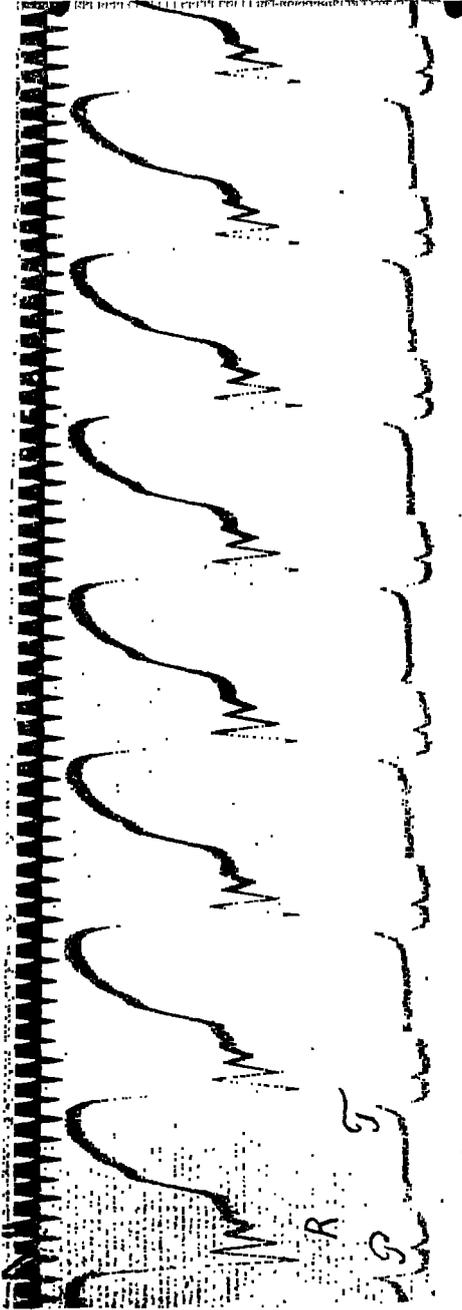


Fig. 1.

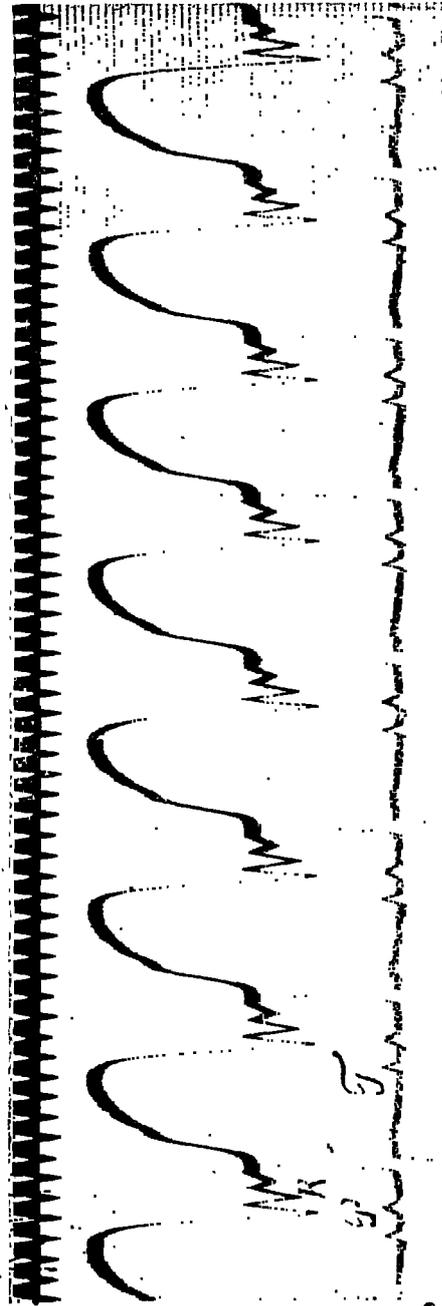


Fig. 2.

¹⁾ The time has not been reproduced in this photograph, but the velocity of the fall of the plate was the same as in the former photographs.

the R-oscillation and the T-oscillation lies now below the position of rest of the string.

Fig. 4 was again photographed 15 minutes after Fig. 3. The R-oscillation has now become exceedingly wide. The T-oscillation is

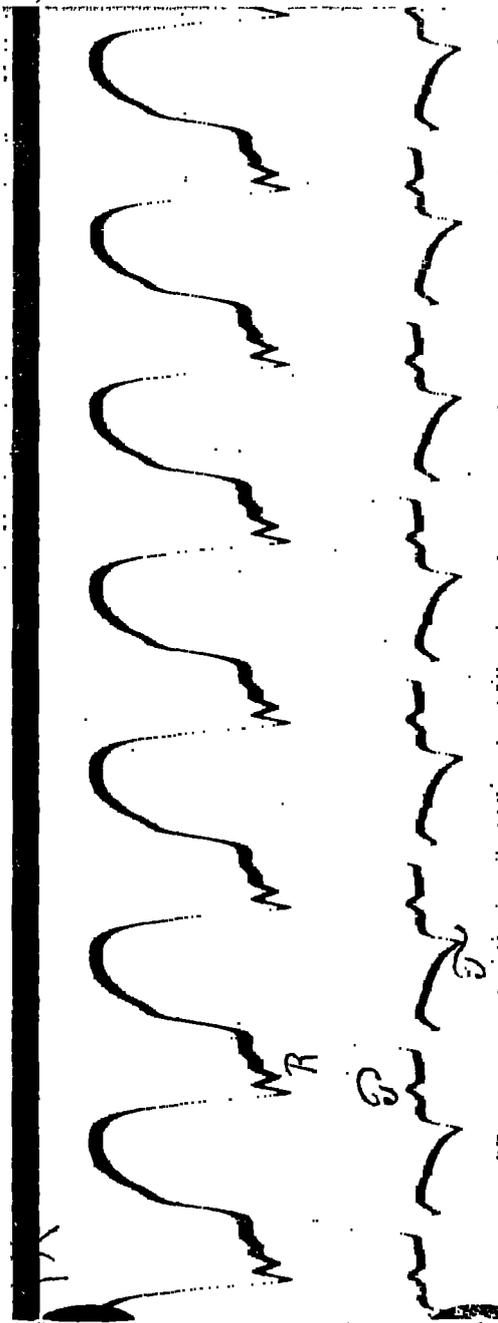


Fig. 3.

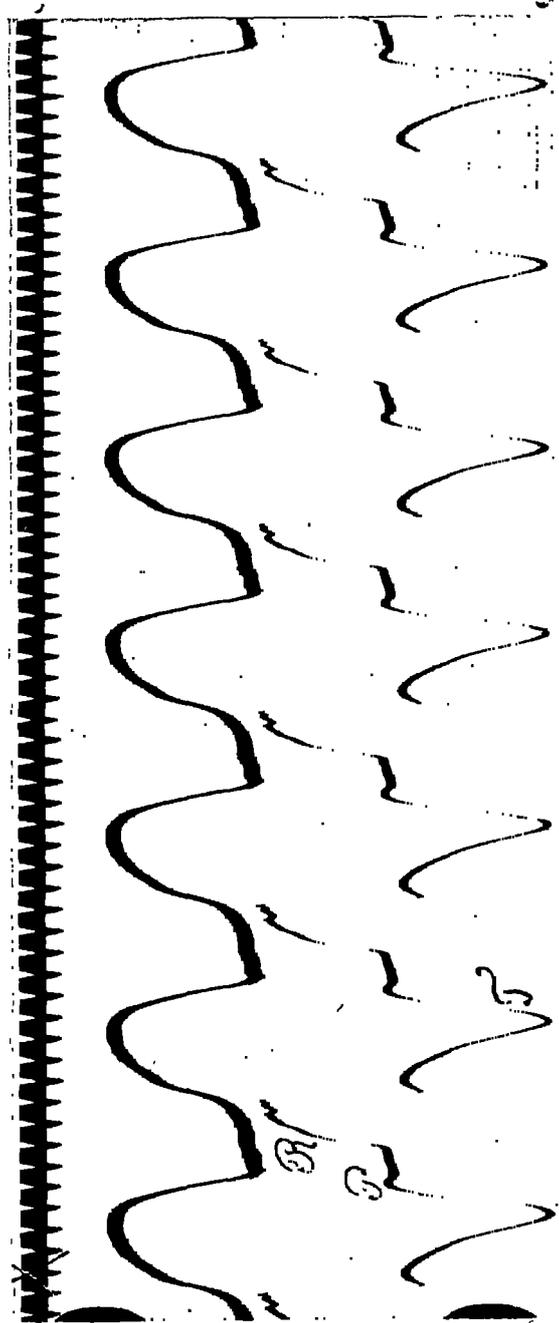


Fig. 4.

now very strongly negative, and the line of connection between the R-oscillation and the T-oscillation has descended more than in the former photogram.

Fig. 5 was taken 15 min. after Fig. 4. In the mean time the rhythm of the ventricle has halved, but after every large ventricle-systole still an abortive systole of the ventricle occurs. This abortive ventricle-systole gives a little nearly triangular electrogram (α). During the halved ventricle-rhythm the velocity of impulse-transmission through the ventricle has again considerably increased. In accordance with this fact the R-oscillation has become again much narrower. The T-oscillation is still negative, but has become considerably smaller than in the former photogram. The line of connection between the R-oscillation and the T-oscillation lies for a part somewhat above the position of rest of the string. If we compare Fig. 5 and Fig. 3, then in Fig. 5 the R-oscillation is narrower than in Fig. 3. In accordance with this fact the T of Fig. 5 is likewise smaller than that of Fig. 3, and the line of connection between the R-oscillation and the T-oscillation in Fig. 5 lies at a higher level than in Fig. 3. After the application of the two poisons mentioned above these results were constantly obtained by me. As long as the poisoning continues, and still before the halving of the ventricle-rhythm has set in, the velocity of the impulse-transmission through the ventricle decreases. The width of the R-oscillation increases accordingly, the T-oscillation changes in a negative sense and the line of connection between the R-oscillation and the T-oscillation descends¹⁾. As soon as halving of the ventricle-rhythm has set in the velocity of impulse-transmission increases again; the width of the R-oscillation decreases, the T-oscillation changes in a positive sense, and the line of connection between the R-oscillation and the T-oscillation rises²⁾.

II. *Artificial and spontaneous modifications of rhythm.*

If we poison a frog's heart with veratrine, digitalis or antiarine

¹⁾ If after the poisoning ventricle alternation appears, then the proportions through the partial ventricle-systole during the little ventricle-systoles are of course different (vide report of the Physiologendag, 20 Dec. 1917). More extensively about this subject afterwards.

²⁾ From Fig. 1 to Fig. 5 included the width of the P-oscillation increases through the poisoning, whilst the auricle-rhythm remains constant. The width of the R-oscillation has consequently decreased in Fig. 5 in consequence of the halving of the ventricle-rhythm, but the width of the P-oscillation has increased, as the rhythm of the auricle has remained unaltered.

the rhythm of the ventricle halves after some time, because the duration of the refractory stage of the ventricle increases. We can then convert the halved ventricle-rhythm into the normal twice as quick rhythm by applying an extra-stimulus to the ventricle at the

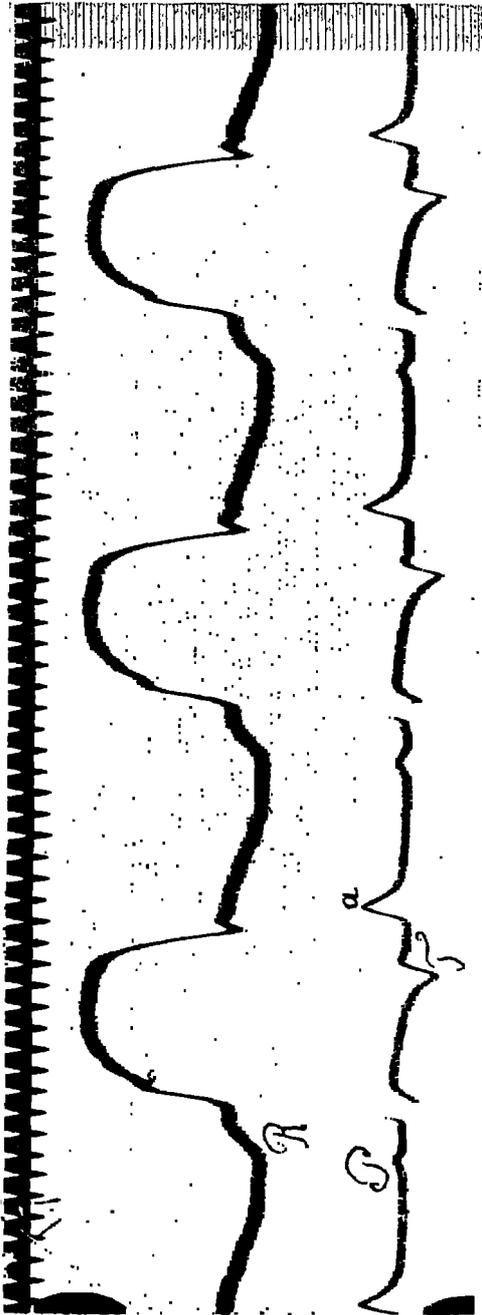


Fig. 5.

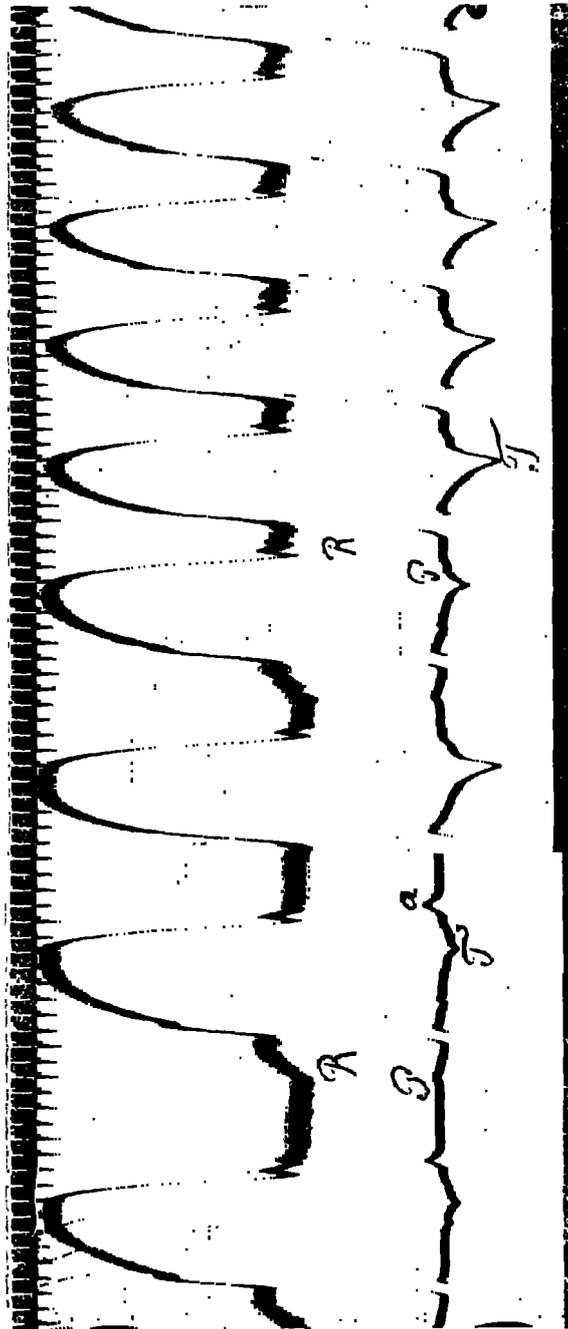


Fig. 6.

end of the diastole or the pause. This was already explicitly discussed by me with regard to veratrine and digitalis to which I refer here¹⁾. The same holds likewise for antiarine, about which I intend to publish a more extensive communication. We can then convert again the normal ventricle-rhythm into the halved one by applying an extra-stimulus to the auricle or to the ventricle-basis in the beginning of the ventricle-systole.

During the normal rhythm the impulse is transmitted slower through the ventricle than during the halved rhythm of the ventricle. It is of course clear that the conductivity inside the ventricle during the normal ventricle-rhythm, in which in the same time twice as many systoles of the ventricle take place than during the halved ventricle-rhythm, is worse than after the halving of the ventricle-rhythm.

In Fig. 6 I reproduce an example of such an artificial modification of the rhythm. In the beginning of the fig. (the first two ventricle-systoles) the rhythm of the ventricle is halved. After every large ventricle-systole occurs another extremely little abortive ventricle-systole, the little triangular electrograms of which are indicated by an α . Both these little ventricle-systoles of the halved rhythm show little negative T-oscillations, and the line of connection between the R- and the T-oscillation lies just below the position of rest of the string. At the rising of the signal the ventricle-basis receives an extra-stimulus towards the end of the pause, after which a great ventricle-systole follows. Thereupon the normal rhythm of the ventricle is restored. The first ventricle-systole of this normal ventricle-rhythm succeeds still after a rather long pause, so that the impulse-transmission through the ventricle is now only unimportantly retarded (compare the width of the R-oscillation of this systole with that of the two preceding systoles of the halved ventricle-rhythm). This slight retardation is however already expressed in an enlargement of the negative T-oscillation and in a descent of the line of connection between the R-oscillation and the T-oscillation. The pauses between the succeeding ventricle-systoles are considerably shortened, and now the width of the R-oscillations has remarkably increased. The ventricle-electrograms show likewise large negative T-oscillations, and the lines of connection between the R- and the T-oscillations have descended considerably, and are gradually converted into the T-oscillations.

In Fig. 7 the halved rhythm of the ventricle was by an

¹⁾ Arch. Néerl. de Physiol. loc. cit.

extra-stimulus on the basis ventriculi converted into the normal one, and the latter again into the halved ventricle-rhythm. The halved ventricle-rhythm was here also obtained by poisoning with antiarine.

The first ventricle-systole of the figure belongs still to the halved rhythm. A short time after the end of the diastole the ventricle-basis receives an extra-stimulus, through which the halved ventricle-rhythm is converted into the normal twice as quick rhythm.

When we compare now the ventricle-electrograms of these two rhythms, we are immediately struck by the fact that the R-oscillations during the normal ventricle-rhythm are wider than those during the halved rhythm.

In the halved ventricle-rhythm the T-oscillations are negative but very little, and the line of connection between the R and the T lies just above the position of rest of the string. In the normal ventricle-rhythm the T-oscillations are likewise negative but rather large, and the line of connection between the R and the T lies now below the position of rest of the string.

The basis ventriculi receives another stimulus at the 2nd rising of the signal, which gives rise to a little abortive systole. After the compensatory pause the ventricle is fixed again into the halved rhythm through the post-compensatory systole. The ventricle electrograms have likewise again obtained the same shape as in the beginning of the figure.

In Fig. 8 the ventricle pulsates in the beginning likewise in the halved rhythm (after poisoning with antiarine). At 1 the ventricle-basis receives an extra-stimulus, causing an extra-systole of the ventricle. After this the halved ventricle-rhythm continues however. When thereupon at 2 the extra-stimulus is repeated a little earlier in the ventricle-period, the conversion into the normal ventricle-rhythm succeeds, but after 3 systoles it changes again into the halved one. During the halved rhythm again little abortive ventricle-systoles occur, the triangular electrograms of which are indicated by an *a*. During the halved ventricle-rhythm the T-oscillation is positive, and the line of connection between the R and the T is above the position of rest of the string. At the quicker normal ventricle-rhythm the R-oscillations are considerably widened, the T is strongly negative and the line of connection between the R and the T has descended far below the position of rest of the string.

We find these proportions not only with poisoned hearts, but not poisoned frogs' hearts show the same phenomena. Fig. 1 of one of

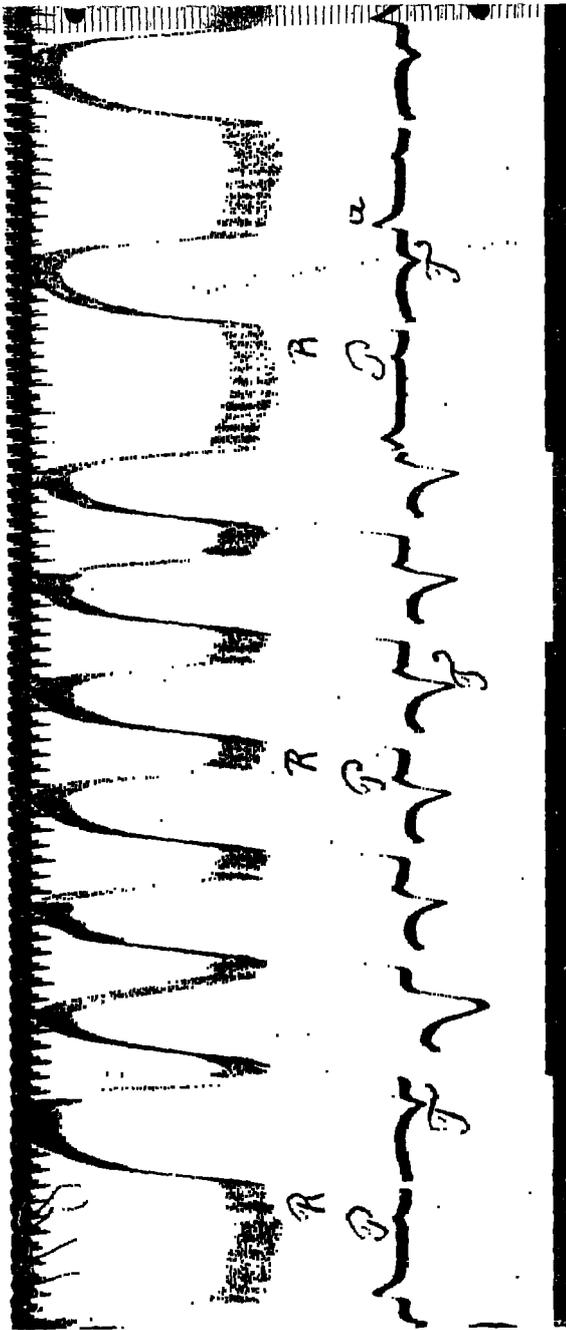


Fig. 7.

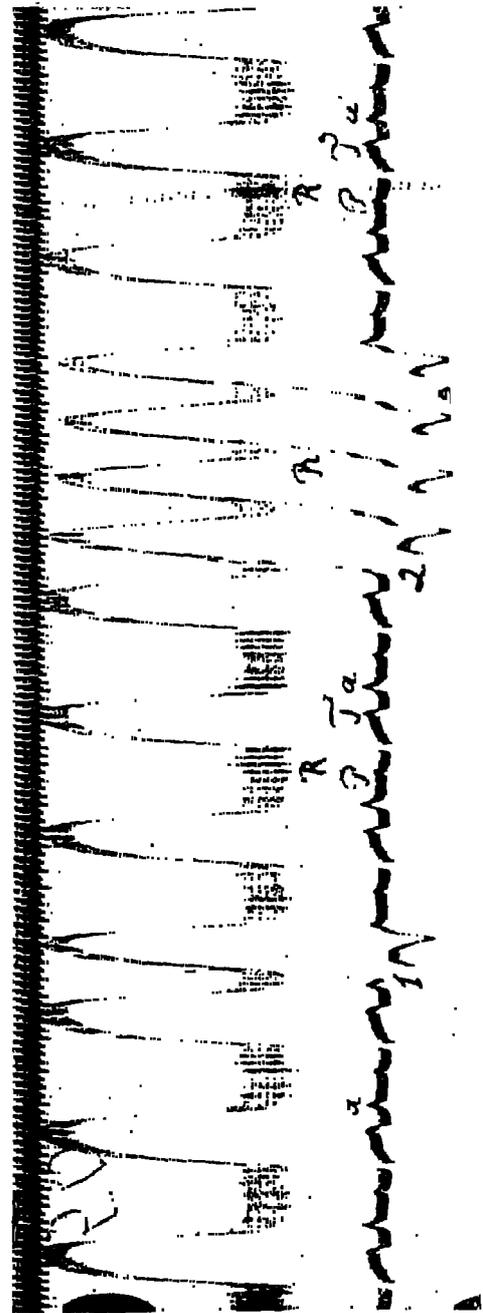


Fig. 8.

my former communications¹⁾ teaches us so. In this figure we see a spontaneous conversion of the normal ventricle-rhythm into the

¹⁾ Koninkl. Akademie van Wetenschappen at Amsterdam. Verslag van de gewone vergadering der Wis- en Natuurk. Afdeeling van 30 Juni 1917 Deel XXVI blz. 424 and Proceedings. Vol. XX, page 404.

halved one in a not-poisoned heart. In both rhythms the T-oscillations are positive but those of the halved rhythm are larger than those of the twice as quick normal one.

During the halved rhythm the width of the R-oscillation in this



Fig. 9.

figure decreases from the first systole to the third included, and the height of the T-oscillation increases. A line of connection between the R and the T is not to be observed in this figure, because the T is immediately connected with the R.

Fig. 9 may still find a place here. This figure shows bigeminus-groups, after poisoning with veratrine, resulting from the falling away of every third auricle- and ventricle-systole. During the second ventricle-systole of each group the impulse-transmission through the ventricle is retarded more considerably than during the first. This appears from the wider R-oscillation of the second ventricle-systole. But the T-oscillation is much more negative, and the line of connection between the R and the T has descended much lower.

The bigeminusgroups, which I published in 1915,¹⁾ show likewise analogous proportions. The R-oscillation of the 2nd systole is here wider, and the positive T-oscillation smaller than that of the 1st systole of each group.

III. *The electrograms of the anticipated ventricle-systoles.*

With regard to this series of experiments a short communication will be sufficient. In a former communication²⁾ these were already mentioned and explained with figures. The anticipated ventricle-systoles were excited by extra-stimulation of the auricle, which brought about extra-systoles of these parts of the heart. After such an extra-systole the impulse proceeded along the atrio-ventricular systems of connection towards the ventricle, which consequently was brought to contraction at an earlier moment of the ventricle-period.

The place where the impulse enters into the ventricle at these anticipated ventricle-systoles, was consequently the same as for the normal periodical ventricle-systoles. For this reason there was no objection to compare the electrograms of these anticipated ventricle-systoles with those of the periodical ventricle-systoles. It is obvious, that the velocity of impulse-transmission through the ventricle during the anticipated ventricle-systoles was inferior to that of the periodical ventricle-systoles and the retardation was the more considerable according to a ventricle-systole being more anticipated. In accordance herewith the R-oscillation of the ventricle-electrograms of the anticipated ventricle-systoles was wider than that of the periodical

¹⁾ S. DE BOER: Die Folgen der Extrareizung für das Elektrogramm des Froschherzens. Zeitschrift für Biologie, Bd 65, 1915, Seite 440, Fig. 8.

²⁾ Koninklijke Akademie van Wetenschappen, Verslag van de gewone Vergadering der Wis- en Natuurk. afdeeling van 30 Juni 1917, Deel XXVI bldz. 422, and Proceedings Vol. XX page 404.

ventricle-systoles, and the wider in proportion as the ventricle-systole was more anticipated. The T-oscillation of an anticipated ventricle-systole changed in a negative sense, and the more so in proportion as the ventricle-systole was more anticipated. The line of connection between the R and the T had descended at an anticipated ventricle-systole, this descent was the more considerable in proportion as the ventricle-systole was more anticipated. At the post-compensatory systole these proportions were exactly the reverse. Then the velocity of impulse-transmission had improved, the R-oscillation was narrower, the T-oscillation had changed in a positive sense, and the line of connection between the R and the T had risen.

These short indications may be sufficient for the present. For further particulars one must compare the figures 6, 7, 8, 9 and 10 of my communication.¹⁾

IV. *Theoretical explanation.*

It has appeared most clearly from the three series of experiments described above, that there is a constantly occurring connection between the width (duration) of the R-oscillation (velocity of impulse-transmission through the ventricle) on one side and the dimension and direction of the T-oscillation and the level, on which the line of connection between the R and the T extends itself, on the other side. When the duration of the R-oscillation increases, then the T-oscillation changes in a negative sense, and the line of connection between the R and the T descends. If on the contrary the duration of the R-oscillation decreases, then the T changes in a positive sense, and the line of connection between the R and the T rises. The modifications that the T-oscillation is subject to, had already distinctly displayed themselves to me by the investigations I made in 1914. I think I am now likewise able to explain more explicitly the modifications, that the line of connection between the R and the T undergoes, and to bring in this way the above mentioned experiments under one point of view.

The normal ventricle-electrogram consists chiefly of an R- and a T-oscillation. Consequently we do not discuss here the Q- and S-oscillation, because the occurrence of these is of no importance whatever for our considerations. These R- and T-oscillations are caused

¹⁾ I intend to explain in a more circumstantial communication more elaborately the electrograms obtained after extra stimulation of the ventricle-basis and point. We can for this purpose compare the electrograms of the more and less anticipated systoles with each other, and not with those of the periodical ventricle-systoles (Vide Fig. 6, 7 and 10 of the former communication.)

by interference of the basal with the apical negativity. The upward-oscillation by which the ventricle-electrogram begins, originates, because the negativity of the basis begins or domineers in the beginning. A short time afterward the apical negativity begins (or the apical negativity increases) and brings the string back to the position of rest. Then there is for some time equilibrium between the basal and the apical negativity, and the string remains in the position of rest.

Thereupon the T-oscillation comes into existence; if this T-oscillation is positive, consequently in the same direction as the R-oscillation, this is caused by the fact, that the basal negativity lasts longer than the apical negativity, or because in the end the basal negativity domineers over the apical negativity. If the T-oscillation is negative, consequently in a direction opposite to that of the R-oscillation, then the apical negativity lasts longer than the basal negativity or then, in the end, the apical negativity domineers over the basal one. In Fig. 10 I have represented the origin of the R and the positive T by interference of the basal negativity $a-b-c$ with the apical negativity $e-f-g$. When now the velocity of impulse-transmission decreases, then the apical negativity will begin (or increase) later after the beginning of the basal negativity, and bring the string back to the position of rest. On account of the retardation of the transmission the position of rest is now reached at a later period.

The width of the R-oscillation increases thereby. But the other part of the ventricle-electrogram is likewise greatly influenced by the

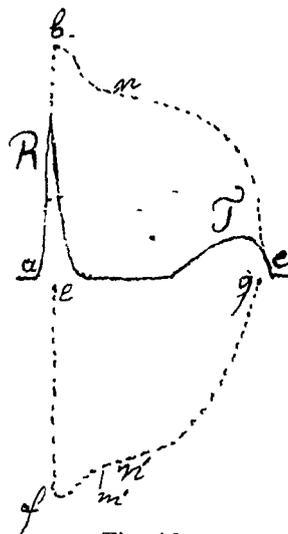


Fig. 10.

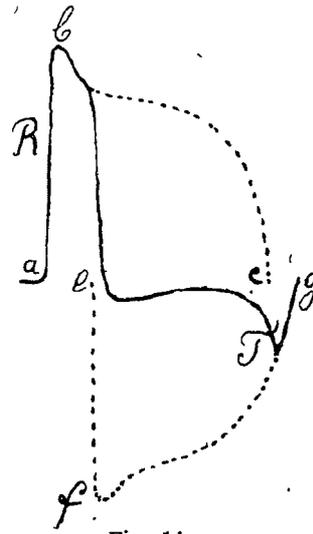


Fig. 11.

retardation of the transmission. The scheme of Fig. 11 may explain this fact. The basal and the apical negativity consist in this scheme of the same curves as those of Fig. 10, but the apical negativity has now removed more backward.

Point *e* is now much farther removed from *a* than in Fig. 10. What is now the consequence of this removal of the apical negativity? In the first place that at the end of the electrogram the apical negativity begins to domineer, and consequently the T becomes negative. If the retardation of the transmission had been less important, then this would only have reduced the positive T somewhat. But the line of connection between the R and the T has likewise descended. This is also to be understood. Whilst in Fig. 10 at a given moment the basal negativity *n* interferes with an equally strong apical negativity *n'* the string remains thereby in the position of rest.

When now, on account of the retardation of the transmission, the apical negativity is removed to the end of the electrogram, then the basal point *n* no longer interferes with *n'* but with *m'*, which is removed farther from the position of rest. This holds now for all points of the basal negativity after retardation of transmission. These interfere consequently all with stronger apical negativities than before the retardation. This is the reason why the line of connection between the R and the T descends. This simple construction teaches us, why at retardation of transmission not only the R-oscillation widens, but also the T changes in a negative sense, and the line of connection between the R and the T descends.

A clear illustration of the experimental data.

At an acceleration of impulse-transmission the R-oscillation will on the contrary become narrower and remove the apical negativity in a contrary direction i.e. to the front. Then each point of the curve of the basal negativity will interfere with a less important apical negativity than before the acceleration. The result is then a rising of the line of connection between the R and the T and an enlargement of the T as the scheme of Fig. 12 indicates.¹⁾

Still a few words about the height or

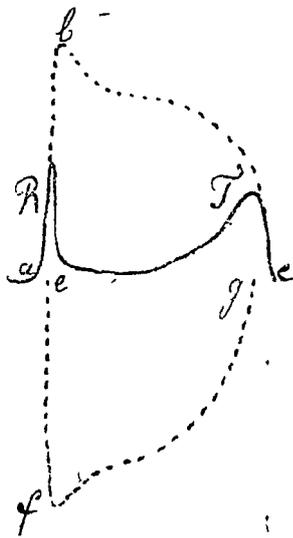


Fig. 12.

¹⁾ I have used in the scheme of Fig. 11 and 12 for the basal and the apical

the R. When the velocity of the impulse-transmission of the ventricle is so great, that apical negativity has already brought back the initial oscillation of the string to the position of rest, before the full basal negativity has developed itself, then the height of the R-oscillation possibly increases at a retardation of the transmission. These proportions are also reproduced in this way in the scheme Fig. 10.

If on the contrary the maximal basis-negativity has already been reached, before the apical negativity brings the string back to the position of rest, then a retardation of the conductivity will no more increase the height of R, but only widen its top. We find these proportions in the frog's heart after the hemorrhage.¹⁾ I hope to come back to this subject more elaborately in a more extensive communication.

It stands to reason that the shape of the ventricle-electrogram is not only determined by the velocity of impulse-transmission. In a former communication of mine I indicated the partial asystole of the ventricle as the cause of the modification of the shape.²⁾ Its shape can likewise change besides by the more or less monophasical deduction (by killing the heart-tissue under one deducting electrode).

I shall restrict myself in this short communication to a few remarks concerning the consequences of the views developed above.

In the first place about the atypical ventricle-electrograms. In these the proportions are as in Fig. 11 viz. a 'high, wide R, descent of the line of connection between R and T and a negative T. In such an electrogram the apical negativity has consequently been removed backward³⁾. This can be caused by retardation of velocity, but in casu the longer distance that the impulse has to cover, will most likely be the cause. In the light of these experiments the shape of the atypical electrograms is conspicuous to us.

components the same as in Fig. 10. It is obvious, that at modification of the velocity of impulse transmission these two components are likewise modified. As these modifications are for in an equal sense, the results are after all as reproduced in Fig. 11 and 12.

¹⁾ Zeitschrift für Biologie, Bd. 65, Seite 428.

²⁾ Archives Néerlandaises de Physiologie de l'homme et des animaux, Tome I, p. 29, 1916 and Zentralblatt für Biologie, Bd. 30, Seite 149, 1915.

³⁾ For the question under consideration it is of no importance, whether we have to do here either with the basal and apical negativity or with the negativity of the left- and the right-ventricle. When the two negativities coincide less, because one of the two commences later, then the atypical shape of the ventricle-electrogram sets in.

In the second place vigorous hearts have a large positive T-oscillation. This is likewise easy to understand, as vigorous hearts possess a good conductivity.

There exists moreover a strong overlapping of the basal and the apical-negativity, and consequently the basal negativity is at the end strongly expressed.

Finally the considerable variability of the T-oscillation is determined in this sense by the velocity of impulse-transmission as has been explained above.

These short remarks may suffice here. I intend to explain these and further results of these experiments in an ulterior more elaborate communication.

Amsterdam, Oct. 1917.

Physiological Laboratory.

Physics. — “*Researches into the Radio-Activity of the Lake of Rockanje*”. By Miss H. J. FOLMER and Dr. A. H. BLAAUW.
(Communicated by Prof. HAGA).

(Communicated in the meeting of September 29, 1917).

§ 1. *Introduction.*

In a treatise on the Lake of Rockanje ¹⁾ ²⁾ I have communicated that an inquiry into the radio-activity of the samples collected by me was being made by an expert. Now that this inquiry, carried out by Miss H. J. FOLMER in the Physical Laboratory at Groningen, has led to fixed results, we wish to bring them before the public. I shall begin with a short explanation from what considerations this inquiry has been planned and elaborated so amply.

When in July 1915 I began my researches into the flora and history of the origin of the Lake of Rockanje I got acquainted with Dr. BUCHNER's researches, which showed what a surprisingly strong radio-activity the latter had found in the Rockanje mud according to his publication in the *Chemical Weekly*. ³⁾ Subsequently Dr. B. G. ESCHER communicated to the Geological Mining Society a report ⁴⁾ made in April 1914. ESCHER discerned in the Rockanje mud organic and mineral parts and came to the hypothesis that the mineral parts and together with these the radio-active substance, had been blown into it from the dunes. In the said meeting and in the above mentioned treatise I have already pointed out that the large mass of mineral substance is nothing but clay, which has settled on the bottom of salt and brackish water in the form of fine slime and mixed with many organic remains.

If, therefore, this mud were so radio-active there would be a far greater chance that radio-active parts had been carried there as slime by the rivers from the mountains of Central-Europe, than that

¹⁾ The Lake of Rockanje in the Isle of Voonne, which forms part of the province of “Zuid-Holland”. It is situated near Hook of Holland, separated from it by the Isle of Rozenburg.

²⁾ A. H. BLAAUW (1917) *Treatise*. Royal Acad. of Sciences Amst. 2nd Section XIX N^o. 3.

³⁾ E. H. BUCHNER (1913) *Chem. Weekly*. Part 10 N^o. 35.

⁴⁾ B. G. ESCHER (1915) *Report Geol. Mining Soc. Gen. Geol. Section Part 2*.

they should belong to the small quantity of dust from the dunes carried into the lake by the wind. But as it must be very well possible to make out by radio-active measurements of samples from the soil, whether the radio-active substance present in that soil had entered into it from the side of the dunes or rather from the side of the slime-carrying rivers, I thought that it was better experimentally to settle a question which was geologically so important.

For that purpose I have collected a great number of samples as will be mentioned below. After Dr. BÜCHNER informed me, in answer to my letter, that he did not intend to continue these researches himself, I was happy enough to find Miss H. J. FOLMER at Groningen willing to undertake them. Consequently this communication is chiefly the result of researches made by her at Groningen.

First samples 2, 4, 6, 8, 9, 10, 11, 12, 13, 17, 20, 23 were destined for inquiry, taken from the boring made at Rockanje. From these it was to appear in what layer the activity was strongest, after that the geological constitution of those layers and the conditions under which they had been thrown down, had already been discussed before in detail. Samples 20 and 23 are, however, from layers which existed long before the origin of the Lake and of the isle of Voorne¹⁾. These samples are called: boring 2, 4, etc.

To these others were added:

R. Taken 25 m. to the North East of the Grotto at 40 cm. depth, consisting of brown, entirely organic mud mixed with some grains of quartz of at most 150—300 μ length.

A. Taken from the bottom of the water, on the side of the Noorddijk, behind the Windgat, where formerly the dike often burst, on the North West side²⁾.

B. Taken from the bottom of a ditch close to the Molendijk in the Strijpepolder, in order to examine whether the mud at a short distance from the Lake is still strongly active.

C. Sand taken from the dunes nearest the Lake (at \pm 800 m. distance) whereabouts formerly the Swyn was situated.

D. Light-grey clay, taken at 25 cm. under the meadow of the Drenkeling behind the Vleerdam Dike of the Lake.

M. Slime, freshly settled, from the Meuse at Grave, which Mr. J. DEN DOOP from Grave kindly provided me with.

¹⁾ Cf. treatise pp. 50—55.

²⁾ Cf. treatise pp. 90—93.

W. Slime, freshly settled, from the Waal at Nymegen, sent to me by the kind interference of Dr. P. TESCH.

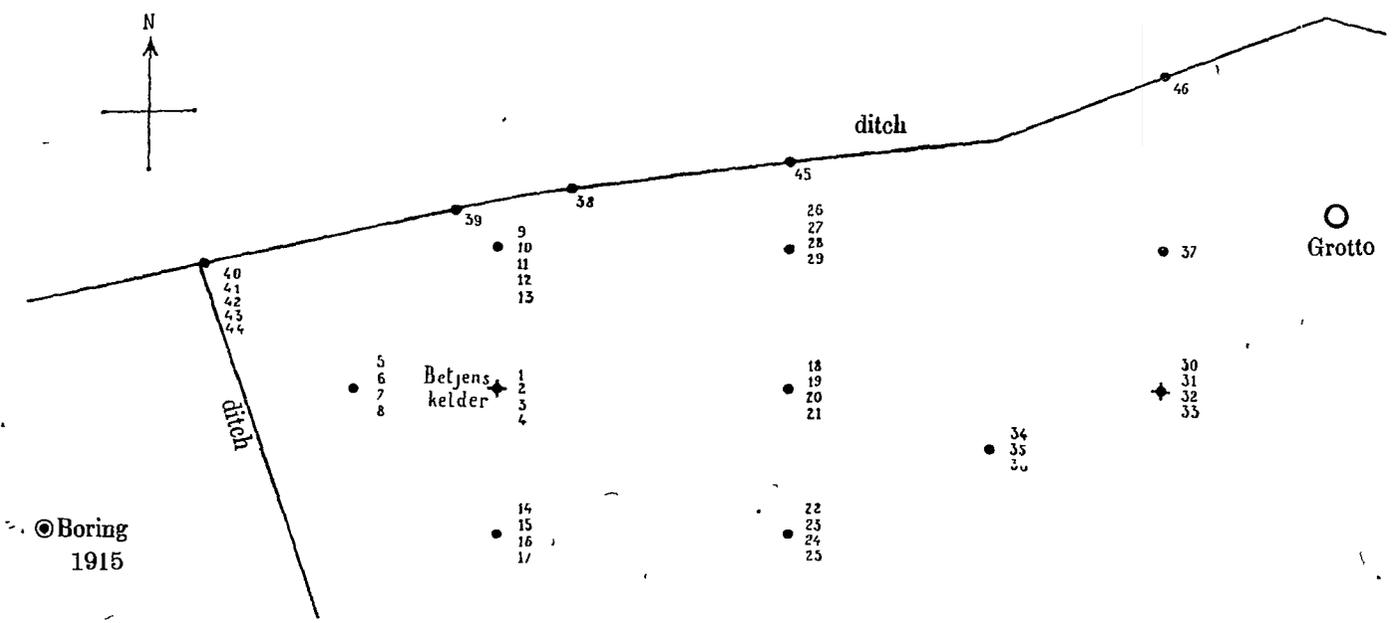


Fig. 1.

Sketch of the shallow borings. Scale $\frac{1}{1340}$.

- = spot of borings; the numbers indicate the samples.
- ◆ = two spots where, besides, samples I, II, and III had already been taken before

These seven samples enable us to compare:

1 the mud of the Lake with that of the environs.

2 the Rockanje mud with neighbouring dunesands and with the slime from the Meuse, the Waal, consequently from the Rhine and Meuse basins.

For purposes of comparison Miss FOLMER still added mould from the garden round the laboratory at Groningen and Fango of Battaglia and of an unknown find-spot.

After this series had been investigated it appeared from reasons to be mentioned below, that it was indeed necessary to extend the number. First Mr. TROUW at Rockanje kindly sent us three samples taken from the same spots where Mr. BÜCHNER collected the samples in 1913, which he found so extremely radio-active.

These samples are called:

I (about 50 m. to the South-West of the Grotto at a depth of 150 cm.)

II (from the South-East Corner of Betjenskelder 60 cm. deep)

III (ibidem 150 cm. deep).

In conclusion we were obliged to collect yet another series of samples scattered over the whole area and at various depths. To that end I have chosen the spots so as to include entirely the area of the spots from which samples had been taken already, which were said to have shown radio-activity by means of radiograms or emanation (cf. fig. I). They were collected 1 from 10 spots at and about those places where the radio-active samples were collected in 1913 (see above) and besides from 5 spots from the bottom of the ditch that skirts the area of the Lake and Betjenskelder on the North. From these 15 spots 46 samples were taken at different depths varying from 30, 60, 90, 120, 150, and 180 cm. All this is sufficiently indicated in the figure together with the numbers of the samples. We have taken these samples by means of a boring machine 2 m. long, consisting of a tube of galvanized iron. Its stock can be pushed through these layers of clay and peat. To the bottom is attached a box in the shape of a hollow cylinder, on the flattened side of which is a slide, which can be opened by means of a thin rod, running upwards through the iron tube; this slide, therefore, can be opened at the top and fastened by a screw, after the boring machine has been placed at the required depth. With the crank at the top of the tube one turns the whole thing round a couple of times, unscrews the slide-rod, closes and fastens the slide again and draws the whole upwards. In this way we made perfectly sure that we drew up only mud from the depth as wanted. These samples Miss FOLMER put

away into small tins shut off by insulating tape, and took them to Groningen for immediate investigation.

Finally a couple of samples, the radio-activity of which was said to have manifested itself by means of radiograms, were added to these; and yet: two other samples 1. dregs of sulphur-bacteria 2. very wet mud from the ditch that skirts the lake. All these samples were investigated by Miss FOLMER, who will describe below more fully her mode of working and the results.

§ 2. *Measurements.*

The researches, the desirability of which was demonstrated by Dr. BLAAUW in his Introduction and which in connection with the experience obtained in the course of the experiment were constantly enlarging, can principally be reduced to the two following parts:

I. To this belongs the investigation (cf. Introduction) concerning the 12 samples of boring, the 7 samples for comparison, the samples I, II, and III, the Fango of Battaglia, already long known to be radio-active and finally the sample: mould. All these have been investigated according to the "emanation method", of which further details will follow below.

II. In contradistinction with the preceding the "direct" measuring method defined more closely below, was yet applied to the second series of experiments in which the emanation obtained from the mud was not investigated, but the mud *itself* with regard to radio-activity. This second series of experiments principally extended over the 48 mud samples (cf. Introduction), all of them taken from the neighbourhood of the Betjenskelder or from the Betjenskelder itself.

A closer consideration of researches I and II may set forth the motive for these two series of experiments performed at such various times, as well as the different choice of methods of investigation.

Part 1.

Description of the investigation according to the "Emanation method".

Here the first part certainly is the laborious dissolving of the various samples for which I used the method as indicated in outline by various investigators.¹⁾ 150 grammes were taken from each sample after having been dried by a slight heat, then sifted minutely and shaken forcibly for five minutes; then 5 grammes of this were

¹⁾ Cf. for this: B. B. BOLTWOOD, Phil. Mag. 1905. J. JOLY, Radioactivity and Geology, 1910. E. H. BUCHNER, Chem. Weekly 1913.

glowed carefully; after having been weighed the remainder was extracted by hydrochloric acid, which was first distilled over chemically pure salt. After this treatment it was filtered, through which a part of the solution to be made, viz.: the acid solution had been obtained. The filter was burnt, the ashes with the dried residue mixed in a platinum crucible with 5 grammes of Na_2CO_3 and 5 grammes of K_2CO_3 .¹⁾ The amalgamation of this mixture took place in a small electric furnace heated for this purpose to about 800 degrees for at least three hours.

Subsequently this melt of molten mass was extracted by water and filtered in such a way that a perfectly pure alkaline solution was obtained. The remainder was dissolved in strong hydrochloric acid and added to the acid solution obtained first, the alkaline solution being preserved separately. If, however, not everything was dissolved completely, it was filtered once more, the residue amalgamated with only a little carbonate and treated again as mentioned above; finally these acid and alkaline solutions were added separately to those prepared first. The solutions obtained i. e. of each sample an acid and an alkaline, were shut off air-tight in a one-litre boiling flask of Jenaglass and put away in order to await the emanation equilibrium, which is almost perfect after 50 days. Even after this time the solutions were still found in an entirely clear state and consequently the chance of occlusion for the formed emanation into a gelatinous precipitate, was absent.

As a second part of the investigation now followed the expulsion of the emanation, which was brought about with the assistance of an arrangement with which the various solutions were made to boil and from which in consequence the emanation could develop itself. This together with the escaped gases — the vapour was condensed in a cooler — were caught into a reservoir over a saturated salt solution. From this the emanation was transferred to a jar communicating with a second in order to make the absorption of gas possible, then all the tubes were rinsed again with air and at last the top of the jar shut off. The emanation which was again present here over a saturated salt solution, was then ready to be investigated electrically.

Hereupon followed the third and last phase of the investigation, viz: the measurement of the ionisation current, caused by the emanation described above. For these electric measurements as well as for those according to the "direct method", the electrometer was

1) Provided by KAHLBAUM "pro analyse" with "Garantieschein."

used by me the principle of which was published in 1914,¹⁾ while the description of the apparatus followed in a second article.²⁾

The method of measuring I arranged as follows:

Before making the solution boil the electrometer was given a definite not over-sensitive state of charge and that: $a + 12$ Volt, $b 0$ Volt, c upwards of -4 Volt. The ionisation cylinder was charged to $+80$ Volt.³⁾ Having attained this, the natural leak in the measuring cylinder was examined a couple of times. The time was so fixed as to make 10 scale-divisions move under the cross wire until the total of one hundred divisions were passed through; this happened in order to be able to include into the calculation the natural leak, when measuring the samples. After this the ionisation space of the apparatus was exhausted, making use of GAËDE'S new single barrel airpump;⁴⁾ with this it was possible to exhaust the space of the measuring cylinder of a volume of 1 litre with the indispensable rubber tubing and manometerspace down to two mm. pressure. The emanation present in the bottle, after having been conducted through drying-tubes with CaCl_2 , P_2O_5 , and a tube with cotton wool, was transferred to the evacuated apparatus. After having awaited the equilibrium of the emanation with the radio-active products, radium *A. B. C.*, so after about 3—4 hours, the measurement proper took place as follows: the time was fixed in which the image of the scale moved under the cross wire, but now, in contradistinction with the determinations just given, over 150 scale-divisions; as this measurement did not last for more than 5 minutes for a sample that is but little active, and also the preceding, viz: that of the natural leak took comparatively little time, the advantage had been obtained by repeating the measurement a couple of times, to be able to include into the average calculation a more exact final value. Herewith the determination proper had come to an end and the radio-activity of the substance could be computed by taking an experiment of the same kind with a normal solution of radium. This I obtained from a quantity of radiumbariumbromide supplied by Messrs. DE HAËN in Hannover, containing 0.0126 m.grammes of radium according to notification.

Here follows, by way of explanation, a calculation of one of the samples examined, viz: N°. I from Betjenskelder.

a. Determination of the natural leak.

1) Royal Acad. of Sciences. Amsterdam. Proceedings of June 1914.

2) Royal Acad. of Sciences. Amsterdam. Proceedings of September 1917.

3) Royal Acad. of Sciences. Amsterdam. Proceedings of June 1914.

taken from 658—600. The latter, obtained in the same way, indicated a displacement from 750—600 in exactly 23.0 seconds.

In order to derive in how much time this normal solution will ionise from 658—600, the ratio of the average sensibility of charge of the distance 658—600 of the scale to that of 750—600 had to be still defined. For this determination I made use of a special experiment taken very accurately and which was of equal importance for the calculation of all the other samples. This consisted in examining the ionisation of a substance of which the ionisation was not too small, from scale-division 750—600, and that in such a way, that the time was continually checked which was wanted for passing through 10 scale-divisions. The values in seconds amounted from 750 to:

first determination: 21, 23, 24, 20, 22, 31, 24, 20, 24, 29, 32,
27, 31, 33, 34.

c. second determination: 31, 27, 29, 21, 25, 25, 29, 26, 30, 25, 36,
34, 34, 28, 28.

From this follows that the charge wanted to displace the needle from 658—600 amounted to $180/411$ of the value, which applies to parts of the scale 750—600. Then the real ionisation time of the normal solution for 658—600 was: $180/411 \times 23 \text{ sec.} = 10.1 \text{ sec.}$ Consequently the sample was $416/10.1 = 41.2$ times weaker than the other, so that every gramme of the sample contained: $\frac{1.25 \times 10^{-10}}{5 \times 41.2} = 0.61 \times 10^{-12}$ grammes of radium. In this way the values for the radio-activity of every sample of part I have been derived ¹⁾.

¹⁾ The calculation might yet be executed somewhat differently and that with the aid of ionisation values of *only* 100 scale-divisions, e.g. of 750—650, and this for a natural leak, emanation as well as for normal solutions, for from the data as given above follows (cf. b) that the substance ionises from 750—650 on an average in 4 min. 16 sec. or 256 sec., whereas the natural leak (cf. a) ionises over the same space in 7 min. 40 sec. or 460 sec. From which follows that the natural leak together with that of the emanation would ionise in 460 sec.

$\frac{460}{256} = 1.8$ time over that part of the scale, (only suppose for the calculation of the sensibility of charge constant from 750—650), so *only* the emanation 0.8 time over that part mentioned in that time. For the final calculation we then derive from c, that the normal solution, that ionises in 23.0 sec. from 750—600, displaces the needle from 750—650 in $\frac{253}{411} \times 23 \text{ sec.} = 14.1 \text{ sec.}$, consequently in 460 sec. $\frac{460}{14.1} = 32.6$ times ionises over the division of the scale mentioned. Finally there

follows from all this that the activity of the normal solution is $\frac{32.6}{0.8} = 40.8$ times

The results obtained are communicated in the subjoined table.

TABLE I.

Indication of the samples	Soil	Depth in Metres	Radio-activity expressed in 10^{-12} gr. rad. pr. gr.
boring 2	lightgrey mud with remains of peat	2.70	0.43
" 4	grey mud and dark clay	4.40	0.54
" 6	grey-black clay	6.05	0.55
" 8	blue-black clay	7.40	0.61
" 9	black fat clay	8.30	0.78
" 10	black mud	9.30	0.66
" 11	bluish-grey clay with grains of sand	9.55	0.62
" 12	blue-black clay	10.50	(2.16)
" 13	black clay with remains of peat.	12.90	0.64
" 17	sand with little slime	\pm 13.50	0.1
" 20	light-grey clay	21.20	0.75
" 23	sand	24.80	0.36
" 23			0.37
A	brown-black peaty mud	—	0.39
B	clay	—	0.78
C	sand of the dunes	—	0.23
D	light-grey clay	—	0.59
M	slime of the Meuse	—	1.09
W	slime of the Waal	—	1.49
R	brown organic mud	0.40	0.24
mould	—	0.96
No. I	blue-black clay	1.50	0.61
No. II	brown-grey clay	0.60	0.49
No. III	blue-black clay	1.50	0.57
	Fango of Battaglia	—	34.0

stronger than the substance investigated. The first calculation is preferable as in it the ionisations could be examined over a larger number i.e. over 150 scale-divisions. Even then the second calculation could be applied, if also the natural leak had been examined down to 600. This, however, is difficult in connection with the length of time of observation, if one makes several and very accurate observations.

From this table it is clear amongst other things that the investigated samples of the boring, as well as those of the Betjenskelder or its neighbourhood only show a radio-activity in the order of 10^{-12} grammes of radium pro gramme; i. e. no larger quantity than is normally found in most rock ¹⁾. The activity of mould is of the same order, whereas only the sample of comparison: Fango exhibits an effect considerably higher. Notwithstanding this small radio-activity, however, it shows in relation to the depth and the nature of the layers, a certain regular course as may appear more distinctly yet from the geological interpretation of the results by Dr. BLAAUW as mentioned below ²⁾. The two values for N^o. 23 which agrée within the limits of errors of observation, relate to the values of activity of two solutions, made and investigated at quite different periods. Having arrived at the end of these experiments we could not but conclude that our results did indeed contrast greatly with the values for samples of mud from the Lake as indicated by Dr. BÜCHNER in 1913; he even found a value of 462×10^{-12} grammes of radium pro gramme in the blue mud from the Betjenskelder.

At the very moment that these researches had proceeded thus far, a circumstance intervened, which especially has been the occasion of our resolving not yet to consider the experiments as being finished; on the contrary: to continue them in a yet more extensive way. From Utrecht Prof. ZWAARDEMAKER sent us two samples of Rockanje mud; from one of these, which Prof. ZWAARDEMAKER had received in 1913 from Mr. TROUW at Rockanje, the radio-activity had been clearly shown in the Utrecht Laboratory, because they had succeeded there in obtaining radiograms through this sample. After all that preceded it was certainly remarkable that, according to the "direct method" of investigation (Cf. Part II) I could determine that this sample certainly possessed radio-activity $1\frac{1}{2}$ times that of Fango of Battaglia. In order to find out whether we might have been mistaken with other samples, Dr. BLAAUW investigated this sample with regard

¹⁾ In the table the values for activity only apply to those of acid solution; in the alkaline solutions, even in the Fango I could find no activity. An experiment with only chemical substances was made to check this with a solution which contained the quantity of chemical substances only necessary for each experiment; also this had a negative result.

²⁾ It is of importance to remark here, that very little information has been given up to now on the relation of the quantity of radium to the depth under the surface of the earth. However, experiments showed no relation. Cf. A. F. EVE and D. Mc. INTOSCH, Trans. Roy. Soc. Canada 1910; E. H. BÜCHNER, Jahrbuch Rad. u. El. 10, 1913; H. E. WATSON and G. PAL, Phil. Mag. 28, 1914.

to Diatoms after which he could ascertain that it was certainly mud from Rockanje and that from a layer agreeing with samples 4 to 6 from the deep boring. Thus the Fango of Battaglia was investigated and it appeared that this is also recognisable by a definite kind of Diatoms. The Diatoms as "characteristic fossils" could again be of use here. When, therefore, the strong radio-activity of the mentioned sample had also appeared in my case, we passed on to a second enlarged investigation with the purpose of obtaining "yet closer indications about the question that concerns us here. This research contains the second series of experiments arranged higher up under Part II (Cf. also Introduction).

Part II.

Description of the method of inquiry, viz.: the "direct method". This is principally to the effect that a part of the dried mud is weighed and placed into the ionisation-space; the radio-active substances, so not *only* the emanations present in it, cause ionisation of the air, which is again measured. This method, introduced already by ELSTER and GEITEL for definitions of the radio-activity of rock and soils and at present still used for these, among others by Prof. GOCKEL in Freiburg, has, however, been disputed on various grounds¹⁾ and it unquestionably has considerable drawbacks as a measuring method; among others this, that when applied as above mentioned it is not possible to obtain an absolute definition or mutual comparison of the quantity of radium, nay a mutual comparison of the activity as a whole cannot even strictly be carried out. For the ionisation may be the consequence of radium and its radio-active products, but at the same time of thorium and other active substances, the rays of which ionise in a very unequal degree. Then, the absorption of the rays is also disturbing, because it gives differences, for the various substances as well as for the divers radiations. Overagainst this we may, however, mention as a very important advantage of the "direct method", that we can get on with it so much quicker; no protracted chemical operations are required as in the case of the emanation method; with the electric measurement we need not await the formation of the equilibrium of the substance employed with the radio-active products to be formed by it. Thus the measurement will only take Prof. GOCKEL an hour, without mentioning the preceding, necessary determination of the natural ionisation. With the use of a sensitive electrometer, however, this advantage is shown more favourably yet. Thus it was possible for me to examine 40 samples

¹⁾ Cf. E. H. BUCHNER. Jahrbuch Rad. u. El. 1913.

quite accurately in 5 hours, among which occur several measurements which were repeated sometimes for the sake of a greater certainty ¹). Nor was it necessary for me to glow the substance before measuring its ionisation. Prof. GOCKEL, namely, experienced the disadvantage that during the hour of the measurement emanation escaped, the radio-active products of which settled on the sides of the vessel, thus causing the ionisation to grow stronger during the measurement; as several circumstances, a. o. the nature of the substance, are of great influence on this so-called "emanating", GOCKEL tries to avoid this difficulty by glowing the substance beforehand, or: to deprive it of all emanation present. This is an uncertain procedure, which BÜCHNER has already pointed out (cf. note p. 725) and I think it is also preferable not to shut out its activity, if the substance should contain some emanation. This is possible if the measurement is but short, as in that time the quantity of escaped emanation need not be taken into account. In my opinion both methods have great value and the importance of the "direct method" should not be underrated; first because of the advantages mentioned in order to determine the order of radio-activity, as in the case of the samples of Part II, by a speedy inquiry, but secondly to penetrate deeper into the radio-active phenomena of the substances itself. It will never be possible to say beforehand what radio-active products, perhaps new ones, one may happen to meet, or whether, as Prof. GOCKEL also remarks, all the products are indeed present, which arise from a series of active substances the emanation of which is found according to the emanation method. With the help of absorption experiments and especially in very accurate measurements it seems to me that especially in the future this method may become of very great value.

In order to complete the above brief description of the method, I may add the following: first of all the placing of the samples into the ionisation space was done in a particular way. Prof. GOCKEL describes the difficulty occurring in his case, viz: that in the space of experimentation a fresh supply of air will always penetrate, which in itself will modify the ionisation. In order to avoid this disturbance the electrometer employed by me was provided with a special

¹) It is important to remark here that a sensitive measuring method, "direct" as well as indirect, possesses advantages over an insensitive one; where up to now, many investigators use the latter, this will explain, though only partly, the remarkable fact that as regards the measuring results of various observers one meets with so much contradiction, where determinations of the radio-activity of similar material are concerned.

closure.¹⁾ When in one of the basins of diameter $11\frac{1}{2}$ cm, 50 grammes of the dried substance were strewn equably, it was possible in a very simple way to exchange the basins without allowing the air to enter the ionisation space. As to the electric measurement, for this the ionisation time was only determined for 50 scale divisions over the same part of the scale. This was subsequently done with all the samples, the results of which are given in the table below; only the ionisation time is mentioned in it as, because of the above-mentioned reasons, a proper calculation of activity will not be possible. Yet the various ionisation times will approximately denote the different values of activity. For a closer meaning of the numbers cf. Fig. 1.

In order to be able to form a somewhat more accurate notion of the order of radio-activity with which such ionisations agree, I have, while supposing among others that the absorptions of the various samples are the same and, besides, that they only contain radium, traced the calculation of activity for sample I (cf. table 2) namely by comparing the ionisation time of I with that of the Fango of Battaglia. It should be taken into consideration here, that the natural leak will also give its share to attain these effects, so that in reality the ratio of the activity of the Rockanje mud to that of the Fango is still less than one might think one could derive directly from these figures. Thus I found N^o. 1 to contain 1.1×10^{-12} grammes of radium pro gramme; i. e. 1.8 times a larger value for this sample than follows for this sample from the emanation method (cf. Table I). That these values do not agree, might partly be caused by the fact that the sample in question contains at the same time thorium. Many minerals are even exempt from radium, whereas they contain a large amount of thorium.

So also this second comprehensive series of experiments had not disclosed an appreciable radio-activity for any of the samples. This notwithstanding, we did not yet consider our experiments as having come to an end and that in connection with the assertion uttered on various sides that radiograms had been obtained by means of Rockanje mud; this had been the matter with the already mentioned sample 1913 and with two samples forwarded by Dr. REYS from the Hague. These samples were investigated, both electrically and photographically; it was already mentioned that according to the first

¹⁾ Cf. also for the drawing: These Proceedings, p. 684. The closure principally consists in this, that instead of the circular bottom plate a ring is fastened to the ionisation cylinder carrying two ways over which 2 metal basins can slide, which alternately form the bottom of the ionisation space.

T A B L E 2.

Number	Depth in cm.	Ionisation time in sec.	Number	Depth in cm.	Ionisation time in sec.
1	90	178	24	150	93
2	120	116	25	180	66
3	150	88	26	90	152
4	180	125	27	120	104
5	90	150	28	150	115
6	120	150	29	180	117
7	150	78	30	60	161
8	180	100	31	90	121
9	60	150	32	120	90
10	90	88	33	150	87
11	120	90	34	90	95
12	150	100	35	120	91
13	180	100	36	150	95
14	90	163	37	60	173
15	120	122	38	60	182
16	150	99	39	60	143
17	180	123	40	60	125
18	90	159	41	90	82
19	120	133	42	120	78
20	150	77	43	150	74
21	180	96	44	180	127
22	90	105	45	30	209
23	120	107	46	30	187
Sample I		130	Sample II		136
Sample III		120	Mould		80
Fango of Battaglia		18			

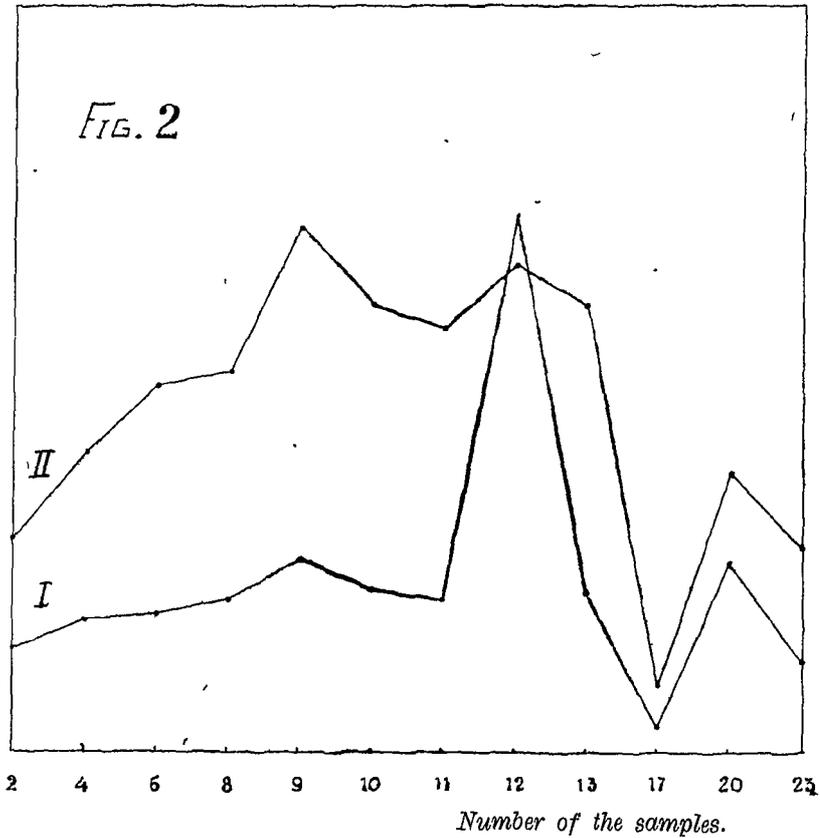
method sample 1913 showed a stronger radio-activity than the Fango. The two other samples, however, could again be ranged under the order of 10^{-12} grammes of radium pro gramme.

But also photographically these and other samples were investigated

with regard to their action. Prof. H. HAGA was willing to undertake the radiogram experiments at our request, of which the results were as follows: The experiments were made in the usual way in which the photographic plate in a black envelope is exposed to the action of the substance to be investigated; in order to be able to state an eventual action some parts of the plate were protected by placing some small metal discs on the envelope, or metal pieces with figures cut into them. In using "Schleussner Röntgen-plates" only a very small action was obtained after a nineteen days' exposure from Fango. Dried mud of Rockanje N^o. 12 and mould would have no action at all. In using "extra speedy Wellington" plates a very strong effect was obtained after a 30 hours' exposure with Uranium-pitchblend, a very weak one with a strip of Uranium glass and no effect at all with a quantity of Rockanje mud 1913. No more was any action obtained after 44 hours by strewing the black envelope with the whole quantity of the last mentioned samples or after a week's exposure with the above-mentioned samples from Dr. REYS. The same negative result was arrived at in experiments in which for a week Schleussner-Röntgen-plates" *without the wrapper* had been placed over a layer of Fango or mud at ± 1 mm. distance or had also been strewn with these substances.

These results agree entirely with the photographic action on radio-active substances as described in the literature on the subject. In such photographic experiments one trial experiment should always be taken with a plate from the same pack without any substance strewn upon it, and one should always be careful with the so-called black paper, some kinds of which transmit a sufficient quantity of daylight to obtain a misleading effect. As the photographic experiments had again given a negative result, there only remained to us to set forth more clearly one side of the question. It has namely been thought that there might exist a relation between organisms and accumulation of radio-activity, when BÜCHNER's definitions of the radio-active intensity of the Rockanje mud were known. As, according to this investigator, radium probably occurs in mud as RaSO_4 , and so many sulphur-bacteria live there, whose sulphur-reserve is oxydated by respiration, so that sulphates again are dissolved into the water, it seemed desirable to us to examine bacteria-dregs and watery mud from the ditch as to their activity. For this purpose Dr. BLAAUW once more took two samples and sent them to me, mixed with much water. The research took place both according to the "direct" as well as to the emanation method. As regards the latter, no emanation equilibrium was awaited, but only the quantity

of emanation present extracted by boiling. If Fango was treated thus, very strong ionisations could again be observed. I shall not mention all the values obtained according to the various methods;



let it suffice to mention here, that also in this case the figures pointed to a radio-activity not exceeding that of 10^{-12} grammes of radium pro gramme.

Finally I will mention one very important experiment taken with the various samples of boring (cf. Part I). From the "conclusions" which Dr. BLAAUW has derived from my data one may notice how he could entirely account for the course of the radio-activity in the series of the borings. I thought it desirable also to apply the "direct method" to these samples of boring to wind up my researches. The result will be found represented graphically in curve II of Fig. 2, whereas curve I fixes the values mentioned in table I according to the emanation method. The conformity in the course will strike one: with the exception in the case of N^o. 12 there occur in both curves corresponding fallings and risings. As not only the quantity of radium influences the values of the "direct method"

(cf page 725) it is certainly remarkable to have to gather from these curves that either these substances contain only the active radium or that also the other active substances in it must show the same course as that element.

Besides, this conformity in the results of the two methods may be looked upon as a valuable check of the one upon the other.

But to what cause do the different values for sample 12 point? One could notice already that this sample is much more active than any of the others in series I, but again looking up the notes taken when I investigated these various samples electrically, I found that it was just for this sample that a very strange course was mentioned of its behaviour with regard to the radio-activity during the day of its measurement. Though, however, N^o. 12 only contains 2.16×10^{-12} gr. of radium pro gramme yet the above mentioned fact considered by itself will be the motivé that this sample will be subject to further investigation.

If then, having come to the end of all the mentioned experiments, we recapitulate results, we will see that neither the electric research, according to various methods, nor the photographic research have disclosed any appreciable values for the radio-activity of the Rockanje mud. The only exception to the large quantity of samples is sample 1913, but, as it did not come to us straight from Rockanje, but was kept in the Utrecht-laboratory for 4 years, we need not take it into serious account.

Our final conclusions from these researches can only be that in our opinion the Lake of Rockanje possesses no radio-activity of any importance.

§ 3. *Conclusions.*

After the detailed researches described above by Miss FOLMER there is no occasion left to me to seek geological explanation for an especially strong, local radio-activity, for not one of the samples shows an action which would be ± 100 times stronger than those of igneous rocks (Cf. BÜCHNER 1913, ESCHER 1915) and all the samples have an activity as has generally been found in soils of the kind.

But though the occasion for further inquiry into an hypothesis for the explanation of a strong local activity may be disregarded by me, I yet want to point out that it is now that this question becomes generally of importance: where do the radio-active parts come from which are found in the alluvium (or in a more general sense in the ground)? In this I will not venture too far on a territory with which others are so much more familiar and better entrusted

and I will only point out some conclusions to be drawn from the values found by Miss FOLMER. This is all the more important, because we are concerned here for the first time with a great number of determinations of radio-activity of a geologically amply described country.

As has been fully described in the treatise (pp 29—31) we are concerned here with clay, organic material, and sand. In the microscopic investigation into the organisms of the samples I have always mentioned the greater or smaller presence of mineral dust, organic remains and grains of sand, together with their size. Of course, it may not be lost sight of that mineral dust need not exclusively be slime from the rivers, but that also part of it may come from the dunes. And the more we meet with grains of quartz in the layer, the greater the chance will be that also part of the finer mineral dust originates in the dunes or the bottom of the sea. Reversely, very small grains of quartz are thrown down in the slime, for in the freshly settled slime of the Meuse and the Waal they are to be found in a small quantity; I shall leave undecided whether they have been blown into it, carried along or rooted up. Yet it is very well possible to conclude from all the figures Miss FOLMER has given, to which of the three mentioned elements: clay, organic remains, or sea- and dunesand the radio-active parts belong.

The quantity of radio-active substance varies in the 24 samples: boring 2, 4 etc. A. B. C. D. M. W. R. I. II. III in 14 of the 24 cases between rather narrow limits: 0.49 and 0.78×10^{-12} gr. of radium pro gramme dried substance.

The following samples possess a lower number:

Boring 2 with 0.43×10^{-12} grammes. Besides fine mineral dust and a few grains of sand of 200—300 μ length at most, especially much organic material.

Boring 17 with only 0.1×10^{-12} grammes. Consists of blue-grey sand (sand with little slime).

Boring 23 with 0.36 and 0.37×10^{-12} grammes of sand; the grains of sand in this sample are at most 450 μ long. Mixed with very fine mineral dust.

A with 0.39×10^{-12} grammes. According to notes in 1915: excessively rich in Diatoms; a great many organic remains, little mineral dust".

C with only 0.23×10^{-12} grammes. According to notes in 1915: "very regular sand without any organic mixtures.

R with only 0.24×10^{-12} grammes. This sample is the same as that described in the treatise p. 17 under No. 2: "brown mud"

where no admixture with the blue-grey mud had as yet taken place; it consists *chiefly of remains from plants and animals* with a few grains of quartz of at most 150—300 μ length.

A higher number was found for the following samples:

Boring 12 with as many as 2.17×10^{-12} grammes. This is the highest amount that has been found. "Blue-black" clay; "consists of *very fine mineral dust*, mixed with very *few* grains of sand, at most 80—120 μ long; *few organic remains*. (Treatise p. 38). Neither is there any sample in this series in which the very fine mineral dust is mixed with so little sand and organic material. It was also pointed out that there was a resemblance between the Diatoms to those from the slime of the Meuse near den Briel. (Treatise p. 51). *M* with 1.09×10^{-12} grammes. *W* with 1.49×10^{-12} grammes.

I think that from this will appear that the quantity of radio-active substance is smallest in samples of soil with much sand or with much organic substance and that this quantity will be the higher as the settled slime of the river lacks these elements. This is clearest in the case of boring 12 and the only samples where the quantity also exceeds 1.00×10^{-12} grammes, are these very slimes from Meuse and Waal. If we have to choose between an origin from the dunes or slime of the river then I think I can safely conclude *that the radio-active substance in the alluvium of Rockanje comes especially from the side of the rivers and in a far less degree from the dunes*.

Apparently there is also radio-active substance in the sand of the dunes (cf. sample C), though in a far less degree. Whether this is the same substance as in the stronger active clay will perhaps be settled later on by others. Moreover it remains possible that also that slight quantity in the dunes yet exists of minerals originally carried along, together with slime of the river and which have settled on the bottom of the sea on the shore. I must still add that, of course independent of the quantity of sand and organic remains, the slime settlements may possess different radio-active intensity, even if they come from the same river. The motion of the water, either by the current or the whirl of an eddy, may cause by fractionated settlement on various spots a varying quantity of active minerals, altering with the strength of that motion.

We will now consider the numbers of the samples of boring (2, 4, 6, 8, 9, 10, 11, 12, 13) a little more closely. They belong to that part where in a deep basin hollowed in the sand, slime of the river was thrown down in salt and later on in brackish water, while in later times the slime of the uppermost layers was mixed

with ever increasing organic remains. We now see that the radio-activity increases chiefly from the top to the bottom, i.e. with the increase of slime of the river and with the decrease of organic material; boring 2 with 0.43, boring 4 with 0.54, boring 6 with 0.55, boring 8 with 0.61, boring 9 with 0.78, boring 12 with 2.16×10^{-12} . But why that slight fall in borings 10 and 11? It is exactly in these two samples that there is a larger quantity of sand. Sample 9 still consists of very black, fat clay with much fine mineral dust, the *few grains of sand* being 100—150 μ long at most. Sample 10: watery mud of very fine mineral dust (slime), mixed with *more grains of sand*, somewhat coarser, at most 350 μ long, Sample 11: Bluish dark-grey, because the slime is mixed with a few *more grains of sand*, very much particularly fine mineral dust, grains of sand at most 300 μ long; small remains of *peat* and wood. (Treatise p. 38). While in going from 9—12 one might expect a further rise of radio-activity, this rise is temporarily suppressed, because layers 10 and 11 again contain more and larger grains of sand, especially 11 a few more remains of peat. Only when this has entirely passed in 12, there appears a rather high number. But in sample 13 the activity falls again to the value of 10 and 11 and concerning this was noted down at the time: fat, black clay, many *remains of peat*, very much fine mineral dust mixed with somewhat *larger grains of sand* at most 200—400 μ long (Treatise p. 39). Then again a fall, if mixed with more organic substance and larger grains of sand. So in its details it also tallies entirely with the conclusion drawn higher up, but at the same time it appears from this of how much geological value accurate sensitive determinations of radio-activity can be.

Finally we may yet draw the attention to the numbers occurring in table 2 as collected by Miss FOLMER. There the radio-activity is the stronger as the given number of seconds is smaller. We refer to the table and to Fig. 1. Where 4 or 5 samples were taken from one spot, one higher than the other, it is again striking that the smallest action is always found in the highest layers that were bored; that first the activity increases in the downward direction, is strongest at 150 cm. depth generally and often decreases again at 180 cm. The same may apply here as to the great boring, that the upper layers contain a larger quantity of organic material. The layer of clay goes down to the depth of 13 m. on the spot of boring, on the spots of these shallow gaugings to 5 m. at most, generally far less deep, so that for the rest one can hardly compare the same depths. Moreover, it will be a good thing to pay attention

to numbers 38, 45, and 46. These are the most weakly active, the only ones where the value rose beyond 3 minutes and it is exactly these samples that consist principally of sand. Besides these 3 samples there are only two left (37 and 39) which also chiefly contain sand, but these too belong to the least active ones. In 37, 38, 39, 45, and 46 the layer of sand was already present at 60, 60, 60, 30, and 30 cm. below the level of the sea.

So here it is once more corroborated, that radio-active action grows less according as the sample of the soil contains more sand or organic substance. The curves in Fig. 2, when compared mutually or with the above-mentioned particularities of the soils may demonstrate clearly, that two very different methods have led to this same conclusion. That sample 12 shows a surprising difference in the two methods is very striking indeed. May be that it points out that the very high number of sample 12 in this series is yet of particular importance.

Mathematics. — “*On Elementary Surfaces of the third order*”.
 (Third communication). By Dr. B. P. HAALMEYER. (Communicated by Prof. L. E. J. BROUWER).

(Communicated in the meeting of September 29, 1917).

It has been proved that F^3 cannot exist if that surface does not contain at least one straight line. It will now be shown that if F^3 contains a line¹⁾, this surface still cannot exist if in no plane through that line the section consists of three lines.

We start from a line a on F^3 and assume that in no plane through a the restcurve consists of two lines. It will be shown that this assumption leads to contradictory results.

Theorem 1: Every point of line a has a tangent plane.

Let A be an arbitrary point of a and β a plane through A not containing a . A cannot be isolated in β because there are points of F^3 on both sides of β inside any vicinity of A . Hence in β a curve passes through A . On this curve we choose a sequence of points A_1, A_2, \dots converging towards A from only one side. Let $\alpha_1, \alpha_2, \dots$ be the planes passing through a and through A_1, A_2, \dots respectively and let α be their limiting plane (obviously α is the plane through a and the tangent at A to the curve in β). In every one of the planes $\alpha_1, \alpha_2, \dots$ is situated a curve of the second order, passing respectively through A_1, A_2, \dots .

Three possibilities are to be considered:

1. The curves of the second order contract towards a or part of a .
2. The curve in the limiting plane α consists of a and an oval which intersects a at A .
3. The curve in the limiting plane α consists of a and an oval which has a for tangent at A .

1. The curves of the second order contract towards a or part of a . This part of a anyway contains the point A . Each curve of the second order divides the corresponding plane α_n in two regions²⁾.

¹⁾ Again *line* will be used for *straight line*.

²⁾ A_n cannot be isolated in α_n because the curve in β intersects the plane α_n . Neither can the restcurve in α_n consist of a line counting double, as we assumed that no second line of F^3 intersects line a .

We call *internal* region that one which contracts towards a or part of a only. Now if A continued to belong to the *external* regions, the curve in plane β would show a cusp in A with both branches arriving from the same side of the tangent. and this is excluded. The possibility might be put forward that for every n the oval in α_n has the line of intersection b_n with β for tangent in A_n , in other words that the two points of F^3 , which b_n carries besides A , coincide.

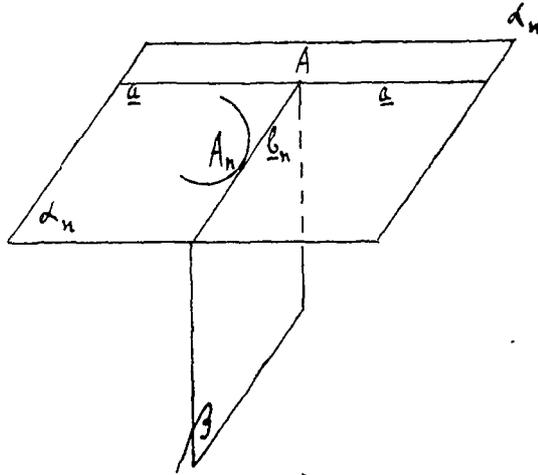


Fig. 11.

As follows can be shown that this possibility is excluded. In the second communication (*Second part, theorem 1*) we proved:

If a line a in a plane α intersects the curve in that plane at an ordinary point A , then lines which converge towards a end up by carrying points of F^3 converging towards A . The demonstration we used there, also holds if A lies on one or more lines of F^3 , provided A is not situated on such a line in plane α . We proceed to apply this theorem to the case of fig. 11. In plane β the line b_n intersects the curve (which is no straight line) at the ordinary point A_n . In plane α_n however it would be possible to find a sequence of lines converging towards b_n but carrying no points of F^3 which converge towards A_n : a contradiction.

Hence A will end up by belonging to the internal regions of the ovals ¹⁾ and considering this region together with its boundary contracts towards a or part of a it follows that *every plane through A not containing line a has a point of inflexion at A with tangent in α .*

¹⁾ We exclude the possibility that A continues to lie on the ovals themselves. The cases in which A belongs to an oval in a plane through a will be dealt with sub 2 and 3.

Sections in planes through a will be dealt with later on.

2. The restcurve in a is an oval which intersects a at A . In a four branches depart from A : AB and AC on a and AE and AD on the oval. Regarding the connection of these branches the JORDAN theorem for space leaves only two possibilities.

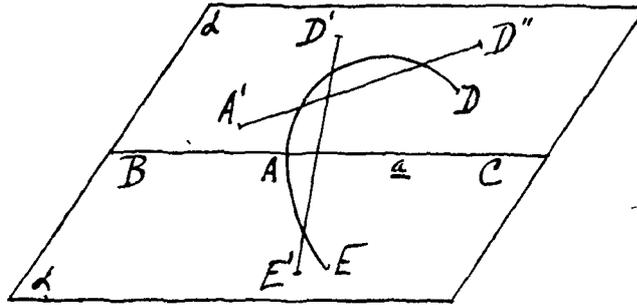


Fig 12.

First possibility: AC and AD are connected by I, AD and AB by II, AB and AE by III and lastly AE and AC by IV. If I and IV were situated on the same side of a then a parallel linesegment converging from that side towards $E' D'$ would end up by having two points in common with I and two with IV: a contradiction.

If I and II were situated on the same side of a , then a parallel linesegment, converging from that side towards $A' D''$, would end up by having two points in common with I and also two with II: a contradiction.

In the same way it can be shown that III and IV cannot lie on the same side of a . Combining these results it appears that the connecting sets of points are situated alternately above and below a .

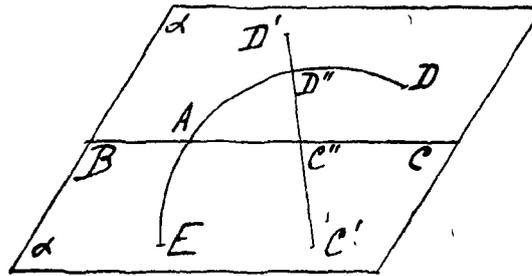


Fig 13.

Second possibility. The following is a representative case: I connects AB and AC above a and III connects AE with AD below a . AC is connected with AD above or below a by II and lastly AB with AE above or below a by IV. Let parallel linesegments converge towards $D' C'$ from that side on which II is situated. This

line ends up by carrying two points of II. Besides it has a point in common with either I or III converging towards C'' or D'' and lastly it carries a point of F^3 converging towards the second point of intersection of $D'C'$ and the oval in a . Altogether four points.

It thus appears that the second possibility is excluded and we need only consider the first.

In § 3 of the first communication we proved: *If A is double point in a plane a , and cusp in not more than one plane, then a is tangent plane*, assuming that no line of F^3 passes through A . Here however one of the branches passing through A , is a straight line. This is the only one, as we assumed that no second line of F^3 intersects the line a on which A is situated. Hence in no plane through A except those passing through a , can the curve contain a line through A and the demonstration of § 3 still holds. The results obtained for planes through the tangents at A in a also remain valid for the planes through the tangent at A to the oval in a . Regarding the curves in planes through the *line* in a however (which line corresponds to the second tangent of the former case) the demonstration says nothing. These shall be dealt with later on. Also the first part of § 3 where the connection of the branches is examined, has to be slightly altered, but this has been done already above.

In order to be able to use the former results here, it remains to prove the following theorem:

If a line of F^3 passes through A , which line is not intersected by a second one, then A cannot be cusp in more than one plane (we give a fresh demonstration as the former one must be altered a good deal).

A is situated on the line a of F^3 and is cusp in a plane β which of course does not contain a . Let α be an arbitrary plane through a not containing the cuspidal tangent in β and b the line of intersection of α and β . Line b carries except A only one point B of F^3 . In plane α the point B cannot be isolated, as the curve in β crosses α . Neither can the restcurve in α (that is: the curve minus a), according to our assumption, consist of two lines and the only remaining possibility is that the restcurve is an oval through B . This oval also passes through A , because b has only the points A and B in common with F^3 (that the oval cannot have b for tangent in B follows from the same reasoning which shows that fig. 11 represents an impossibility.)¹⁾

¹⁾ Here we are not entitled to use the theorem given at the end of the first communication, because this was only proved for points not situated on a line of F^3 , and it is not excluded that B lies on such a line.

Hence in every plane through a , not containing the cuspidal tangent in β , the restcurve is an oval through A . Passing on the limiting case, it appears that in the plane through a and the cuspidal tangent in β the curve consists of a only, or a together with an oval through A .

Furthermore it appears that an arbitrary line through A ($\neq a$) carries at the utmost one point of F^3 different from A . But in no plane can A be isolated (because a furnishes points of F^3 inside any vicinity of A , on both sides of every plane not containing a), hence in any plane which does not contain a the point A is either cusp or double point. Concerning the planes through a it appeared that A is double point in every one of these with the possible exception of the one through a and the cuspidal tangent in β , in which case the curve in that plane consists of a only.

So far we only assumed A to be cusp in a single plane β . Now let A be cusp in two planes β and γ . We shall consider separately the cases that only one or more than one line can be cuspidal tangent at A :

First case. A is situated on the line a of F^3 . Let b denote the only line through A which can be cuspidal tangent and let α be the plane through a and b . The foregoing results show that there are only two possibilities:

- I. The curve in α consists of a and an oval through A .
- II. The curve in α consists of a only.

I. Let c be a line through A in α , not being tangent to the oval and not coinciding with a or b . Only line b can be cuspidal tangent at A hence in every plane through c ($\neq \alpha$) A is double point, but A is double point in α also, hence A would be double point in every plane through c , and c cannot be tangent in any of these planes because c carries besides A a second point of F^3 . This however cannot be, as may be shown in the same way as in § 3 of the first communication. The fact that here A lies on a line of F^3 makes no difference as the demonstration merely depended on the connection of the branches dictated by the assumption that F^3 is a twodimensional continuum.

II. Again let c be a line through A in α not coinciding with a or b . In every plane through c ($\neq \alpha$) A is ordinary double point and in α the curve consists of a only.

Let σ be an arbitrary plane through c ($\neq \alpha$). In this plane σ the line c is tangent at the double point A , hence in σ on both sides of c at least one branch joins A with the line at infinity (on

one side there even can be three, when the loop reaches the line at infinity, but in any case there is at least one on either side). Now let δ revolve round c . The curve in a limiting plane is the limiting set of the curves in the converging planes (no isolated points are possible here). Besides a sequence of infinite branches has an infinite limiting branch. Hence it follows that in every plane through c ($\neq \alpha$) we can choose on both sides of c an infinite branch such that they merge in each other in continuous fashion when δ revolves round c . If we add the line a in α these branches are just sufficient to give F^3 the character of a twodimensional continuum in the neighbourhood of A and the branches departing from A , which we have left out, cannot be fitted in anymore. This contradicts our assumption that F^3 is a twodimensional continuum (of course the neighbourhood of a point on a twodimensional continuum can in an infinite number of ways be represented on the neighbourhood of a point in a plane, but the neighbourhood of a point in a plane can by (1,1) continuous transformation in the plane never be transformed in anything but the neighbourhood of a point).

Second case. A is situated on the line a of F^3 and is cusp in β and γ . The cuspidal tangents do not coincide, hence the line of intersection b of β and γ cannot be cuspidal tangent in either of these planes. It follows that b carries besides A a second point B of F^3 and the curve in the plane α through a and b consists of a and an oval through A and B . The line b divides β in two semiplanes: in the one the cuspidal branches depart from A , hence in the other A is isolated. In the same way A is isolated in one of the semiplanes in which b divides γ .

Now a foregoing demonstration (§ 5, second communication) shows that in this case A is isolated inside the entire angle ($< 180^\circ$) between these semiplanes. Hence the line α belonging to F^3 cannot pass through this angle and it follows that the semiplanes of β and γ in which the cuspidal branches depart from A , are situated on the same side of the plane α through a and b , let us say below α . In α four branches arrive at A , consecutively AP , AQ , AR and AS (two on a and two on the oval). Suppose above α , AP is connected with AQ and AR with AS . Then line b must lie inside the angles QAR and PAS , because planes pass through b in which A is isolated above α . Let c be a line in α through A inside the angles PAQ and SAR (this is impossible when the oval in α has a for tangent at A , which case we shall consider separately). The foregoing results show that A is double point or cusp in every plane

through c . In any such plane however two branches arrive at A from above α , one on the set which joins AP to AQ and the other on the set by which AR is connected with AS . Now if A were cusp in a plane through c then, considering the branches arrive from above α , at the utmost one plane could pass through b in which A is isolated above α and this contradicts the above results. Hence A must be double point in every plane through c : a contradiction.

It now remains to consider the case that the oval in α has a tangent at A . We shall consider separately the following possibilities:

I. There exists a semiplane through b above α in which A is not isolated.

II. No such semiplane exists.

I. A is not isolated above α in a plane δ through b . Then in the semiplane of δ above α two branches depart from A , because A is cusp or double point in every plane not containing α and line b has a second point B in common with F^2 . From the way in which the branches meeting at A in α are connected, follows that in every plane through b two branches arrive from below α , hence A is ordinary double point in δ . Here, there is no danger of a line as we assumed that no second line of F^2 intersects α . If δ revolves round b then in one of the two directions A will remain ordinary double point till δ coincides with α .

From this it follows that the semiplanes of β and γ in which the cuspidal branches depart from A are situated on the same side of δ , let us say below δ . In δ we now choose a line d through A separated from b by the tangents at A . The same reasoning used before shows that A would have to be double point in every plane through d . Only for the plane through α and d a slight alteration is required, which however is selfevident. The impossibility of assumption I has thus been proved.

II. A is isolated in every semiplane through b above α . In every plane through A not containing α the point A is double point or cusp, hence in every plane through b ($\neq \alpha$) A is cusp and all the branches arrive at A from below α . It follows that A must be cusp in every plane except α , all branches arriving at A from below α . This however is only possible if the cuspidal tangents form one plane ε through α , which plane has nothing but line α in common with F^2 . Let a sequence of planes $\varepsilon_1, \varepsilon_2, \dots$ all passing through α converge towards ε . In each of these an oval passes through A .

Now suppose the oval in ε_n crosses the line α at A . Then four

branches arrive at A in ε_n , forming finite angles. These branches are connected alternately on different sides of ε_n . Through A in ε_n we can at once find a line through which pass two planes having a cusp in A and such that in both the cuspidal branches arrive from the same side of ε_n . Then in the same way as before we can once more obtain a contradiction.

It now remains to consider the possibility that for every n the oval in ε_n has a for tangent at A . For increasing n these ovals contract either towards A only or towards a connected part of a containing A .

If A is the only limiting point, then the contracting ovals would give to A the character of a point of a twodimensional continuum and a sequence of points on a having A for limiting point, could not be fitted in anymore.

If on the other hand the limiting set is an interval on line a then the internal points of this interval would, in planes not containing a , be cusps with both branches arriving from the same side of the tangent and this is also excluded.

We thus have proved that *every plane through A , containing neither line a , nor the tangent at A to the oval in a , has an ordinary point in A with tangent in a . The planes through the tangent at A to the oval in a have point of inflexion in A with tangent in a .*

There remain to be considered the curves in planes through a . These shall be dealt with presently.

3. We now come to the third possibility mentioned on page 736. The restcurve in a consists of an oval having a for tangent in A . In a there depart from A two branches AB and AC on a and AE and AD on the oval. In almost the same way as before it appears that here AC is connected with AD , AD with AE , AE with AB and lastly AB with AC . The connecting sets of points are again situated alternately above and below a . This being established the further reasoning used for case 2 holds here without any alteration (again we remind the reader of the assumption that no second line of F^3 intersects a). Results: *In every plane which does not contain line a , the point A is ordinary point with tangent in a (in all these planes the branches depart from A to the same side of a).*

The curves in planes through a must be considered still.

In each of the three above cases, a was found to possess the

character of tangent plane, only we had no certainty with regard to the curves in planes through a . Now all possibilities have been considered it appears that for no point A two different planes can pass through a both possessing one of the examined characters (we obtain an immediate contradiction by considering a plane through A not containing a). It follows that in the three above cases no plane through a ($\neq a$) can contain branches departing from A (except a itself). This completes the demonstration that a is tangent plane.

Theorem 2: If A moves continuously along a , then the tangent plane also changes in continuous fashion.

Let the points A_1, A_2, \dots on a converge towards A . Tangent planes $\alpha_1, \alpha_2, \dots, \alpha$ all passing through a . We assume that $\alpha_1, \alpha_2, \dots$ have a limiting plane α' different from α and shall prove that this leads to a contradiction. Let $\beta_1, \beta_2, \dots, \beta$ be planes respectively passing through A_1, A_2, \dots, A and all $\perp a$. The line of intersection of α_1 and β_1 we denote by b_1 , the one of α_2 and β_2 by b_2 , etc. Lastly let b be the line of intersection of α and β and b' the one of α' and β . According to our assumptions b' and b do not coincide and b' is the limiting line of b_1, b_2, \dots .

Now b is tangent at A to the curve in β and in the converging planes β_1, β_2, \dots the curves have for tangents at A_1, A_2, \dots respectively the lines b_1, b_2, \dots converging towards b' in β .

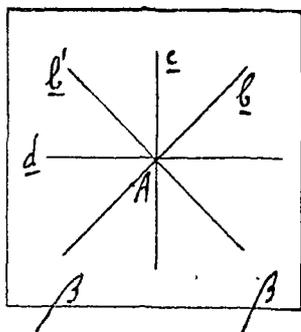


Fig. 14

According to *theorem 2* of the second communication the curve in β is the limiting set of the curves in β_1, β_2, \dots (with the possible exception of an isolated point).

Let c and d be lines through A in β separating b from b' . The corresponding planes through a shall be denoted by γ and δ .

For n large enough a branch departs in β_n from A_n in both directions inside those opposite angles between γ and δ in which b' is situated. Loops contracting towards A are evidently excluded, hence in order that in β no branch departs from A inside those angles of c and d which contain b' , it is unavoidable that in the converging planes the above mentioned branches leave these angles via points of the planes γ and δ (or one of these) converging towards A . Hence in at least one of the planes γ and δ the point A would be limiting point of points of F^3 not situated on a . This means that in one of those planes a branch departs from A different from a , but this is a contradiction

considering that only in the tangent plane a a second branch can pass through A . This completes the demonstration of *theorem 2*.

Let an oval in a cross the line a at A . This oval and the line a have a second point of intersection B and the points A and B have the tangent plane a in common. If A moves continuously along a then, according to *theorem 2*, the tangent plane a also changes in continuous fashion and the point B also moves continuously.¹⁾ From this follows that a point A at which an oval crosses a , can only be limiting point of points of a possessing the same character. Besides it is easy to prove that the tangent to the oval at A also changes continuously. This result however will not be needed, but we do want the following:

Let A_1, A_2, \dots on a converge towards A . Tangent planes $\alpha_1, \alpha_2, \dots, \alpha_n$. If the oval in a crosses a at A it follows from the above that for n larger than some finite value the plane α_n also shows an oval which crosses a at A_n .

Now suppose all these ovals in α_n turn at A_n their concave sides to the left. The oval in a is the limiting set of the ovals in α_n and considering a sequence of finite concave branches cannot converge towards a finite convex branch, it follows that the branch in a through A also turns its concave side to the left.

Taking these results together we obtain:

Theorem 3: A point of line a in the tangent plane of which an oval crosses a , can only be limiting point on a of points having the same kind of tangent plane also with regard to the side to which the ovals through those points are concave or convex.

Theorem 4: F^3 cannot exist if the restcurve does not degenerate in any plane through a .

We consider the case in which the curves of the second order in the planes $\alpha_1, \alpha_2, \dots$ (passing through a and converging towards a), contract towards part of a . We call *internal region* of these ovals that region which contracts to nothing but a . We found that the points of a belonging to this limiting part must be situated in the internal region of the oval in α_n for n larger than some finite number. From this follows that the part of a belonging to the

¹⁾ This theorem and some others which shall be formulated presently concerning the directions in which A and B move, have already been given by JUEL, Math. Ann. 76, p. 552. The existence and continuous changing of tangent planes is simply postulated by that author.

internal region of the oval in α_n must diminish for increasing n because if the oval in α_n crosses a at A_n and B_n then α_n is tangent plane at A_n and in case A_n ended up by being situated inside ovals, α also would be tangent plane at A_n : a contradiction.

Hence if the ovals have the *entire line* a for limiting set, α can have points in common with a . An idea of this case may be got by imagining a sequence of hyperbolas of which the angle between the asymptotes (inside which the hyperbola is situated) tends towards 180° and such that the centre is situated on a and both asymptotes converge towards a .

In this case everything is in favour of counting a as a *triple* in α . In no plane through a a branch would depart from any point of a , and except α , F^3 would contain no straight line.

A second possibility we wish to consider separately is that in the tangent plane of *every* point of a the oval has a for tangent. Let A be a point of a with tangent plane α . The line a divides α into two semiplanes, in the one A is isolated and in the other an oval has a for tangent at A .

Now let A move along a . The plane α turns round a . If A moves on in the same direction the plane α goes on turning in the same direction, for otherwise two points of a might be found with the same tangent plane and this cannot be as in either point an oval in the tangent plane must have a for tangent.

If A goes round the entire line a the tangent plane meanwhile turns 180° round a . The ovals in the tangent planes merge continuously into each other, hence after turning 180° the branch having a for tangent is situated in the wrong semiplane. This means that on the way the branch must change from the one semiplane to the other and this is only possible either via a tangent plane in which the restcurve consists of two lines through A , or via a tangent plane in which the oval has contracted to nothing but point A . The first possibility is excluded according to our assumption and the second would mean that a sequence of ovals in the converging planes contract towards a point of a not belonging to the internal region of the converging ovals. This was found to be impossible hence the assumption that every point of a has a tangent plane with a having a for tangent, leads to contradictory results.

Leaving apart both cases treated above, there certainly exists a plane through a in which an oval has two different points A and B in common with a . Let this plane α revolve continuously in

certain direction round a . The points A and B then also move along a continuously¹⁾. Two assumptions are possible: A and B can move in the same or in opposite directions. Let the direction be the same. In the time that B has described the original segment BA , the point A has gone further, hence all this time we keep tangent planes with ovals having two different points in common with a .

When B arrives at the original place of A the plane a must have turned an angle of 180° , but if the branch through B has originally been concave to the left, it must now be concave to the righthand side, and this is not possible as on the way the concave side in B cannot jump round and no change from concave to convex can have taken place via a degeneration of the oval in two straight lines (according to our assumptions).

The second possibility was that A and B move in opposite directions. Let the tangent plane successively turn round a in opposite directions, then we obtain two different points in which A and B meet. Such a meeting takes place either when the two points of intersection of a and the oval converge to one point or when the entire oval contracts to nothing but a single point on a . In both cases the concave sides of the branches through A and B face each other. A priori it seems possible that before the meeting the convex side of the branches through A and B face each other, but then these branches would be connected on both sides via the line at infinity and in the limiting plane the oval would degenerate in two straight lines²⁾ through the point where A and B meet and this contradicts our assumptions.

Now we start from the original position of A and B and we observe A only. Let the branch through A turn its concave side to the left. If we turn the tangent plane in such a way that A moves to the right, then the concave side goes on being turned to the left. But before the meeting with B takes place the concave side must be turned to the right (that is in the direction in which A moves) and this means a contradiction because the curvature cannot change its sign discontinuously, neither can it change via a degeneration of the oval in two straight lines (according to our assumption). This completes our demonstration.

Remark. Above we spoke about the possibility that the oval

¹⁾ If a goes on turning in the same direction A and B obviously cannot change the direction in which they move for then points of a would exist with two different tangent planes.

²⁾ The oval does not converge towards a .

through A and B contracts to the point where A and B meet. The most rational thing to do is to consider this meeting point as a special kind of oval in the tangent plane. We can also imagine that the oval through A and B contracts to a *segment* of a . All points of this segment would have the same tangent plane (tangent plane of the first kind, examined at the beginning). Now the admission of this possibility has the disadvantage that we should be more or less forced to consider the line segment in the tangent plane as a special sort of oval and going back to the definition of elementary curves we should not only have to admit isolated points, but line segments also. This would cause the development of the theory to become a good deal more complicated but the enlargement of the results would probably remain very trivial. To mention an example; to the elementary surfaces of the second order would be added the plane convex regions including the boundary and the line segment.

Far greater would the changes become if we also dropped the condition that the convex arc is not to contain line segments. This however would mean an entirely different problem.