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Physics. — "*The rectilinear diameter of helium*" ¹⁾. By E. MATHIAS, C. A. CROMMELIN, H. KAMERLINGH ONNES and J. C. SWALLOW. (Communication from the Physical Laboratory at Leiden).

(Communicated at the meeting of March 28, 1925).

§ 1. Our investigations of the density-curve and the diameter of helium cover the temperature range between the critical point (5°, 19 K.) and the boiling-point (4°.22 K.) of this substance; they are the continuation of our determinations concerning the density-curves and diameters of oxygen, argon, nitrogen, hydrogen and neon ²⁾.

§ 2. We have made use of a helium cryostat in which the helium boils under a pressure greater than atmospheric. In this way the critical point can be reached without danger to the apparatus, as the critical pressure only amounts to 2.26 atm.

The temperature was determined by means of vapour-tension measurements, while of course the pressure measurements gave no difficulties at all. The helium originated from the evaporation of liquid helium and so could be considered perfectly pure.

We have adopted for the weight of a litre of gaseous helium under normal conditions the value of RAMSAY and TRAVERS, 0.1787 grammes.

§ 3. In the following table we have given the numbers obtained for the densities $\varrho_{liq.}$ and $\varrho_{vap.}$ of the liquid and of the saturated vapour respectively in grammes per cm^3 . at the same temperature θ (thermodynamic scale) and for the ordinates of the diameter $y = \frac{\varrho_{liq.} + \varrho_{vap.}}{2}$; we have included some liquid densities at and below the boiling-point determined by Dr. BOKS and one of us (H. K. O.) ³⁾; we have calculated the vapour densities by means of the isotherms at low temperatures, also determined by Dr. BOKS and one of us ³⁾.

In calculating the linear formula of the diameter by the method of least squares we have neglected the measurements at the temperatures

¹⁾ A detailed communication about this subject will shortly be published as N°. 172b of the Comm. from the Phys. Lab. Leiden.

²⁾ These Proceedings Febr. 1911, Oct., Dec. 1912, Jan. 1913; Vol. 17 p. 953, Vol. 23 p. 1175. Ann. de physique (9) 19 (1923), p. 231.

³⁾ 4th Int. Congress of Refrigeration. Travaux de la première commission internationale p. 215. Comm. Leiden N°. 170b. Thesis for the doctorate J. D. A. BOKS. Leiden, July 1924.

θ (Celsius scale in Kelvin degrees)	T (Kelvin scale in Kelvin degrees)	$\rho_{liq.}$	$\rho_{vap.}$	$y(W)$	$y(R)$	O—C abs.	O—C in %
—268°.38	4.71	0.1139	0.02699	0.07045	0.07015	+0.0003	+0.43
268°.50	4.59	1165 ¹⁾	2389 ¹⁾	702	703 ⁵⁾	— 15	—0.21
268°.86	4.23	1253	1637	708 ⁵⁾	710	— 15	—0.21
268°.87	4.22	1255	1618	708 ⁵⁾	710	— 15	—0.21
269°.19	3.90	1311	1176	714 ⁵⁾	715 ⁵⁾	— 1	—0.14
269°.79	3.30	1395	06435 ³⁾	729 ⁵⁾	726 ⁵⁾	+ 3	+0.41
270°.53	2.56	1457 ²⁾	02079 ³⁾	739	739 ⁵⁾	— 0 ⁵⁾	—0.07
270°.72	2.37	1466	01368	740			
270°.79	2.30	1469	01159	740 ⁵⁾			

2°.30 and 2°.37 K. The curve of the liquid densities shows a maximum at about 2°.30 K., so that the linear relation no longer applies to the continuation of the diameter.

The formula of the diameter becomes:

$$y = -0.40263 - 0.0017616 \theta.$$

The inclination coefficient of the diameter is thus:

$$a = 0.0017616.$$

The above mentioned formula gives for the critical density at the critical temperature —267°.90 C. (5°.19 K.)

$$\rho_k = 0.06930.$$

¹⁾ Values experimentally determined (MATHIAS, CROMMELIN, ONNES, SWALLOW).

²⁾ Values experimentally determined (ONNES and BOKS); these observations were relative, as the normal volume left something to be desired. They have been corrected therefore by means of the numbers under ¹⁾ (of which the normal volume was determined much more accurately).

³⁾ Values calculated from the formula

$$\rho_{vap} = \frac{kp}{A_A \{ 1 + B^{(p)} p + C^{(p)} p^2 \}}$$

k = weight in gr. of 1 cm³ of helium at normal circumstances.

p = pressure in international atmospheres.

$B^{(p)}$ and $C^{(p)}$ are the coefficients in the series

$$p\nu_A = A_A \{ 1 + B^{(p)} p + C^{(p)} p^2 + \dots \}$$

The values of $B^{(p)}$ and $C^{(p)}$ have been calculated from the isotherms of helium at helium temperatures of ONNES and BOKS i.e.

The critical coefficient becomes:

$$K_4 = \frac{RT_k \varrho_k}{p_k} = 3.270$$

a value almost equal to that of hydrogen (3.276).

§ 4. The deviations of the rectilinear diameter are small (though greater than for hydrogen and neon). So we can conclude that helium obeys the law of the rectilinear diameter in the same way as the other substances investigated. The deviations all being smaller than $1/2\%$, are somewhat too great to be considered as experimental errors; besides, the systematical character of these deviations is indisputable. This systematical character is of the same sort as that of argon, neon and nitrogen, that is convex to the temperature-axis at low temperatures and concave at higher temperatures.

This investigation has been made with the aid of financial help of the Caisse des Recherches out of which the Académie des Sciences at Paris placed a subvention at our disposal. For this subvention we return our cordial thanks.

Physics. — "*Helium in earth-gases of the petrol sources*". By Dr. J. CLAY.
(Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of March 28, 1925).

Both from a geological and a technical point of view it is of importance to know whether helium occurs in the earth gases of the petrol sources in India. In other places namely sources have been found containing so much helium that the balloons of large airships can be filled with it.

The Bat. Petrol. Company was so kind to take carefully considerable quantities of gases from their sources and to present these to the physical laboratory of Bandoeng for our researches.

Some samples were first freed from their and expediated in shut drums of 5 L. but most samples were transported in large drums of 100 L. or in steel high pressure tubes.

In all cylinders care was taken for a sufficient overpressure (shut by water) so that no air could enter.

In order to investigate spectroscopically the presence of helium in the gas, we had to be sure that it did not contain traces of hydrogen, as the hydrogen spectrum can render that of helium imperceptible. This was the greatest difficulty with most samples.

The absorption of the hydrogen by palladium proved to be insufficient. As the only method to get rid of the hydrogen we mixed the gas with a considerably surplus of oxygen and then burned the hydrogen in a Drehschmidt capillar tube.

Thereto we mixed the gas with five times its volume of oxygen and made it flow through the capillar so often till no longer a decrease of volume was observed.

Then the remaining oxygen was taken away by pyrogallol solution, while the carbonic acid was absorbed by a potassium solution. Finally the remaining gas was led into a reservoir of known volume, while the pressure could be read. Then the gas was let into that part of the apparatus where at the temperature of liquid air it comes in contact with cocosnutcoal. Here all gases were absorbed except helium. Though at atmospheric pressure the absorption of helium at the temperature of liquid air amounts to 20 %, it may be neglected at the low pressure we finally had in the apparatus (surely below 1 mm. mercury), the absorption being proportional to the gaseous pressure. The latter could be measured in a MAC LEOD vacuummeter. In order to treat a large quantity of gas the reservoir was generally filled 5 times, while the new quantities were

introduced while it contained still the gas left when the coal is regenerated by heating and evacuation by the air pump.

The finally obtained gas rest was then collected in a fresh tube with coal and brought at the temperature of liquid air.

Each time the nature of the gas was examined in a spectral tube by means of a HILGER spectrograph (of constant deviation) the spectrum being compared with that of pure helium. In this way helium was stated in the samples from

Ledokput	158	Tjepoe	Java
Ledokput	135	"	"
Banjoeasin	17	"	"
Djerigi put	15	"	"
Tg. Lontar I, V, VI Pladjoe Sumatra.			

The following gases contain small traces of helium, probably still less than the given percentages. The latter reserve must be made as very small traces of other gases might be present, though these have not been stated spectroscopically. Always the mercury spectrum was visible. The pressure of the mercury vapour however is not measured in the MAC LEOD vacuummeter:

Gaboes	0,0014 ‰	Tjepoe	Java
Semanggi 66.	0,0013 ‰	"	"
Semanggi 62.	0,0017 ‰	"	"
Banjoebang 15.	0,0020 ‰	"	"
Nglabo	0,0033 ‰	"	"
Zuid-Perlak	0,0030 ‰	Pankalanbrandan	Sumatra
P. Soesoe	0,0015 ‰	"	"
Papa Drien	0,0006 ‰	"	"

*Bosscha Laboratory Techn. Highschool
Bandoeng (Java).*

July 1924.

Physics. — "*Electric phenomena in the atmosphere*". By Dr. J. CLAY.
(Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of March 28, 1925).

§ 1. All investigators of the electric phenomena in the atmosphere agree that in the first place we want observations at different places and of long duration, as we have not yet a sufficient insight in these phenomena.

It seemed to me of importance to make observations at a place, where the meteorological states vary more regularly than in the temperate regions where until now most data have been collected. Especially I intended to investigate the different parts of the phenomena at the same time.

The different phenomena to be investigated are:

1st, the value and the variation of the electric charge of the earth, which can be determined by the potential gradient,

2nd, the charge and the conductivity of the atmosphere and their variation,

3rd, the percentage of emanation in the air and in the earth,

4th, the penetrating radiation of the earth and of cosmic origin. These two latter phenomena cause the ionisation of the air,

5th, the electric charge of the rain.

These are the electric phenomena that have been put on the preliminary working programme of the Bandoeng laboratory.

Since a few months we have started a photographic registration of the potential gradient, as well as also determinations of conductivity and number of ions, while preliminary experiments are made on the percentage of emanation, on the penetrating rays and on the electric charge of the rain.

§ 2. As to the potential gradient, this is determined by means of a ionium collector projecting 75 cm. above the *top* of the physical institute while the ridge itself is earthed by means of two thick iron wires.

The collector is isolated on amber, which has been dried by means of sodium brought into its immediate neighbourhood in a glass tube.

The connecting wire of the electrometer is lead through a glass tube; through the roof and the ceiling, it directly goes to the electrometer.

The electrometer has been made in the Bandoeng laboratory; it is a binant electrometer of the CURIE type but it has a fixed and a rotating cylinder instead of a box with a needle. Further it has the advantage

that by means of a mirror the rotation of the cylinder can be registered, while quite independently a second mirror makes continuous* direct reading on a fixed scale possible.

In order to fix the absolute value we compared during several days

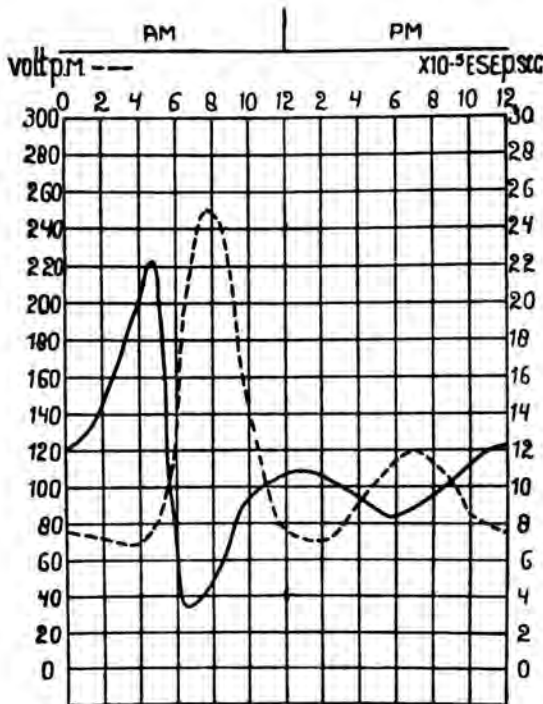


Fig. 1. Potential gradient and conductivity of the air.

The dotted line in this figure indicates the value of the potential gradient while the value of the conductivity is given by the uninterrupted line.

the obtained values of the potential gradient with those found at different places of the open land belonging to the Technical Highschool. The reduction factor proved to be 2.2. This means that the value of the potential at the roof has to be divided by this factor.

From fig. 1 we see the most striking feature of the diurnal variation of the potential gradient. It is a highly developed maximum at 8 $\frac{1}{2}$ a.m. local time. This maximum is about 2 to 2.5 times as high as the mean value over the day and about 4 to 5 times as great as the immediately preceding and following values.

The mean value is about 90 volt, the maximal value 250 volt pro meter.

A second much smaller maximum is found at 8 $\frac{1}{2}$ p.m., while the weak minimum lies of at about 4 a.m.

On the whole the variation curve resembles very much that found by KÄHLER in July at Potsdam. The only difference is that at Bandoeng the a.m. maximum is much stronger developed.

The time of this maximum does *not* agree with the results of the investigations of S. J. MAUCHLY¹⁾, who compares the data collected on the cruises of the „Carnegie” through different oceans and also those found at the coast stations. He comes to the conclusion that the diurnal variation has a maximum which occurs for all stations at about the same time viz. at about 17 G.M.T. For Bandoeng this would be at about midnight local time.

The theory of EBERT explains the negative charge of the earth.

¹⁾ S. J. MAUCHLY. On the diurnal variation of the potential gradient. Terr. Magn. a. Atm. Electricity Vol. 28, p. 61, 1923.

According to it the high potential gradients should occur *after* the falling of the barometer, which does not agree at all with the Bandoeng results.

How to explain then the high maximum?

To this purpose we shall want in the first place other simultaneous data f.i. on the conductivity and the number of ions.

We have tried whether the great variation of the gradient is connected with the change of the degree of moisture. During the time of the measurements (dry season) the amount of water vapour varied from 6—9 in the morning on an average from 11.5 to 14.5 that is by 25%. This might reduce the mobility of the ions somewhat, but not enough to explain the change of the conductivity.

In the meantime the relative degree of moisture fell from 90% to 50%.

§ 3. Finally we may remind that recently from different sides a connexion has been sought between the value of the potential gradient and the solar activity. HUNTINGTON's "Earth and Sun" (published in the beginning of 1924) gives a detailed account of these investigations. He wants to prove that it is of great importance to investigate the variation of the gradient in order to have a measure for the solar activity, which again strongly influences all meteorological factors.

March 1924 L. A. BAUER¹⁾ published a calculation according to which during the two last sun spot periods 1901—1923 a variation of the sun spot number by 100 corresponds to an increase of 20 to 35% of the mean potential gradient. For the correlation coefficient he gives 0.75, which suggests an intimate connexion.

§ 4. The electric state of the atmosphere was determined by two different methods. First by measuring the dispersion of the electricity by a conductor of 14.4 cm. capacity connected with a bifilar Wulf electrometer. According to theoretical considerations of SWANN²⁾ the form of the electrically charged body is of no importance, while the charge, emitted by a body with charge Q is given by $4\pi Qnev$, where v denotes the mobility of the electric charges, e the charge and n the number of charges pro cm^3 . When we write for the capacity of the conductor as far as it is surrounded by air C , for the capacity of conductor and electrometer together C_1 , for the potential V , we have

$$-C_1 \frac{dV}{dt} = 4\pi CVnev.$$

or integrated

$$C_1 \lg \frac{V_1}{V_2} = 4\pi nevCT,$$

¹⁾ L. A. BAUER. Correlations between solar activity and atmospheric electricity. Terr. Magn. a. Atm. Electr. March 1924 p. 23.

²⁾ W. F. G. SWANN. The theory of electrical dispersion into the free atmosphere. Terr. Magn. a. Atm. Electr. Vol. 19, p. 81 1914.

when V_1 is the initial potential and V_2 the potential after T seconds.

By means of this formula nev can be calculated. This quantity is called the conductivity of the air. Both for positive and negative charges it was determined during several days with intervals of a few hours, so that the diurnal variation could be found. This conductivity too was proved to vary strongly.

From fig. 1 we see, that at four o'clock in the night a strongly defined maximum occurs, which is shortly followed (at about half past six) by a minimum. Generally the potential gradient has a maximum, when the conductivity shows a minimum, as might have been expected. It is of importance to find out which of the two is primary and perhaps the cause of the other. It is most suggestive that the variation of the potential gradient is caused by that of the conductivity.

It is interesting to investigate which is the cause of the variation of the conductivity as we have two factors that may undergo a change viz. the number of charges pro unit of volume and the mobility.

To this purpose it is desirable to determine at the same time both conductivity of the air and the number of ions pro cm^3 , which may be done by the method of EBERT. We took a cylindrical tube of 1 m length and 15 cm. diameter in which an isolated tube is suspended.

The air is pumped through this tube, which is kept at a potential of 200–300 volt, so that *all* charges of the same sign are driven towards the rod, which is connected with a binant electrometer. The capacity of rod and electrometer as a whole is 75 cm. The sensibility of the electrometer is 120 mm. pro volt. Generally the charge is measured up to 200 mm. Before the natural leakage has been determined. The quantity of air pumped through the tube is sufficient to cause a charging of the electrometer to 1,66 volt in 1–2 minutes. The velocity of the air is controlled by a tested venturimeter.

In this way the charge of a definite kind of ions pro unit of volume of the air is determined directly, so that the quantity ne is known.

On different days the conductivity does not vary in the same way exactly as the number of ions, though these two quantities often correspond very well. So we found f.i. on one day for the ratio between the conductibilities at noon and at 8 a.m. 1,30, and for the ratio of the number of ions at the same moments 1,29.

From these data we find for the mean number of positive ions pro cm^3 . 260 and for that of negative ions 220 both at noon.

Several recent researches suggest that the different variation of the mobility on different days is due to the different degree of moisture of the air. As has been found by J. J. THOMSON and stated by a recent research of NOLAN ¹⁾ the ions are bound to small clumps of 14–36 water molecules, which give a mobility of resp. 1,87–2,24 cm. sec. pro

¹⁾ J. J. NOLAN. The constitution of gaseous ions. Physical Review July 1924 p. 16.

unit of potential gradient. The above mentioned value of 260 ions gave a mean mobility of 2.4 cm., which can be explained partially by the higher temperature and the lower pressure, compared with those used by NOLAN.

A better insight will not be possible before numerous other observations will have been collected.

§ 5. Further we must investigate by which ionising actions the ionisation of the air is maintained.

A few observations have been made already on the percentage of emanation of the air.

Through a second cylinder equal to the first one air was pumped during 2—3 hours, while the rod was kept at 1500 volt, so that the emanation settles down on the rod. Afterwards the loss of charge of the rod is measured. The quantity of air passed through the tube was known, while the loss of charge could be compared with that found, when a known quantity of emanation from a standard solution of RUTHERFORD was introduced into the tube. For the emanation we found in this way 3.10^{-19} Curie pro cm^3 . This is a rather low value, which agrees with the small number of ions that was found.

§ 6. Incidentally the potential gradient and the conductivity were measured at some mountain tops of Java, from which then the number of ions was derived. We were struck by the exceedingly high gradient as well as by the fact, that the number of negative ions sometimes exceeded that of the positive ones.

On the Tjikoray (2824 m.) we found in October as 7 a.m. 400 volts pro meter, at noon 700 volt pro m. at 5 p.m. 800 volt pro m. Thus the variation is quite different from that on the plateau of Bandoeng.

In May we found on the Pangerango (3025 m) 350 volt at 7 a.m. gradually rising to 450 volt at 5 p.m. Both here and on the Tjikoray it was impossible to measure during the night because of the condensation of watervapour on the supporting rod by the strong heat radiation. For the number of ions pro cm^3 . we found:

			+	—
October	Tjikoraj	2824 M.	347	425
May	Pangerango	3024 M.	207	365
June	Patoea	2400 M.	85	151
May	Weltevreden	10 M.	212	179
Aug.	Bandoeng	760 M.	260	220

These detached data do not yet allow many conclusions. It is only evident that generally the number of ions is small.

September 1924.

*Bosscha Laboratory of the Technical
Highschool. Bandoeng. Java.*

Physics. — "*Magnetic researches. XXVII. Magnetic properties of some paramagnetic chlorides at low temperatures.*" By H. R. WOLTJER. (Communication N^o. 173b from the Physical Laboratory at Leiden). (Communicated by Prof. W. J. DE HAAS.)

(Communicated at the meeting of May 30, 1925).

§ 1. *Introduction.* The strong increase at low temperatures of the specific magnetic susceptibility χ , according to the law of CURIE $\chi T = C$, had raised, as soon as further researches on this subject were undertaken (first oxygen, then powdered salts) the question whether such substances on sufficiently continued cooling would show ferromagnetism.¹⁾ It then soon appeared²⁾, that obedience to the law of CURIE only means a special case of obedience to a more general relation $\chi(T + \Delta) = C$, Δ being an individual constant for each substance, which at first was always found to be positive. For ferromagnetic substances above the CURIE-point a similar law holds, the law of WEISS $\chi(T - \theta) = C$ deduced by him from his theory. So, as θ is ascribed to the appearance of a molecular field, Δ may be connected with a negative molecular field, as already mentioned by WEISS and FOËX in their research on the magnetisation of ferromagnetic substances above the CURIE-point.³⁾

It is evident that substances with a positive Δ cannot be cooled down to the CURIE-point; moreover the later so called cryomagnetic anomaly⁴⁾ appears. The substances with negative Δ form a different group, to which, as found by CABRERA⁵⁾, nearly all chlorides belong. Now, a negative value of Δ is in itself not sufficient argument for expecting ferromagnetic phenomena at temperatures below $-\Delta$, e.g. one has to be prepared for the appearance of the cryomagnetic anomaly. This circumstance is left out of consideration by THEODORIDES⁶⁾ in his

¹⁾ H. KAMERLINGH ONNES and A. PERRIER, these Proceedings 12, p. 799; Leiden Comm. N^o. 116.

²⁾ H. KAMERLINGH ONNES and E. OOSTERHUIS, these Proceedings 15, p. 322; Leiden Comm. N^o. 129b.

³⁾ P. WEISS and G. FOËX, Arch. des Sc. Phys. et Nat. 31 (1911) pp. 4, 89.

⁴⁾ H. KAMERLINGH ONNES, Rapport 3e Cons. de Phys. Solvay 1921, Leiden Comm. Suppl. N^o. 44a I.

⁵⁾ J. de Chim. Phys. 16 (1918) p. 442, cf. p. 490.

⁶⁾ Diss. Zurich 1921, p. 83.

conclusion that one may presume a real CURIE-point for the chlorides as their molecular field is positive. The researches of ISHIWARA¹⁾ showed however, that the cryomagnetic anomaly for anhydrous CrCl_3 , CoCl_2 and NiCl_2 has not yet appeared in the temperature domain of liquid air. So it was important, as CABRERA had already pointed out, to investigate those substances at very low temperatures.

In 1921 KAMERLINGH ONNES²⁾ was able to communicate as a preliminary result of this research that the cryomagnetic anomaly appeared indeed for these substances in the temperature region of liquid hydrogen, but at the same time other anomalies appeared in so far as the susceptibility became dependent on the field strength³⁾. Since then the problem has been investigated at helium temperatures also. This research confirmed the particular shape of the magnetisation curves of CoCl_2 and NiCl_2 and pointed out more clearly how far ferromagnetism can be spoken of for CrCl_3 . These results will be treated in a following communication. Here we deal with the measurements undertaken in order to confirm and to test the results of the preliminary investigation of the substances mentioned down to the triple point of hydrogen.

§ 2. *Materials, method etc.* Prof. VAN ITALLIE and Miss Dr. STEENHOUWER of the Pharmaceutical Laboratory have been so kind as to furnish us with pure anhydrous CrCl_3 , CoCl_2 and NiCl_2 . In order to avoid hydration the substances were transferred to the experimental tubes in an atmosphere of dry CO_2 . Moreover the tubes that served for the final experiments were heated for some time before being sealed off. The preliminary experiments were carried out according to the „rod-method“; as at hydrogen temperatures the susceptibility appeared to become dependent on the field strength, the final experiments were carried out by measuring the attraction experienced by a „sphere“ in an inhomogeneous magnetic field. In the following we mention the results of the final series only. In this the attraction was measured by electrodynamic compensation⁴⁾ except for CrCl_3 in liquid hydrogen, as here the forces became too large for this method. For the corrections to be applied we refer to a previous communication⁵⁾. Here we mention only that the temperature determination of the liquid bath was considerably improved as compared with previous measurements, a stirrer⁶⁾ and a resistance thermometer being used.

¹⁾ T. ISHIWARA, *Tôhoku Sc. Rep.* 3 (1914), p. 303.

²⁾ *I.c.*, § 5e footnote.

³⁾ If the susceptibility depends on the field strength one can only speak of cryomagnetic anomaly, if the results for a given value of the field strength are compared.

⁴⁾ H. KAMERLINGH ONNES and A. PERRIER, *these Proceedings* 16, p. 689; *Leiden Comm.* N^o. 139a.

⁵⁾ H. R. WOLTJER, *these Proceedings* 26, p. 613; *Leiden Comm.* N^o. 167b.

⁶⁾ A. PERRIER and H. KAMERLINGH ONNES, *these Proceedings* 16, p. 901; *Leiden Comm.* N^o. 139d.

§ 3. Results and discussion.

a. Above hydrogen temperatures,

TABLE I.
CrCl₃ anh.

T	$10^6 \chi$	$10^5 \chi (T - 32.5)$
288°.0 K	41.0	1048
285.9	40.6	1028
285.0	40.0	1010
248.3	47.8	1031
239.2	49.3	1018
224.3	54.0	1035
211.1	56.8	1015
199.2	60.7	1013
199.1	62.2	1036
170.7	74.0	1023
153.1	85.0	1025
136.1	99.6	1032
64.2	294.7	934

For CrCl₃ (table I) down to the lowest ethylene temperature the relation $\chi(T - \theta) = C$ holds.

θ , determined graphically from a $1/\chi$, T -diagram, equals 32°.5. The CURIE

TABLE II.
CoCl₂ anh.

T	$10^6 \chi$	$10^5 \chi (T - 20)$
288°.7 K	90.8	2441
287.9	90.8	2433
249.6	105.0	2411
195.5	139.7	2452
169.7	163.3	2444
137.2	206.5	2420
77.5	421.1	2423
64.0	544.9	2396

constant then becomes 0.01025 corresponding to 17.9 magnetons. From ISHIWARA's measurements we derive: $\theta = 44^\circ.2$, $C = 0.01102$, n (number of magnetons) = 18.53. Usually the ion Cr^{+++} is supposed to have 19 magnetons.¹⁾

For CoCl_2 (table II) down to liquid nitrogen the relation $\chi(T - \theta) = C$ holds.

θ , determined graphically from a $1/\chi, T$ -diagram, equals 20° . The CURIE constant then becomes 0.02432 corresponding to 24.93 magnetons. From ISHIWARA's measurements we derive: $\theta = 33^\circ$, $C = 0.02401$, $n = 24.77$.

THEODORIDES (determinations above 0° C.)²⁾ gives $\theta = 47^\circ.2$, $C = 0.02426$, $n = 24.96$.

To explain by moisture the difference between THEODORIDES and us as regards θ a water content of 9 % (if additivity holds) in our salt must be supposed. As traces of moisture change the colour of CoCl_2 to violet and our salt was slatish blue, this explanation seems to be excluded and the difference remains as yet unexplained.

TABLE III.
 $\text{NiCl}_2 \text{ anh.}$

T	$10^6 \chi$	$10^5 \chi (T - 67)$
291 $^\circ.9 \text{ K}$	42.2	950
291.2	42.3	949
291.1	43.1	966
289.6	44.0	980
288.7	44.1	979
249.7	51.8	947
249.0	53.6	976
230.0	59.1	963
211.0	67.6	973
195.2	76.0	974
194.7	77.1	985
169.7	94.2	968
137.6	136.5	963
77.6	414.1	438
63.9	600.1	—

¹⁾ P. WEISS, J. de Phys. et le Rad. (4) 5 (1924) p. 129.

²⁾ Diss. Zürich 1921 ; Paris C.R. 171 (1920) p. 948; J. de Phys. et le Rad. (4) 3 (1922) p. 1.

For NiCl_2 (table III) down to the lowest ethylene temperature the relation $\chi(T-\theta)=C$ holds.

θ , determined graphically from a $1/\chi, T$ -diagram, equals 67° . The CURIE constant then becomes 0.00971 corresponding to 15.7 magnetons.

From ISHIWARA's measurements we derive:

above 220° K. $\theta = 94^\circ$, $C = 0.00933$ $n = 15.4$
 below „ $\theta = 70^\circ$, $C = 0.01100$ $n = 16.7$.

THEODORIDES (determinations above 0° C.) gives $\theta = 77^\circ.6$, $C = 0.01004$, $n = 16.00$.

b. In the temperature region of liquid hydrogen, in which these three substances are below their θ -temperatures, all of them show the anomaly that the susceptibility (calculated from the attraction in the ordinary manner) becomes dependent on the field strength. At higher temperatures nothing is to be seen of this, except perhaps for CoCl_2 at $64^\circ.0 \text{ K.}$ and 5 amp. through the magnet coils, in this case however the force is very small and the result of the measurement uncertain. Table IV and figs. 1—3 show the susceptibility as a function of the field strength at different temperatures: for CrCl_3 not χ , but χT has been plotted, as otherwise the diagram would have become too large.

TABLE IV.

<i>I</i>	H_0	$10^5 \chi \text{ CrCl}_3$			$10^5 \chi \text{ CoCl}_2$			$10^5 \chi \text{ NiCl}_2$		
		$64^\circ.2$	$20^\circ.3$	$14^\circ.6$	$64^\circ.0$	$20^\circ.4$	$14^\circ.4$	$63^\circ.9$	$20^\circ.4$	$14^\circ.2$
5	3.3	—	416 ¹⁾	915	49.1	152	138	—	63.1	61.3
10	6.6	—	420	712	54.5	182	168	59.3	70.3	69.6
15	9.9	29.3	387	611	54.1	200	191	60.6	73.4	74.1
20	12.9	29.4	360	540	54.3	208	204	59.7	77.3	77.0
30	17.3	29.4	321	462	54.1	217	213	60.0	81.0	81.1
45	20.2	29.6	299	413	54.9	223	—	60.1	82.6	82.7
60	21.6	29.4	288	389	54.9	225	—	60.0	83.4	83.7
70	22.2	—	282	378	—	—	—	—	—	—

The first column of table IV gives the current in the magnet coils, the second the field strength in the middle of the interferrum in kilo-gauss; at the place of the samples H is about $0.8 H_0$. The hydrogen values for CrCl_3 are corrected for demagnetisation²⁾. The

¹⁾ In the whole of the determinations concerning CrCl_3 this point is exceptional and in drawing the curve of fig. 1 it has been left out of account.

²⁾ H. R. WOLTJER, I.C. § 3b.

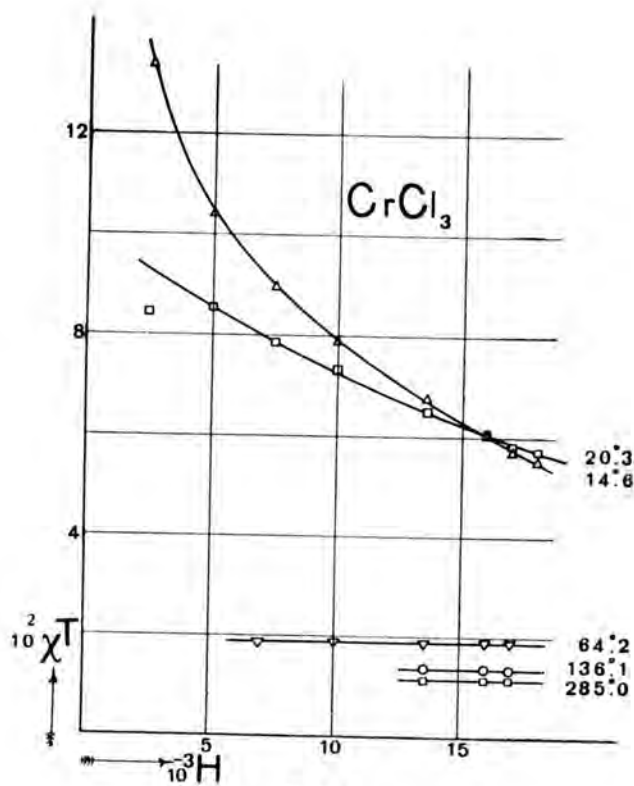


Fig. 1.

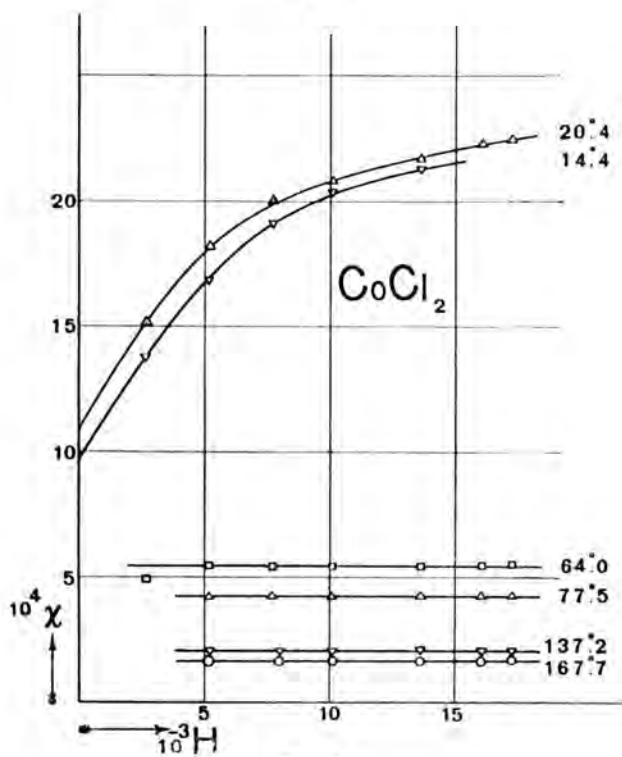


Fig. 2.

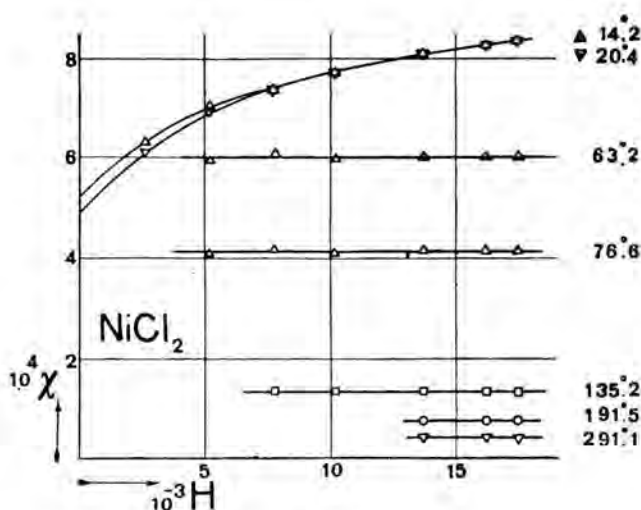


Fig. 3.

diagrams and table IV show, that for CrCl_3 the dependence on the field strength is opposite to that for CoCl_2 and NiCl_2 and, as corresponds to ferromagnetism, χ decreases with increasing field strength. In this sense it can be said, that CrCl_3 below $32^\circ.5$ K shows ferromagnetism. The magnetisation curves will be given at the same time as those for CoCl_2 and NiCl_2 in the following communication. For the latter substances the susceptibility increases with increasing field strength. This is a very uncommon feature. For CrCl_3 the dependence of the susceptibility on temperature is in the liquid hydrogen region still strong and, as regards the sign, normal; the susceptibility of CoCl_2 decreases though, slightly, with falling temperature; the susceptibility of NiCl_2 is independent of temperature except for weak fields in which the same phenomenon appears as for CoCl_2 .

If the inverse initial susceptibilities are plotted as functions of temperature, the curves are, at higher temperatures, rectilinear for these three substances and in the nitrogen region convex to the T -axis, for yet lower temperatures those of CoCl_2 and NiCl_2 show a minimum.

§ 4. Summary.

1. For anhydrous CrCl_3 , CoCl_2 and NiCl_2 as instances of substances with negative J , the susceptibility has been investigated for dependence on field strength and temperature.

2. For all of them down to the temperature region of liquid nitrogen the susceptibility is independent on the field strength. Down to the lowest ethylene temperatures all of them satisfy the relation $\chi(T-\theta) = C$ in which θ is found to be $32^\circ.5$, 20° and 67° resp.

3. In the temperature region of liquid hydrogen for all of them the

susceptibility depends on the field strength; for CrCl_3 it decreases, for CoCl_2 and NiCl_2 it increases with increasing field.

4. With a given field strength the susceptibility of CrCl_3 increases with falling temperature, for CoCl_2 it decreases a little, for NiCl_2 the initial susceptibility decreases a little.

I have pleasure in thanking Prof. KAMERLINGH ONNES very heartily for his invitation to this research and his continued interest and Mr. E. C. WIERSMA for his strong support in the final experiments and the calculation of their results.

Physics. — "*Further experiments with liquid helium. Z. Magnetic researches. XXVIII. Magnetisation of anhydrous CrCl_3 , CoCl_2 and NiCl_2 at very low temperatures.*" By H. R. WOLTJER and H. KAMERLINGH ONNES.

(Communicated at the meeting of May 30, 1925).

§ 1. *Introduction.* In the preceding communication the magnetic anomalies shown by anhydrous CrCl_3 , CoCl_2 and NiCl_2 at the temperatures of liquid hydrogen have been pointed out. It seemed to be important to extend this research to the very low temperatures obtainable with liquid helium. The following questions came to the foreground: as regards CrCl_3 whether the initial susceptibility would increase with decreasing temperature as strongly as in the liquid hydrogen region and whether in strong fields saturation phenomena would appear; for the other substances whether the decrease of the susceptibility with decreasing temperature that seemed to be indicated by the measurements in liquid hydrogen would be continued.

§ 2. *Method.* With the same samples to which the preceding communication refers, the magnetisation was determined from the attraction, exerted on a small quantity of the substance in an inhomogeneous magnetic field following exactly the method described in full in connection with the investigation of gadoliniumsulphate ¹⁾.

§ 3. *Results.* For CrCl_3 two series of measurements in helium have been carried out and three in liquid hydrogen; for each of both other substances one series in liquid helium followed in each case by a measurement in liquid hydrogen.

It seems superfluous to give here all the figures concerning CrCl_3 . In table I we give part of the series of 12 and 15 July 1922. These observations have been plotted in fig. 1. The curves in that diagram have been obtained by smoothing the *whole* observational material. This smoothing was performed thus: with the aid of the preliminary isotherms the curves $H = \text{constant}$ have been drawn in a σ, T -diagram (σ is the specific magnetisation, H the field strength after correction for demagnetisation) (fig. 2) and from this the final σ, H -diagram has been traced.

In table II are given the forces (in grammes) exerted on the samples of CoCl_2 and NiCl_2 (resp. 0.2990 and 0.2515g.) at different temperatures

¹⁾ These Proc. 26, p. 614; Leiden Comm. N^o. 167b.

TABLE I. CrCl_3

T 20°.3 K		14°.6		4°.23		2°.36		1°.23	
H	σ	H	σ	H	σ	H	σ	H	σ
2.6 Kg.	11.5	2.5	25.2	2.3	35.2	2.3	36.0	2.3	36.3
5.1	22.5	5.0	38.2	4.8	47.3	4.8	48.6	4.8	49.4
7.7	31.1	7.5	49.1	7.4	57.3	7.4	58.6	—	—
10.1	38.3	9.9	57.4	9.8	66.5	9.8	66.9	9.8	67.2
13.7	45.4	13.5	65.3	13.3	77.1	13.3	78.0	13.3	78.8
16.3	49.4	16.0	68.2	15.9	83.0	15.9	84.2	15.9	85.1
17.5	51.7	17.3	69.9	17.1	86.3	—	—	17.1	88.5
18.1	52.7	17.9	70.6	17.7	88.0	17.7	89.5	—	—

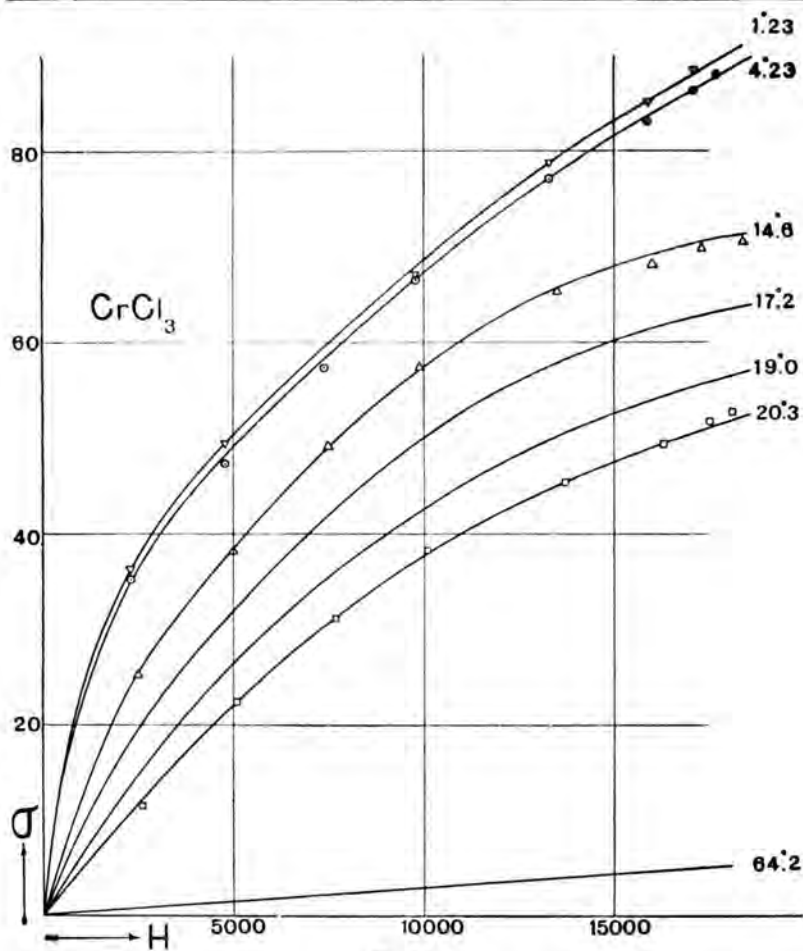


Fig. 1.

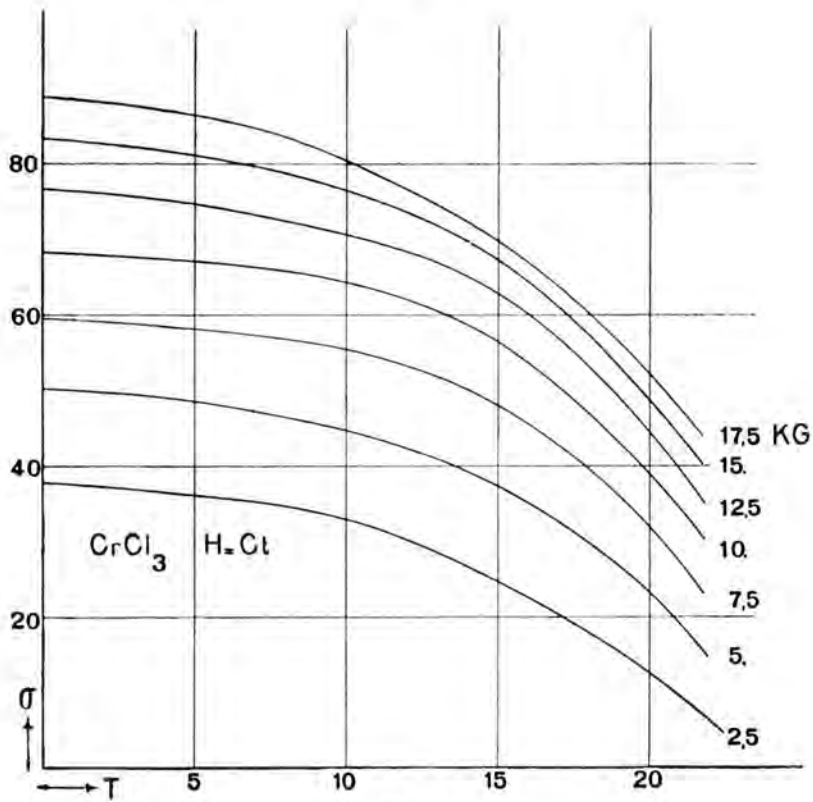


Fig. 2.

TABLE II.

I	3	4	5	10	15	20	30	45	60	70
CoCl_2										
20.4 K	—	—	0.9	3.9	9.9	17.9	31.9	41.9	45.4	—
14.0	—	—	0.8	3.8	9.6	17.6	31.6	41.6	45.2	46.8
4.2	—	—	0.8	3.7	9.5	17.7	31.8	41.8	45.4	47.1
2.31	—	0.4	0.7	3.7	9.5	17.7	31.7	41.8	45.4	47.1
1.48	—	—	—	—	—	—	32.2	—	45.9	—
NiCl_2										
20.4	—	—	0.3	1.3	3.0	5.4	9.6	12.5	13.8	—
14.6	—	—	0.3	1.3	3.0	5.4	9.7	12.5	13.8	—
4.22	—	—	0.3	1.2	3.0	5.3	9.5	12.6	13.7	14.3
2.30	0.11	0.18	0.3	1.2	3.0	5.2	9.6	12.5	13.8	14.3
1.48	—	—	—	—	2.9	—	—	—	13.8	14.3

and different currents in the magnetcoils. It shows that the change of the susceptibility is very small for CoCl_2 and entirely out of the experimental accuracy for NiCl_2 . The magnetisation being so slightly dependent on temperature, in table III and in figs. 3 and 4 only one magnetic isotherm is given, that for 2.03 K.^1

TABLE III, $T = 2.03\text{ K.}$

NiCl_2		CoCl_2	
H	σ	H	σ
1.6	1.1	—	—
2.2	1.3	2.2	2.6
2.7	1.6	2.7	3.5
5.2	3.6	5.2	9.1
7.7	5.7	7.7	15.8
10.2	7.9	10.1	22.5
13.7	11.3	13.6	31.3
16.2	13.6	16.1	38.0
17.4	14.9	17.3	41.2
18.0	15.6	17.9	43.1

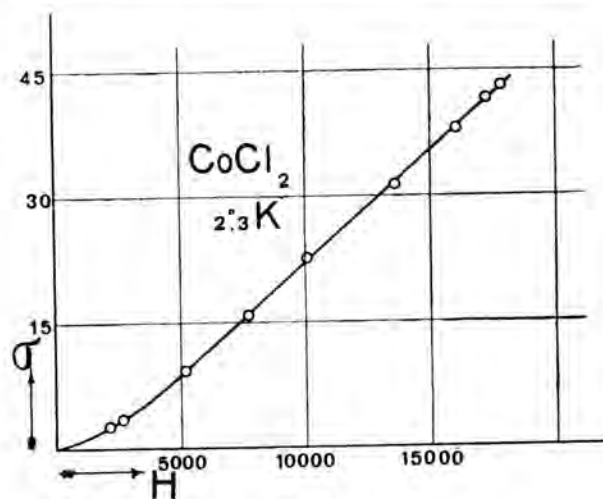


Fig. 3.

¹⁾ If σ over H is taken, values for χ are found slightly different from those given in table IV of the preceding communication for CoCl_2 and NiCl_2 at 14.02 K. , even if the circumstance is taken into account, that in table III of the present communication corrections

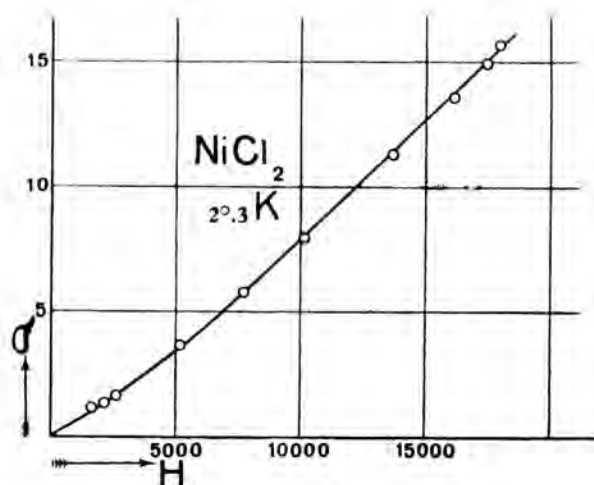


Fig. 4.

§ 4. *Discussion.* The magnetisation curves show some resemblance to those found by WEISS and FORRER ¹⁾ for nickel in the neighbourhood of the CURIE-point, but there are also striking differences: there is no question of saturation magnetisation and the slope of the isotherm for large fields is at helium temperatures even greater than at hydrogen temperatures ²⁾. WEISS's theory of ferromagnetism does not seem to be applicable here. The highest specific magnetisation attained by us is 89.5 e. m. C.G.S. corresponding to 12.6 magnetons, and the saturation would correspond to 18 magnetons. Neither for CrCl_3 nor for the other chlorides have we found hysteresis or residual magnetism.

For CoCl_2 and NiCl_2 the magnetisation curves are for smaller fields convex to the H -axis, for larger ones nearly linear; the susceptibility approaches asymptotically a limit for large fields. Formally, this feature may be explained thus: the magnetisation may be considered to be a result of two components, one proportional to the field strength (in the diagram it would be represented as a straight line through the origin

for the demagnetisation are applied. Nearly as large differences are found, if, not the calculated susceptibilities, but the values of the attraction at hydrogen temperatures found here are compared with those on which the χ -values of table IV on the preceding communication are based. The present observations have been made by means of a different apparatus and on another occasion to those of the preceding paper. The latter are no doubt more accurate, but the former are better comparable with the observations in liquid helium, since they are taken within a small interval of time, using the same method and the same apparatus. As regards NiCl_2 the differences remain nearly within the accuracy of the experiments (about 20%), for CoCl_2 they are larger (above 40%) and not yet quite explained.

¹⁾ Paris C.R. 178, p. 1046.

²⁾ This remark only holds if the large magnetisation of the CrCl_3 does not influence the distribution of the lines of force and the calibration of the large magnet remains valid.

parallel to the straight part of the curve); and a second in the opposite direction to the field, which develops under influence of the field from zero to a maximum amount. However it seems difficult to see the physical meaning of this last component. As regards CrCl_3 the measurements do not favour the conclusion that there is a limit to the susceptibility; there seems to be no reason for replacing the last parts of the curves for $1^\circ.23$ and $4^\circ.23$ K in fig. 1 by straight lines. If there was a limit, one could perhaps think of a superposition of paramagnetism and ferromagnetism, as recently found by PESCHARD¹⁾.

For CrCl_3 it seems important to investigate the magneto-caloric effect in order to ascertain whether there is yet a spontaneous magnetisation notwithstanding the absence of saturation phenomena²⁾.

§ 5. Summary.

1. For anhydrous CrCl_3 , CoCl_2 and NiCl_2 the magnetisation curves have been determined at the temperatures of liquid hydrogen and helium, at which temperatures these substances are below their "CURIE-temperature"³⁾.

2. CrCl_3 shows ferromagnetism in so far as the susceptibility decreases with increasing field strength; saturation spontaneous magnetisation, or hysteresis has not been found.

3. NiCl_2 and CoCl_2 show an unusual type of magnetisation curve, first convex to the H -axis, then linear for higher fields. At low temperatures the law connecting magnetisation and field strength seems to approach asymptotically to a definite form (different for CrCl_3 and for CoCl_2 and NiCl_2) and so to become independent of temperature; for CoCl_2 and NiCl_2 this form has been reached nearly at hydrogen temperature; for CrCl_3 there is only a small change in magnetisation on cooling from $4^\circ.23$ to $1^\circ.23$ K.

¹⁾ Paris C.R. 180 (1925) p. 1836.

²⁾ The lines $\tau = ct$ in a H, T -diagram from which, as shown by WEISS and FÖRRER for nickel, the spontaneous magnetisation also may be derived, do not give much information in our case, mainly on account of the temperature gaps above and below the liquid hydrogen region [note added in the translation].

³⁾ Here by „CURIE-temperature“ the temperature θ in the relation $\chi(T - \theta) = C$ is meant.

Mathematics. — "*Representation of the Pairs of Points that are Associated relative to a Conic, on the Points of Space*". (Second communication). By G. SCHAAKE. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of May 30, 1925).

In these Proceedings, XXVIII, p. 267, the author has treated a representation of the pairs of points associated relative to a conic, on the points of space. In the following paper we shall indicate a way of producing the same representation which differs from the one given l.c.

§ 1. The system of the pairs of points of a plane α is a system of ∞^4 individuals, the same as that of the straight lines of space. Both systems have moreover the property in common that we may define their figures by six homogeneous coordinates between which there exists a fundamental relation. For the straight lines of space these are PLÜCKER's coordinates.

In order to find the coordinates of a given pair of points (P_1, P_2) of α we remark that the two pencils of rays that have P_1 and P_2 as vertices, form a degenerate class-conic, i.e. that these two pencils form together a degeneration of the system of straight lines which envelop a conic. The product of the first members of the equations of P_1 and P_2 in line coordinates gives the first member of the equation of the aforesaid class-conic k_2 . Hence this equation has the form:

$$p_{11} \xi_1^2 + 2p_{12} \xi_1 \xi_2 + 2p_{13} \xi_1 \xi_3 + p_{22} \xi_2^2 + 2p_{23} \xi_2 \xi_3 + p_{33} \xi_3^2 = 0 \quad (1)$$

Now we consider the six coefficients p_{ik} as homogeneous coordinates of the pair of points (P_1, P_2) . As k_2 is degenerate they must satisfy the relation:

$$\begin{vmatrix} p_{11} & p_{12} & p_{13} \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{vmatrix} = 0 \quad (2)$$

It is obvious that inversely six quantities p_{ik} which satisfy the relation (2), define a pair of points of α , the pair of the two points into which the class-conic represented by equation (1), degenerates.

If the homogeneous coordinates of P_1 and P_2 are resp. x_1, x_2, x_3 and x'_1, x'_2 , and x'_3 , we have:

$$p_{ik} = \frac{1}{2} (x_i x'_k + x_k x'_i),$$

hence:

$$p_{ii} = x_i x'_i.$$

§ 2. If we consider p_{11}, \dots, p_{33} as homogeneous coordinates of a point Q in R_5 , (2) is the equation of a cubic variety of R_5 . If we associate to each other the pair of points (P_1, P_2) of α and the point Q of V_4 which have the same homogeneous coordinates, we find a one-one correspondence between the pairs of points of α and the points of V_4 and accordingly a representation of the system of the pairs of points of α on the above mentioned cubic variety ¹⁾.

This representation has neither singular points nor singular conics. By transformation to another system of coordinates in α the formulas of transformation for the p 's are also linear. We see, therefore, that the geometry of the pair of points in the plane is identical with that on a cubic variety in R_5 .

§ 3. If we have two conics:

$$S_1 \equiv \sum a_{ik} x_i x_k = 0 \quad \text{and} \quad S_2 \equiv \sum b_{ik} x_i x_k = 0,$$

and if A_{ik} is the minor of a_{ik} in the discriminant of the form S_1 ,

$$\sum A_{ik} b_{ik} = 0$$

is the condition that must be satisfied if the conic $S_1 = 0$ is to be harmonically inscribed in $S_2 = 0$.

The A 's are the coefficients of the class-equation of the conic $S_1 = 0$. Hence

$$\sum p_{ik} a_{ik} = 0$$

is the condition that must be satisfied if the conic $p_{ik}^2 = 0$ is to be harmonically inscribed in $a_{ik}^2 = 0$.

Accordingly a linear four-dimensional space R_4 in R_5 represents all the conics p_{ik}^2 that are harmonically inscribed in a given conic k^2 . The intersection with V_4 is the representation of the system of the pairs of points that are associated relative to k^2 . For if we choose a polar triangle of k^2 the conics inscribed in this triangle which have degenerated into a pair of points, always consist of an angular point of this triangle and a point of the opposite side. Accordingly the conics harmonically inscribed in k^2 which have degenerated into a pair of points, always consist of two points associated to each other relative to this conic, and obviously the inverse also holds good.

Consequently the system Σ of the pairs of points associated relative to a conic k^2 , is represented on the cubic variety V_3 in which V_4 is cut by R_4 . On this variety lies the curve of the image points of the coincidences of Σ , for which P_1 and P_2 coincide in a point of k^2 .

The order of this curve is equal to the number of points of inter-

¹⁾ Cf. CAYLEY: On the curves which satisfy given conditions, *Philosophical Transactions of the Royal Society of London*, vol. 158, p. 75, where the representation is treated of the pairs of lines of a plane on a cubic variety in R_5 .

section with another linear four-dimensional space R'_4 , of which the points on V_4 are the images of the pairs of points which are associated to each other relative to another conic k'^2 . The points that are common to R_4 , R'_4 and V_4 are the images of the pairs of points which are associated to each other relative to k^2 as well as relative to k'^2 and which define, therefore, a quadratic involution in α . This involution contains four coincidences, to wit the points of intersection of k^2 and k'^2 ; hence the locus on V_3 of the images of the double points of Σ is a biquadratic rational curve k^4 . This appears also analytically if we substitute for x_1 , x_2 and x_3 in the equations

$$p_{ik} = x_i x_k$$

expressions that are quadratic in a parameter t .

A straight line of V_3 represents a tangential pencil of conics of which all the individuals have degenerated into two plane pencils. The vertices of these pencils form in the first place the associated pairs of points of a line l , which define an involution λ . The image line k of λ is a chord of k^4 as each system λ contains two coincidences. If these coincidences lie in the points A_1 and A_2 of k^2 , k is the line which joins the image points K_1 and K_2 on k^4 of these coincidences. As each pair of points associated relative to k^2 belongs to one system λ , we find:

The variety V_3 consists of the chords of k^4 .

Further we have systems π of which the pairs consist of a fixed point P and the points of the polar line p of P relative to k^2 . These are represented on straight lines s of V_3 , which, as a system π does not contain any coincidence, do not have any point in common with k^4 . The transition between the systems π and λ is formed by the systems τ which consist of a point T of k^2 and the points of the tangent t to k^2 at T . To a system τ there corresponds a tangent to k^4 .

A straight line through a point of k^4 is the image of a special tangential pencil of conics. For an arbitrary straight line the image points of the three degenerations of the corresponding tangential pencil lie in the points of intersection of this line with V_3 . In the special case which we considered, one of the conics of the tangential pencil has degenerated into a double point. As we know that this double point counts for two degenerations of the tangential pencil, two of the points of intersection of a line cutting k^4 with V_3 coincide in the intersection of the line with k^4 , and k^4 is therefore a double curve of V_3 .

§ 4. We choose a point K on k^4 and we project V_3 out of K on a three-dimensional space R_3^1 of R_4 . The projection S of a point Q of V_3 on R_3^1 may be considered as the image point of the pair of points (P_1, P_2) of α corresponding to Q . In this way we have found a representation of the pairs of points associated relative to k^2 on the points of R_3^1 . The projection k^3 of k^4 out of K on R_3^1 consists of points that are singular

for the representation. For if we choose S on k^3 , the whole line KS lies on V_3 . Consequently S is the image of all the pairs of points of the line BP that are associated relative to k^2 if the coincidences lying in the points B and P of k^2 are resp. represented on K and the other intersection of KS and k^4 .

The curve k^3 is the locus of the singular image points. k^3 always contains the image point of one of the ∞^2 pairs of points of which the carriers pass through B .

As k^3 is the projection of k^4 out of K on R_3^1 , k^3 is in particular the locus of the image points of the coincidences among the pairs of points associated relative to k^2 .

An arbitrary R_3 of R_4 cuts V_3 in a cubic surface Ω which has four conical points in the points of intersection of this R_3 with k^4 . The projection of this surface, a cubic surface Ω' with four conical points lying on k^3 , is the image of the system of the pairs of points that are associated relative to the conics of a pencil and which form, accordingly, a quadratic involution. If we have a space which touches k^4 at K , two of the conical points of Ω coincide in a biplanar point of this surface.

The tangent planes are the planes through the tangent k at K to k^4 and the other two conical points. For an arbitrary plane through k cuts Ω along k and a conic which touches k at K . For each of the two above mentioned planes this conic degenerates into two lines through K one of which passes through another conical point of Ω . Hence any line through K in such a plane has three points of intersection coinciding in K with the intersection of Ω and the plane, so that the pencil in this plane which has K as vertex, consists of tangents of Ω .

The quadratic hypercone of the tangents of V_3 at K is accordingly cut by an R_3 touching k^4 at K along the two planes through k and the two points of intersection outside k of the R_3 with k^4 . If k cuts the space R_3^1 in the point A on k^3 , these planes are projected out of k on R_3^1 in two generatrices of the cone κ which projects k^3 out of A .

To the coincidence in B there corresponds on V_3 the point K . For the projecting ray we may now choose any tangent to V_3 at K .

Consequently the representation of the pairs of points (P_1, P_2) associated relative to k^2 on the points S of R_3^1 , contains one cardinal pair of points, the one for which P_1 and P_2 coincide in B . To this pair the points of the quadratic cone K are associated.

If a point Q of V_3 approaches to the point K of k^4 , the chord of k^4 through Q approaches to the chord KL of this curve which lies in the plane through k and the tangent q at K to the curve along which Q approaches to k^4 . The pair of points (P_1, P_2) corresponding to Q approaches to the coincidence in B , so that the line $P_1 P_2$ approaches to the join of B and the point P of k^2 which corresponds to the point L of k^4 . The tangent q which is the limiting position of the projecting line KQ , cuts R_3^1 in a point of the generatrix of κ which joins A to the point of k^3 that corresponds to P .

To a pair of points for which P_1 and P_2 coincide in B and $P_1 P_2$ is defined, there correspond accordingly the points of a generatrix of κ . This generatrix joins A and the point of k^3 which corresponds to the point different from B where $P_1 P_2$ cuts k^2 .

§ 5. The intersection of a space touching k^4 at K with V_3 , the surface Ω , has the line KK_1 which joins the biplanar point K to a conical point K_1 , as torsal line. By making two conical points of an arbitrary surface Ω approach K we can easily see that the plane through KK_1 and k becomes a tangent plane to Ω at all points of KK_1 .

In the same way the intersection of V_4 with the space through KK_1 which touches k^4 at K_1 , has the line KK_1 as torsal line, and the plane through KK_1 and the tangent k_1 to k^4 at K_1 becomes a tangent plane to the surface. Hence V_3 has the same tangent space along a chord of k^4 , the space which is defined by the tangents to k^4 at the points where this chord cuts k^4 .

The tangent spaces of V_3 along the generatrices of this variety through K cut R_3^1 along the tangent planes of κ through A .

To a system of ∞^1 pairs of points associated relative to k^2 containing a pair for which P_1 and P_2 do not coincide and the carrier passes through B , there corresponds a curve on V_3 which cuts a generatrix of V_3 through K . The projection of this curve must touch κ at the projection on k^3 of the point of intersection.

If the image curve in R_3^1 of such a system cuts k^3 but does not touch κ at this point of intersection, this point is the image of a coincidence. For the point of the curve which corresponds to this curve on V_3 of which the aforesaid point of intersection is the projection, must necessarily lie on the double curve of this variety.

Analogous remarks may be made about the image surface of a system of ∞^2 pairs of points that are associated relative to k^2 .

§ 6. A system λ of the ∞^1 pairs of points of a line l associated relative to k^2 , is represented on a chord of k^4 which is projected out of K in a chord of k^3 .

Accordingly the system λ of the ∞^1 pairs of points of a line l which are associated relative to k^2 , is represented on a chord of k^3 .

A system π which consists of the pairs of points associated relative to k^2 for which one point lies in a given point P and the other, therefore, on the polar line p of P , is represented on a straight line of V_3 that does not cut k^4 . This line cuts a generatrix of V_3 through K in the image point of the pair that consists of P and the intersection of BP and p . Consequently its projection s on R_3 touches κ on k^3 at the point which corresponds to the point of intersection outside B of the line BP and k^2 .

A system π is represented on a line s which touches κ on k^3 .

§ 7. The representation of the pairs (P_1, P_2) on the points S of R_3^1 may also be brought about without more-dimensional considerations. We consider the one-one correspondence between the points of k^2 and those of k^3 . The image point S of (P_1, P_2) must lie on the chord k of k^3 corresponding to the system λ of $P_1 P_2$ and on the two lines s which correspond to the systems π that are defined by P_1 and P_2 . The chord k joins the points of k^3 which correspond to the points of intersection of $P_1 P_2$ and k^2 . The lines s lie in the tangent planes of κ at those points of k^3 that are associated to the points of intersection outside B of BP_1 and BP_2 with k^2 .

The image point S is a common point of the two above mentioned tangent planes and the chord k .

If k^2 is the projection of k^3 on a plane α out of a point A of k^3 and if the corresponding points of k^3 and k^2 always lie on a projecting ray, hence on a generatrix of κ , the projections of the lines s on α are the tangents to k^2 at the points of intersection outside B of BP_1 and BP_2 with k^2 . The intersection of these tangents lies on $P_1 P_2$. For the pairs (K_1, K_2) of these points of intersection which may be derived from the pairs (P_1, P_2) of the involution defined on $P_1 P_2 = l$ by k^2 , form an involution on k^2 of which the double points lie in the points of intersection of l with k^2 and which, accordingly, has l as axis.

The point S , i.e. the intersection of the lines s , has the intersection of the two aforesaid tangents as projection and lies moreover on the chord k of k^3 corresponding to $P_1 P_2$, i.e. the chord k of k^3 that does not pass through A , lying in the plane through A and $P_1 P_2$.

In this way we have come back to the way of producing our representation which has been treated in the paper mentioned at the beginning.

Mathematics. — "*An Involution in the Rays of Space through which a Quadratic Scroll is Associated to a Plane Pencil*". By G. SCHAAKE.
(Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of May 30, 1925).

§ 1. We start from a linear complex C , a straight line m which does not belong to C , and a straight line n lying in C . By the aid of these we can associate to any line l of space a line l' in the following way.

We consider the scroll ϱ defined by l , m and n . This has one more straight line o in common with C besides n . We associate to l the generatrix l' of ϱ which is harmonically separated from l by m and o . The ∞^4 pairs of rays (l, l') define an involution I in the rays of space.

§ 2. If l is chosen in n , there are ∞^3 scrolls ϱ , hence ∞^3 lines l' . Accordingly a complex N of lines n' is associated to n in our involution of rays I .

In order to find the number of generatrices n' of N in a given plane pencil (T, τ) , we remark that a straight line n' lying in (T, τ) belongs to a scroll ϱ which has the transversal t_1 of m and n through T and the transversal t_2 of m and n lying in τ as directrices, as t_1 and t_2 must cut at least three straight lines in ϱ .

Consequently the straight line o corresponding to n' , which is at the same time a generatrix of ϱ , must lie in the plane pencil which has as vertex the point T' which is harmonically separated from the point t_1m by T and the point t_1n and of which the plane passes through t_2 . As this line o must belong to C , the pencil in question contains only one line o , which corresponds to a straight line n' of (T, τ) . Accordingly (T, τ) contains only one line n' of N so that N is a linear complex.

In order to find the plane pencil of N that has an arbitrary point T of space as vertex, we consider the transversal t_1 of m and n through T and we determine the point on t_1 that is harmonically separated from the point of intersection of t_1 and m by T and the intersection of t_1 and n . The plane of the pencil of C that has this point as vertex, contains the transversal t_2 of m and n . The plane through T and t_2 is, therefore, the plane of the pencil of N that has T as vertex.

If we have a straight line n' which cuts n , the scroll through m and n containing n' must degenerate into a plane pencil ψ containing n and a plane pencil φ containing m which has one ray in common with ψ .

If ψ does not belong to C , o lies in φ but not in ψ and the same holds good for the line n' , that is harmonically separated from o and m by the line $\varphi\psi$, so that in this case we do not get a straight line cutting n .

If, however, ψ belongs to C , all the complex rays in ψ may be considered as lines o and also as lines n' , as each line n' is harmonically separated from n by o and the line that is common to φ and ψ . Accordingly N has all the plane pencils containing n in common with C .

The line n is, therefore, for I a singular line of the third rank¹⁾. To n there corresponds a linear complex N which contains the special bilinear congruence I' of the lines of C that cut n .

To any line l of a plane pencil ψ containing n , there corresponds as line l' the generatrix of the plane pencil φ corresponding to ψ which is harmonically separated from the lines m and o in φ by the line $\varphi\psi$. As there are ∞^2 plane pencils ψ containing n , we find ∞^2 singular lines, which all cut m and, as they also correspond to n in I , belong to N .

Accordingly the bilinear congruence B of the lines of N that cut m , consists of straight lines that are singular for I . To each of these lines a plane pencil containing n is associated. To each line cutting n there corresponds a line of B .

For a straight line l which belongs to a plane pencil ψ of C containing n , all the lines of ψ are lines o , hence also lines l' .

Consequently the lines of the special bilinear congruence I' of the rays of C which cut n , are also singular for our representation. To each line of I' there correspond as lines l' all the lines of the plane pencil of this congruence which contains l .

If we choose l in m there are ∞^3 scrolls ϱ , but on each of these scrolls the line l' which is harmonically separated from l by m and o , coincides with l .

Hence the line m is an isolated double ray of our involution and C consists wholly of double rays.

§ 3. For the rays l belonging to a given plane pencil (T, τ) the scroll ϱ always has as directrices the transversal t_1 through T of m and n and the transversal t_2 of these lines lying in τ . Hence the scroll λ associated to (T, τ) belongs to the bilinear congruence that has t_1 and t_2 as directrices. As (T, τ) has one ray in common with the linear complex N and contains one line which cuts n , n is a generatrix of λ and this surface has one line in common with the bilinear congruence B . The lines o corresponding to the lines l of (T, τ) form the scroll π of C that has t_1 and t_2 as directrices.

Through a point of t_1 there passes only one generatrix of λ , the genera-

¹⁾ A singular straight line of the rank n is a straight line to which ∞^n rays are associated.

trix of the scroll ϱ which is defined by l , m and the line of π passing through the point of t_1 that is harmonically separated from the intersection of t_1 and m by T and the chosen point.

Suppose that through a point of t_2 there pass x lines of λ ; in this case this scroll is of the order $x+1$, the same as the surface that is associated to the plane pencil which has a point on t_2 as vertex, which surface has t_2 as single and t_1 as x -fold directrix. The two scrolls have $(x+1)^2 - 2x = x^2 + 1$ generatrices in common. These are in the first place the line n and further the line l' which is associated to the common line l of the two plane pencils. Hence $x^2 + 1 = 2$ or $x = 1$.

Consequently to a plane pencil of lines l there corresponds a quadratic scroll of lines l' which contains n and has one line in common with the bilinear congruence B^1).

If (T, τ) contains one line of B , a plane pencil containing n splits off from the associated scroll and there remains a plane pencil that has one line in common with B .

For a line l cutting m ϱ degenerates into a plane pencil φ containing m and a plane pencil ψ containing n . The line o lies in φ the same as l' , which line is harmonically separated from l by m and o . A plane pencil with vertex on m , which accordingly contains one line of B , is therefore transformed into a plane pencil that has the same vertex. In the same way it appears that to a pencil in a plane through m , there corresponds a pencil in the same plane and that a plane pencil containing m is transformed into itself.

If (T, τ) has a straight line in common with l' , the plane pencil of l' which contains this line, splits off from λ . n belongs to this pencil and it has a line in common with B as it lies in the linear complex N together with B . Accordingly there remains a plane pencil that has no line in common with B but that has a line in common with l' . This line lies in the plane pencil of l' which contains the common line of (T, τ) and l' .

We saw that to a line l cutting n there corresponds a line which passes through the point of intersection of the plane (n, l) with m and which lies in the plane through m and the point ln . If, therefore, we have a plane pencil with vertex on n , a pencil of B corresponds to it which lies in the plane through m and the vertex on n and of which, accordingly, the vertex lies on the line m' which is associated to m relative to the complex N . On the contrary to a pencil of lines l of which the plane passes through n , there corresponds a pencil of B of which the vertex lies in the intersection of m and the plane through n , and which lies in a plane through m' .

¹⁾ Another involution of rays, which transforms a plane pencil into a quadratic scroll, has been indicated and investigated by Prof. JAN DE VRIES, these Proc., XXII, p. 462. In this involution, however, the image of a sheaf is not a bilinear congruence, but a congruence (3,1).

§ 4. To a sheaf of lines l with vertex P there corresponds a congruence Σ of lines l' that has the transversal p of m and n through P as directrix, as this line is a directrix of all the scrolls ϱ of the lines l of the sheaf P . For a line l through P of which the associated line l' passes through a given point Q , the scroll ϱ must also have the transversal q of m and n through Q as directrix. Hence such a line l must lie in the pencil that has P as vertex and of which the plane passes through q . One generatrix of the scroll λ corresponding to this pencil passes through Q . The sheaf-order of Σ is accordingly one.

In the same way the pencil that has P as vertex and which lies in a plane through the transversal b of m and n in a plane β , must contain each line l through P for which the associated line lies in β . One generatrix of the scroll λ corresponding to this pencil lies in β . Accordingly the field-order of Σ is also one.

The congruence Σ contains n , as this line is associated to the plane pencil of lines l which the sheaf P has in common with the complex N . As further the sheaf P contains a pencil of lines l in a plane through n , Σ has in common with B a pencil with vertex in the intersection M of p and m in a plane through m' . Σ also contains the plane pencil of l' which contains the line of l' through P .

To a sheaf P there corresponds accordingly a bilinear congruence Σ which contains n , has a pencil in common with B that has its vertex on m and lies in a plane through m' , and has a pencil in common with Γ .

The lines of Σ through P form the plane pencil of double rays belonging to C which has this point as vertex. The directrix of Σ different from p is the transversal of n and m' lying in the plane of this pencil.

If P lies on n there corresponds to the sheaf a pencil of singular lines belonging to B in a plane through m and P of which the vertex lies on m' .

As to a line cutting m there corresponds a ray which cuts m in the same point, a sheaf with vertex on m is transformed into itself.

If P lies on m' there splits off from the corresponding bilinear congruence the sheaf of which the vertex S lies in the intersection of n with the plane through m and P , as this sheaf corresponds to the plane pencil which the sheaf P has in common with the congruence B . Consequently there remains a field of rays that must have a pencil in common with B in a plane through m' , so that the plane of this field is the plane (S, m') .

From the field-order of the congruences Σ , i.e. the number of pairs of the involution of which one line passes through a given point and the other lies in a given plane, it ensues that to a field of rays α there corresponds a congruence Φ with sheaf-order one. For the pairs of rays (l, l') of which l lies in α and l' in a plane β , the scrolls ϱ have the transversals a and b of m and n in these planes as directrices, so that l lies

in the plane pencil in a which has the intersection of b with a as vertex. The plane β through b contains one generatrix of the scroll corresponding to this pencil. Accordingly the field-order of Φ is also one.

Φ contains again n and the plane pencil of Γ to which the ray of Γ in a belongs. But a contains a plane pencil with vertex on n , so that Φ has a pencil in common with B in a plane through m of which the vertex lies on m' . The plane of the latter pencil passes at the same time through the point of intersection of a and n .

Consequently to a field of rays a there corresponds a bilinear congruence Φ containing n which has a pencil in common with B with vertex on m' and lying in a plane through m , and which has a plane pencil in common with Γ .

The rays of Φ in a are double rays of our involution and form the pencil of C in this plane. The transversal of m and n through the vertex of this pencil is the directrix of Φ different from a .

If a passes through n there corresponds to the field a plane pencil of singular lines belonging to B . The vertex of the pencil lies in the point of intersection of m and a , its plane passes through m' .

A field containing m is transformed into itself because to a line l cutting m there corresponds a ray in the plane (m, l) .

If a passes through m' there splits off from the associated bilinear congruence the field of rays of which the plane σ is defined by n and the point of intersection of a and m , as this field corresponds to the pencil of B lying in a . Accordingly there remains a sheaf of rays which must have a plane pencil in common with B of which the vertex lies on m' , so that the vertex of the sheaf associated to a lies in the point of intersection of this line with σ .

§ 5. As a linear complex L has two straight lines in common with a scroll λ , the corresponding complex A contains two generatrices of any plane pencil. Hence A is quadratic. The complex A contains n , as this line is associated to all the lines which L has in common with N . Accordingly a plane pencil containing n to which there corresponds a line of B , generally outside L , does not contain any line of A besides n , so that n is a double line of this complex.

As L has one line in common with any plane pencil containing n and with any plane pencil of Γ , the congruences B and Γ belong wholly to A .

The lines of A issuing from a point P of n , form the plane pencil of Γ which has P as vertex, and the plane pencil corresponding to the line which L has in common with the pencil of B in the plane (P, m) .

To a linear complex L there corresponds a quadratic complex A which contains the congruences B and Γ and which has n as double line.

If L contains the line n , the linear complex A containing n , B and Γ

splits off from N and, accordingly, there remains a linear complex to which n belongs.

A linear complex containing B or Γ always becomes such a complex.

If L is a special complex with axis a , Λ consists of congruences Σ as well as of congruences Φ . The directrices of the congruences Σ form two scrolls of which the first has a , m and n as directrices, the second a' , m' and n , if a' is the straight line associated to a relative to C . In this way the directrices of the congruences Φ form two scrolls of which the first has a , m and n , the second a' , m and n as directrices.

§ 6. We consider a scroll κ of the order μ which has n as ν -fold line and which contains resp. β and γ lines of B and Γ . This has in common with the quadratic complex Λ corresponding to a linear complex, $2\mu - 2\nu - \beta - \gamma$ lines that are not singular for the involution, which number indicates the order of the scroll κ' corresponding to κ . As κ has $\mu - \nu - \beta - \gamma$ lines outside B and Γ in common with N , κ' contains the line n as $\mu - \nu - \beta - \gamma$ -fold generatrix. The number of generatrices of κ that are not singular for our involution, i. e. the number of these lines which belong at the same time to the special linear complex with axis n , is $\mu - 2\nu - \gamma$. Further there corresponds to any common line of κ and Γ a line of κ' which belongs at the same time to Γ .

To a scroll of the order μ which has n as ν -fold line and which contains resp. β and γ lines of B and Γ , there corresponds a scroll of the order $2\mu - 2\nu - \beta - \gamma$ which has a $\mu - \nu - \beta - \gamma$ -fold generatrix in n and which has $\mu - 2\nu - \gamma$ lines in common with B and γ lines different from n in common with Γ .

Accordingly to an arbitrary scroll of the order μ there corresponds a scroll of the order 2μ which has a μ -fold generatrix in n and which has μ lines in common with B .

Let us now examine the congruence Ψ' corresponding to a congruence Ψ (s, v) which has a p -fold line in n , which has a scroll in common with B of which m is an a -fold, m' a b -fold directrix and which contains c generatrices of any plane pencil of Γ .

Ψ has resp. $s + v - p - a - c$ and $s + v - p - b - c$ non-singular generatrices in common with a congruence Σ and a congruence Φ . Hence a plane pencil of B with vertex on m , to which there corresponds a field of rays containing n , contains $v - p - c$, a pencil of B in a plane through m , to which a sheaf with vertex on n is associated, contains $s - p - c$ lines of Ψ' .

Through a point of n there pass b non-singular lines of Ψ' , in a plane through n there lie a non-singular lines of the congruence, as a sheaf with vertex on n and a field through n correspond resp. to a plane pencil of B with vertex on m' and a plane pencil of B with vertex on m .

Consequently to a congruence Ψ with sheaf-order s and field-order v with a p -fold line in n which has a scroll in common with B for which

m is an a -fold, m' a b -fold directrix, and which contains c generatrices of any plane pencil of Γ , there corresponds a congruence Ψ' with sheaf-order $s+v-p-a-c$ and field-order $s+v-p-b-c$ which has a scroll in common with B that has m as $v-p-c$ -fold, m' as $s-p-c$ -fold directrix, which contains c lines of any plane pencil of Γ and has an $s+v-p-a-b-2c$ -fold line in n .

Ψ' has as many plane pencils in common with Γ as Ψ contains lines of Γ that are not singular for the involution, hence $s+v-2p$.

Accordingly to an arbitrary congruence $\Psi(s, v)$ there corresponds a congruence $\Psi(s+v, s+v)$, which has a scroll in common with B that has m as v -fold, m' as s -fold directrix, and which has an $s+v$ -fold generatrix in n . Ψ' has $s+v$ plane pencils in common with Γ .

Finally we examine the complex K' which corresponds to a complex K of the order κ of which the rays of the congruences B and Γ are resp. δ - and ε -fold lines, and which has n as π -fold line.

The complex K contains $2\kappa-\pi-\delta$ generatrices of a scroll λ . A plane pencil containing n has δ lines of K' besides n , so that n is a $2\kappa-\pi-2\delta$ -fold line of K' . A plane pencil which contains a line of B and to which such a plane pencil is associated, has $\kappa-\delta$ lines in common with K which are not singular for I . Hence the lines of B are $\kappa-\pi$ -fold lines of K' . In the same way it ensues from the fact that a plane pencil through a line of Γ contains $\kappa-\varepsilon$ lines of K , non-singular for I , that the lines of Γ are $\kappa-\pi-\delta+\varepsilon$ -fold lines of K' .

Accordingly to a complex K of the order κ that has n as π -fold line and of which the rays of the congruences B and Γ are resp. δ - and ε -fold lines, there corresponds a complex K' of the order $2\kappa-\pi-\delta$ which has n as $2\kappa-\pi-2\delta$ -fold line and of which the rays of B and Γ are resp. $\kappa-\pi$ - and $\kappa-\pi-\delta+\varepsilon$ -fold lines.

Hence an arbitrary complex K of the order κ is transformed into a complex K' of the order 2κ which has n as 2κ -fold line and of which the rays of B and Γ are κ -fold lines. The lines of K' passing through a point of n form, therefore, besides a plane pencil of Γ , a cone of the order κ .

§ 7. The involution of rays examined in this paper may e.g. be applied to determine the numbers of scrolls λ that contain a given line n , have a line in common with a congruence B and which satisfy besides a five-fold condition.

Let us try to find e.g. the number of the scrolls λ which contain a line l and which pass through two given points. By means of our involution these scrolls are transformed into the plane pencils through a given line l' which have a straight line in common with each of two bilinear congruences Σ_1 and Σ_2 . We find the number of these plane pencils by considering the correspondence on l' which arises in the following way. Through a point P of l' we draw the line s_1 of Σ_1 . To P we associate

the point P' where l' is cut by the generatrix of Σ_2 in the plane (l', s_1) .

The (1,1) correspondence (P, P') has two coincidences.

Accordingly there are two scrolls which contain two given straight lines, have one ray in common with a bilinear congruence, and pass through two given points.

We can also try to find the number of the scrolls λ which contain a line l and have a straight line in common with a plane pencil w_1 . The corresponding plane pencils must pass through l' and have a straight line in common with the scroll λ_1 corresponding to w_1 . Their vertices lie in the points of intersection of l' and λ_1 .

Consequently there are two scrolls with two given generatrices which have one line in common with a bilinear congruence and with a plane pencil.

Chemistry. — "*Equilibria in systems in which phases, separated by a semi-permeable membrane*" X. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of June 27, 1925).

Systems with several semipermeable membranes. Double-membranes.

We now take the osmotic equilibrium:

$$E = E_1 \mid E_2 \mid E_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the separate systems E_1 and E_2 and also E_2 and E_3 are separated from one another by a semipermeable membrane. Of the many possible cases we now shall consider only the case, that the two semipermeable membranes allow to pass one substance only viz. the same substance W (water). We find the equations for equilibrium by expressing:

a. that the phases of the system E_1 are in equilibrium, taken for themselves; also those of E_2 and those of E_3 .

b. that the O.W.A. of E_1 is equal to that of E_2 and that of E_2 equal to that of E_3 ; consequently the three separate systems have the same O.W.A.

Consequently we get the same equations for equilibrium, independent which of the three separate systems in (1) is situated between the two membranes. Therefore, if one of the three osmotic systems:

$$E_1 \mid E_2 \mid E_3 \quad E_2 \mid E_1 \mid E_3 \quad E_1 \mid E_3 \mid E_2$$

forms an osmotic equilibrium, then both the other ones do also.

In fig. 1 in which only a part of triangle WXY is drawn, the lines drawn represent isotonic curves. We now take into consideration the osmotic system.

$$L_1 \mid L_2 \mid L_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which L_1 , L_2 and L_3 are liquids, represented by the points 1, 2 and 3. It is apparent from the situation of those points that

$$\text{O.W.A. of } L_1 < \text{O.W.A. of } L_2 < \text{O.W.A. of } L_3.$$

Consequently we may write for (2):

$$L_1 \rightarrow L_2 \rightarrow L_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which the arrows indicate the direction in which the substance W

water) diffuses. Consequently in fig. 1 the liquids L_1 and L_3 move in the direction of the arrows, drawn in the points 1 and 3; we shall refer later to the movement of L_2 , which takes place of course along the line $2W$.

At last a definite osmotic equilibrium shall be formed from system (3); then the three liquids are situated on an isotonic curve. It may be converted f.i. into one of the osmotic equilibria:

$$L_c \mid L_b \mid L_a \text{ or } L_h \mid L_g \mid L_f \dots \dots \dots (4)$$

and accidentally also into:

$$L_e \mid L_2 \mid L_d \dots \dots \dots (5)$$

so that liquid L_2 at the finish of the osmose is again the same as at the beginning.

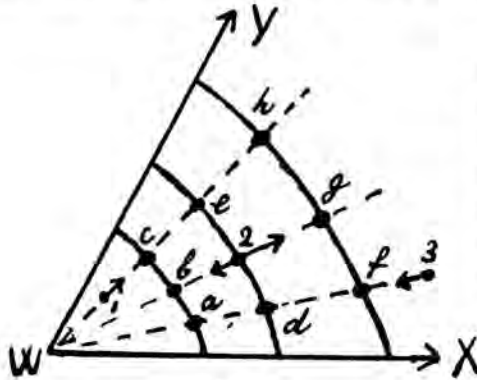


Fig. 1.

If, besides the compositions, still also the quantities n_1 , n_2 and n_3 of the liquids L_1 , L_2 and L_3 are known, then we know also the quantities n'_1 , n'_2 and n'_3 and the compositions of the liquids L'_1 , L'_2 and L'_3 which arise at last. We represent the composition of L_1 by $x_1 X + y_1 Y + (1 - x_1 - y_1)W$ that of L'_1 by $x'_1 X + y'_1 Y + (1 - x'_1 - y'_1)W$ those of the other liquids by

substituting the index 1 by 2 and 3. As the quantity of water in the whole system must remain constant and also the quantities of X and Y in each of the three separate systems, we find the equations:

$$\left. \begin{aligned} n_1 + n_2 + n_3 &= n'_1 + n'_2 + n'_3 \\ n_1 x_1 &= n'_1 x'_1 & n_2 x_2 &= n'_2 x'_2 & n_3 x_3 &= n'_3 x'_3 \\ n_1 y_1 &= n'_1 y'_1 & n_2 y_2 &= n'_2 y'_2 & n_3 y_3 &= n'_3 y'_3 \end{aligned} \right\} \quad (6)$$

Further we still have the two equations:

$$\varphi'_1 = \varphi'_2 = \varphi'_3 \dots \dots \dots (7)$$

in which

$$\varphi = \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y};$$

they express that the three liquids L'_1 , L'_2 and L'_3 are in osmotic equilibrium at last. We now have 9 equations for the definitions of the 9 unknowns which occur in (6) and (7); the quantities and compositions of L'_1 , L'_2 and L'_3 are defined, therefore. From this appears also that the

result of the osmose depends not only on the composition of the original liquids, but also on the ratio of their quantities.

The quantity of a substance W , which diffuses in a definite time by a membrane, depends not only on the difference of the O.W.A. of the two liquids, but also on the active surface of the membrane. By changing this surface, we may, therefore, regulate also the quantity of water, which diffuses in a definite time through this membrane.

Let us assume now that the system:

$$L_1 \rightarrow L_2 \rightarrow L_3 \text{ is converted into } E=L_c \mid L_b \mid L_a \text{ (fig. 1),}$$

As L_1 only gives water and L_3 only takes water in, those two liquids shift during the osmose always in the same direction viz. L_1 from point 1 towards c and L_2 from point 3 towards a (fig. 1). Although liquid L_2 arrives at last from point 2 in b , we yet may distinguish different cases.

a. L_2 goes without change in direction from 2 towards b .

b. L_2 goes starting from point 2 firstly in the direction towards g , returns then towards point 2 and goes further towards b .

c. L_2 goes starting from point 2 firstly towards point b , then a little further in the direction towards W and returns then towards b .

In both the latter cases we shall say that the liquid varies or swings; in case b it swings over point 2, in case c over point b .

The case, mentioned sub b , may be realised when we regulate the surface of the two membranes in such a way, that at the beginning more water diffuses from L_2 towards L_3 than L_2 takes from L_1 . The case mentioned sub c can occur when the membrane between L_1 and L_2 is very large and the quantity of L_1 is large with respect to the quantity of L_2 . Corresponding phenomena can occur, when system (3) is converted into one of the other equilibria (4) and (5).

If we let the liquids change places in system (2) then we get:

$$L_2 \leftarrow L_1 \rightarrow L_3 \quad (8a) \qquad L_1 \rightarrow L_3 \leftarrow L_2 \dots \dots (8b)$$

in which the arrows indicate again the direction in which the water diffuses at the beginning of the osmose. With a single example we shall show that the liquids in those systems may swing during the osmose. Let us assume that in (8a) the osmose between L_1 and L_3 takes place extremely slowly, but that between L_2 and L_1 extremely quickly. As the osmotic equilibrium between L_2 and L_1 is reached then practically almost immediately, we then get a system:

$$L'_2 \mid L'_1 \mid L'_3 \dots \dots \dots (8c)$$

in which L'_3 differs only very little from L_3 , L'_2 and L'_1 now have

almost the same O.W.A., which is larger than that of L_1 but smaller than that of L_2 , also smaller than that of L_3 or L'_3 , therefore. Water now shall diffuse, as is indicated in:



viz. firstly from L'_1 towards L'_3 and afterwards from L'_2 towards L'_1 . The liquid L_2 in (8a), therefore, takes water in at the beginning of the osmose, but later it gives water again.

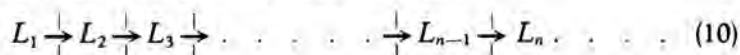
The equations (6) and (7) are valid not only for the conversion of system (3) but also for the systems (8a) and (8b). Consequently for the end-equilibrium it is indifferent which of the three liquids is between the two membranes; this has influence only on the way in which this equilibrium is formed.

In the osmotic system:



we have n liquids and $n-1$ membranes. We are able to show also that the osmotic equilibrium which arises at last from this, depends only on the quantities and the composition of the liquids, but that it is independent on their series. The way, in which the equilibrium sets in is dependent, however, on the series of the liquids and also on the surface of the membranes.

Let us assume that the O.W.A. of the liquids in (9) increases, according the index of the liquid being larger. We then have:



in which the arrows indicate the direction in which the water diffuses. We now may imagine that L_1 and L_n during a long time change their O.W.A. only imperceptibly or not; this can take place f.i. when both liquids are present in a very large excess. This may be the case also when L_1 is f.i. water and L_n watervapour under a very low constant pressure.

While L_1 en L_n then remain unchanged, the other liquids change their composition until the same quantity of water diffuses through each membrane in the same time. As soon as this stationary state has established itself, all liquids have a definite composition and O.W.A. This stationary state depends not only on the original composition and quantities of the different liquids, but also on the surface of the different membranes.

A similar stationary state shall occur also when the liquids $L_2 L_3 \dots L_{n-1}$ have the same O.W.A. at the beginning; further, of course it is indifferent whether those liquids have the same composition or not and which substances they contain.

Double-membranes.

If we compare the two osmotic systems:

$$L_1 \mid L_2 \text{ and } L_1 \mid D \mid L_2 \dots \dots \dots (11)$$

with one another, then we see that in the first one the two liquids L_1 and L_2 are in osmotic contact with one another with the aid of a single semipermeable membrane; in the second one the water, in order to diffuse from L_1 towards L_2 , must pass through two semipermeable membranes, between which a phase (or system) D is found.

We now may consider the two semipermeable membranes with the included phase D as to form together a new semipermeable membrane; we call this "double-membrane with the phase D " or only "double-membrane" and we shall represent it by $\mid D \mid$ or $\mid \mid$.

We now may say that the liquids L_1 and L_2 in the second system (11) are in osmotic contact with one another with the aid of a double-membrane. Further we shall see that a double-membrane sometimes may play quite a different part as the single membrane.

We now take the osmotic system:

$$L_1 \mid Y \mid L_2 \text{ fig. 1 Comm. III. } \dots \dots \dots (12)$$

in which L_1 and L_2 are separated from one another by a double-membrane with the solid substance Y . The liquids L_1 and L_2 are represented by points within the field $WwvX$ of fig. 1 Comm. III. Further we shall see that system (12) may pass into one of the osmotic equilibria:

$$E = L_1 \mid L \mid L_2 \quad (13a) \quad E = L_1 \mid Y + L_w \mid L_2 \dots \quad (13b)$$

in which all liquids are isotonic, therefore, or into the complex

$$K = L_1 \mid Y \mid L_2 \dots \dots \dots (14)$$

in which the two liquids are not isotonic. In the latter case, therefore, the double-membrane plays the part of a wall, which is impermeable for water.

As the result of the osmose depends on the composition of the liquids L_1 and L_2 we distinguish three cases.

1. L_1 and L_2 are situated both within the field Wwm fig. 1 Comm. III. The O.W.A. of the solid substance Y is, therefore, greater than that of the liquids L_1 and L_2 ; at the beginning of the osmose water shall diffuse, therefore, as well from L_1 as from L_2 towards the solid substance Y . Consequently there arises a system:

$$L_1 \rightarrow Y \leftarrow L_2 \dots \dots \dots (15)$$

1. The water diffuses through the double-membrane, so that an osmotic equilibrium is formed. The double-membrane behaves itself with respect to the water-diffusion as a single membrane. This is the case when both the liquids are situated within the field Wwm and may take place also when the liquids are situated on different sides of the curve $w m$.

Yet there is a difference between the equilibrium which is formed with the aid of a single membrane and that which is formed with the aid of a double-membrane; sometimes this difference can be very great.

When L_1 and L_2 are situated in the field Wwm , then the result of the osmose is, that both liquids are situated also within the field Wwm ; the one viz. shifts away from point W and the other towards point W , till they arrive on the same osmotic curve.

If, however, we use the double-membrane $\begin{array}{|c|} \hline Y \\ \hline \end{array}$ with a large quantity of Y , then, as we have seen above, both liquids shift at last towards the isotonic curve $w m$. (fig. 1 Comm. III).

2. The double-membrane prohibits the diffusion of the water; it behaves itself, therefore, as a wall, which checks the water, notwithstanding the two liquids have a different O.W.A.

This is the case, when both liquids are situated in the field $w m X v$ (fig. 1 Comm. III).

3. The water diffuses firstly through the double-membrane; then the diffusion stops, although the O.W.A. of both the liquids is still different. This case may occur, when both liquids are situated on different sides of curve $w m$.

We now take the osmotic system

$$L_1 \begin{array}{|c|} \hline Y \\ \hline \end{array} L_2 \quad \text{fig. 1 Comm. V.} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

in which L_1 and L_2 represent liquids of the field $W a c b$. Also here for (17) is valid, what is deduced above for system (12); of course we now have to replace the isotonic curve $w m$ and the fields Wwm and $w m X v$ of fig. 1 Comm. III by the isotonic curve $a m$ and the fields $W a m$ and $a m b c$ of fig. 1 Comm. V.

If the double-membrane contains the solid substance X , then we have the osmotic system:

$$L_1 \begin{array}{|c|} \hline X \\ \hline \end{array} L_2 \quad \text{fig. 1 Comm. V} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

then the isotonic curve $b d$ and the fields $W b d a$ and $b c d$ play a corresponding part.

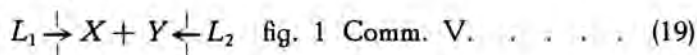
Hence is apparent that the solid substance, which is present in the double-membrane, may have great influence on the osmose. The double-membranes $\begin{array}{|c|} \hline X \\ \hline \end{array}$ and $\begin{array}{|c|} \hline Y \\ \hline \end{array}$ are viz.

both permeable for water of liquids of the field $W a m$;

both impermeable for water of liquids of the field bdc ;
but $\left| X \right|$ is permeable and $\left| Y \right|$ is impermeable for water of liquids of the field $ambd$.

When therefore, L_1 and L_2 represent, two liquids of the field $ambd$, then system (17) remains unchanged, also when the two liquids are not isotonic, system (18), however, passes into an osmotic equilibrium.

If we take in the double-membrane a mixture of solid X and Y , then we have the osmotic system:

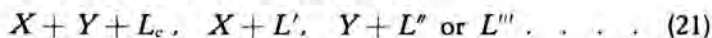


in which the double-membrane is permeable for water from all liquids of the field $Wbca$.

As the O.W.A. of solid $X + Y$ is equal to that of liquid L_c and, therefore, greater than that of the liquids of the field $Wbca$, in (19) the water shall diffuse in the direction of the arrows. It now depends on the composition of the liquids L_1 and L_2 and on the ratio's of the quantities of XYL_1 and L_2 which equilibrium shall be formed from (19). If we represent this by:

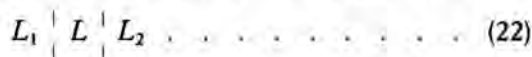


then $E_1 D$ and E_2 can be one of the equilibria:

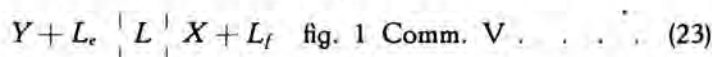


Herein L' represents a liquid of the saturation-curve bc , L'' a liquid of the saturation-curve ac and L''' an unsaturated liquid.

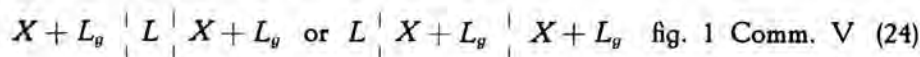
System (20), therefore, can represent a.o. the osmotic equilibrium:



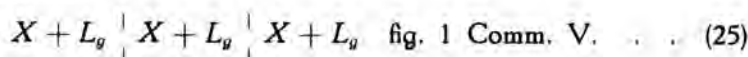
in which three unsaturated liquids, represented by points of an isotonic curve; it can represent also the osmotic equilibrium:



liquid L then is situated on the isotonic curve ef . It can represent also an osmotic equilibrium:



in which L is a liquid of the isotonic curve, going through point g . In each of the two osmotic equilibria (24) two identical liquids L_g occur; even it is possible that an osmotic equilibrium is formed with three identical liquids, f.i.



This is possible only then, when the liquids L_1 and L_2 of system (19) are situated both in the field Wbc and when the complex $X + Y$ of the double-membrane is represented by a point between X and c' (imagine c' to be the point of intersection of the side XY with the line Wc , which is not drawn).

In the osmotic system

$$L_1 \mid X \mid L_2 \text{ fig. 1 Comm. IX. (26)}$$

L_1 represents a liquid with the components $W + X + Y$ and L_2 with the components $W + X + Z$. Consequently liquid L_1 is situated in triangle WXY and L_2 in triangle WXZ of fig. 1 Comm. IX.

If L_1 is situated within the field Wdr_1 and L_2 within the field Wdr_2 then (26) passes into one of the osmotic equilibria:

$$L'_1 \mid L \mid L'_2 \text{ (27a)} \quad L'_1 \mid X + L_d \mid L'_2 \text{ (27b)}$$

When in (27a) L is represented f. i. by point q then L'_1 is situated on qq_1 and L'_2 on qq_2 . When the double-membrane contains much solid X then the equilibrium (27b) is formed, L'_1 is situated then on curve dr_1 and L'_2 on curve dr_2 .

The osmotic system

$$L_s \mid X \mid L_w \text{ fig. 1 Comm. IX (28)}$$

may pass into an osmotic equilibrium (27a) with three unsaturated isotonic liquids; it can form also one of the systems:

$$E = L_t \mid X + L_d \mid L_u \quad K = L_t \mid X \mid L_u \text{ (29)}$$

The first is an osmotic equilibrium; the latter is a complex in which L_u has a greater O.W.A. than L_t . The diffusion of water, however, is also prohibited by the double-membrane.

The reader may easily deduce the other cases, also when we use the double-membranes $\mid Y \mid$ or $\mid X + Y \mid$. I only wish to draw the attention to the fact that the double-membrane $\mid X \mid$ is impermeable for water from liquids of the fields dr_1ab and dr_2Zg , the double-membrane $\mid Y \mid$ for water from liquids of the fields acb and $ehZg$ and the double-membrane $\mid X + Y \mid$ for water from liquids of the field $fiZg$.

(To be continued).

Chemistry. — "*The fictitious heats of solution of enantiotropic modifications at their transition point*". By Prof. ERNST COHEN and Mr. H. L. BREDÉE.

(Communicated at the meeting of April 25, 1925).

Introduction.

1. In his "Recherches expérimentales et théoriques sur les Equilibres Chimiques" ¹⁾ LE CHATELIER, a long time ago, has pointed at a highly interesting relation which must exist at the transition point of enantiotropic modifications. If we call these two modifications, which are in equilibrium with each other at the temperature of transition T_0 , α and β , the temperature coefficients of the solubility at T_0 $\left(\frac{dc}{dT}\right)_\alpha$ and $\left(\frac{dc}{dT}\right)_\beta$, respectively, the fictitious heats of solution Q_α and Q_β , then, according to LE CHATELIER we have at T_0 :

$$\frac{\left(\frac{dc}{dT}\right)_\alpha}{\left(\frac{dc}{dT}\right)_\beta} = \frac{Q_\alpha}{Q_\beta} \quad \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (1)$$

About this point LE CHATELIER observes: "Il serait intéressant de vérifier cette conséquence de la formule, qu'au point de transformation le rapport des tangentes est égal au rapport des chaleurs de dissolution:

$$\frac{\frac{dc}{dT}}{\frac{dc'}{dT}} = \frac{L}{L'}$$

Only recently P. MONDAIN MONVAL ²⁾ has taken up the testing of this "Law of Tangents", choosing for his object those modifications of ammonium nitrate (the β -rhombic and the α -rhombic, which we shall indicate by the names of modification III and IV) which have their transition point ³⁾ at 32°.3 C. From his experiments he deduces:

$$\frac{Q_\alpha}{Q_\beta} = 1.158; \quad \frac{\left(\frac{dc}{dT}\right)_\alpha}{\left(\frac{dc}{dT}\right)_\beta} = 1.17.$$

¹⁾ Paris 1888: pag. 165.

²⁾ C. R. Paris 177, 175 (1923); Thèses, Paris 1924; Ann. de Chimie 3, 72, 121 (1925).

³⁾ ERNST COHEN and J. KOOY, These Proceedings 27, 65 (1924); also Zeitschr. f. physik. Chemie 109, 81 (1924).

Here he observes: „Si nous rapprochons les valeurs de ces rapports nous voyons que l'écart qui existe entre elles est d'environ 1 %. Cet accord excellent tient évidemment en partie à une heureuse coïncidence. En égard à la difficulté des mesures et à la précision respective avec laquelle elles ont été effectuées, un écart de 4 à 5 % n'aurait rien que d'acceptable", and his final conclusion is: „Les mesures que nous avons effectuées sur les modifications allotropiques du nitrate d'ammonium aux environs de 32° vérifient donc plus exactement qu'on ne pouvait l'espérer la loi du rapport des tangentes".

2. We cannot agree with this opinion. For, the agreement which MONDAIN MONVAL assumes from his measurements, does not really exist. It seems to exist, because he chooses quite arbitrary values out of his experimental data. Here again we have a case as is so often found in the literature, when we have to test thermodynamic relations. MOESVELD ¹⁾ has already directed attention to this fact, and we wish to point out here, that it is of great importance to trace the cause of this non agreement, when it seems that there is a discrepancy between theory and experiment, as such an investigation often leads to the discovery of new phenomena. For instance, during our investigations on the metastability of matter ²⁾, new phenomena have been brought to light, and these could be studied quantitatively, because we chose for our starting-point the divergencies between calculation and experiment which had appeared, when the equation of CLAPEYRON-CLAUSIUS was applied to the modifications III and IV of ammonium nitrate.

3. While, in an investigation by COHEN and HELDERMAN ³⁾, the curves of the intermediate heats of solution of the two forms of ammonium nitrate mentioned, had been accurately determined, we have very carefully measured the values of $\left(\frac{dc}{dT}\right)_\alpha$ and $\left(\frac{dc}{dT}\right)_\beta$ at the transition temperature (32.3 C.) in order to test the relation of LE CHATELIER. In the present paper we describe the investigation referring to it, and in conjunction with it, a discussion of the results of MONDAIN MONVAL.

A. The Materials used.

4. The ammonium nitrate which we used in our investigation was obtained by recrystallizing an already pure commercial preparation several times out of carefully distilled water. An analysis, to show the degree of purity finally attained was made, according to the method, described

¹⁾ The Testing of BRAUN's Law, Utrecht 1918, page 7.

²⁾ These Proceedings 27, 65; 28, 1 (1924); Zeitschr. f. physik. Chemie 109, 81; 113, 145 (1924).

³⁾ These Proceedings 28, 2 (1924); Zeitschr. f. physik. Chemie 113, 145 (1924).

in KRAUCH "Die Prüfung der Chemischen Reagentien auf Reinheit" ¹⁾). No impurities were found.

5. We have also ascertained the purity of our material by determining the solubility of crystals prepared by successive crystallizations, according to the method described hereafter. In this way a certain crystallization gave at 20°.00 the values of 65.24 and 65.24. Crystals of the next crystallization gave the values of 65.25; 65.24 and 65.26.

B. The solubility determinations.

1. General observations.

6. The greatly divergent values which are found in the literature for the solubility of ammonium nitrate at one and the same temperature ²⁾, prove already that it is very difficult to carry out reliable determinations for this highly soluble salt. For this reason we have taken very great pains with these measurements, and have succeeded in carrying out the determinations with an accuracy of 0.02 to 0.03 %₀, in which equilibrium was always reached, starting from unsaturated as well as supersaturated solutions. Great accuracy is required, as, when LE CHATELIER's equation is to be tested, it is just the point to fix the differential quotients, which from their very nature are very susceptible to slight errors in the values of solubility. All the determinations were carried out in triplicate, while the weighings (on a BUNGE balance, which allowed an accuracy of the weighings to 0.1 mgr.) were reduced to vacuum. Our weights were calibrated according to the well known method of F. KOHLRAUSCH. The thermometers used were compared with an instrument graduated in tenths of a degree, and calibrated by the Physikalisch-Technische Reichsanstalt at Charlottenburg, the zero point of which we have controlled. In our thermostats, in which the equilibrium of solution was attained by shaking water with excess of salt, was always a BECKMANN thermometer, divided into hundredths of a degree. The regulation of the temperature was brought about by a regulator according to OSTWALD (capacity of the bulb about 500 cc), which we filled with tetrachlorethane, a liquid which has the advantage over toluene in being non-inflammable, which is very convenient when filling the bulb. The time of shaking varied between 4 and 48 hours. The temperature variations of the thermostat during a short period were not greater than 0.01 degree, at 5° and 10° two hundredths of a degree at most. The shaking of the solutions in the thermostat was done by means of the acatène-apparatus, which has been described by COHEN and BRUINS in a former paper ³⁾.

¹⁾ Berlin, 1896. Dritte Auflage, S. 32.

²⁾ A synopsis is found in MONDAIN MONVAL. See note 2 page 377.

³⁾ Zeitschr. f. physik. Chemie 93, 43 (1918).

7. In the analysis of the saturated solutions, which, also at the higher temperatures, had to be carried out without loss of liquid (owing to evaporation) the method was followed which had been indicated by COHEN and MOESVELD¹⁾: the curve was determined which represents the specific volume of aqueous solutions of ammonium nitrate as function of the concentration (at a definite temperature). The concentration of the saturated solutions is then found by determining their specific volume (at the temperature for which the curve mentioned has been fixed) and by calculating the concentration from the equation which represents the relation between specific volume and concentration.

8. As the temperature coefficient of the solubility of ammonium nitrate is very great, the pycnometer, into which the saturated solution is pressed, must, during this manipulation, be totally immersed in the thermostat in which equilibrium of solution is reached. For particulars of this technique we refer to the paper by ERNST COHEN, WILHELMA A. T. DE MEESTER and A. L. TH. MOESVELD²⁾ on the influence of pressure on the solubility of substances V, especially par. 11.

2. The determination of the solubility of Ammonium nitrate IV.

9. The range of stability of modification IV lies³⁾ between -16° and $+32^{\circ}.3\text{ C.}$

Our determinations of solubility have been carried out at $0^{\circ}.00$; $5^{\circ}.00$; $10^{\circ}.00$; $15^{\circ}.00$; $20^{\circ}.00$; $25^{\circ}.00$; $30^{\circ}.00$ and $32^{\circ}.00\text{ C.}$

In order to determine the concentration of saturated solutions between 0° and $32^{\circ}.3\text{ C.}$ we might actually have used the equation previously found by COHEN, HELDERMAN and MOESVELD⁴⁾, which represents the relation between specific volume and concentration of solutions of ammonium nitrate at $32^{\circ}.3\text{ C.}$:

$$(\nu_e)_{32.3} = 1.00507 - 0.00392087c + 0.0000051003c^2 - 0.00000000566c^3. \quad (2)$$

Meanwhile we have again determined this relation.

10. For this purpose we prepared solutions of accurately known concentration by weighing (in flasks, similar to those which were used for the determinations of solubility) salt (which had been strongly dried under particular precautions which have previously been described⁵⁾) and water

¹⁾ Zeitschr. f. physik. Chemie **94**, 482 (1920).

²⁾ These Proceedings **28**, 108 (1924); also Zeitschr. f. physik. Chemie **114**, 321 (1924).

³⁾ ERNST COHEN and J. KOOY, These Proceedings **27**, 65 (1924); also Zeitschr. f. physik. Chemie **109**, 81 (1924).

⁴⁾ See these Proceedings **27**, 565 (1924), especially par. 9. Also Zeitschr. f. physik. Chemie **112**, 135 (1924), especially par. 9.

⁵⁾ See these Proceedings **27**, 565 (1924). Also Zeitschr. f. physik. Chemie **112**, 135 (1924), especially par. 9.

the specific volume of these solutions was then determined at 32°3 C. in the way described in par. 8. Great care was taken that no evaporation could take place during the solving of the salt, which was brought about by heating: the flasks were closed during the heating.

The results thus obtained are given in table 1.

TABLE 1.
Temperature 32°3 C.

Concentration in gr. per 100 gr. of solution	Spec. vol. found C. and B.	Spec. vol. calculated C. and B. equation (3)	Spec. vol. calculated C. H. and M. equation (2)
25.00	0.91012	0.91011	0.91015
34.99	0.87377	0.87375	0.87387
44.98	0.83829	0.83830	0.83850
54.98	0.80374	0.80372	0.80398
64.98	0.77003	0.77002	0.77028
70.65	0.75125	0.75129	0.75152

According to the method of least squares we find from the values in the first and second columns:

$$(\nu_c)_{32^{\circ}3} = 1.00529 - 0.00392915c + 0.0000049640c^2 - 0.00000000333c^3. \quad (3)$$

From the second and third columns of table 1 we see that this equation describes the observations. Further we observe that the differences in concentration which the equations (2) and (3) yield for a given specific volume, attain at most an amount of 0.08 per cent.

11. The results of the solubility determinations of modification IV are summarized in table 2. By means of the method of least squares we find from it for $c_{IV} = f(t)$:

$$c_{IV} = 54.241 + 0.6106t - 0.00297t^2 \quad . \quad . \quad . \quad (4)$$

Columns 6, 7 and 8 of table 2 prove that this equation holds good.

3. The determination of the solubility of Ammonium nitrate III.

12. The range of stability of this modification (III) lies between 32°3 and 84°2 C. Our solubility determinations within this range have been made at 33°00; 36°00; 39°00; 42°00; 45°00 and 48°00 C.

The curve which represents the specific volumes of solutions of ammonium nitrate as function of the concentration, has been fixed for

TABLE 2.
Solubility of Ammonium nitrate, Modification IV, in water.

Temp.	Period of shaking in hours	v_c found	v_c mean	Solubility; gr. of salt per 100 gr. of solution			$c_{\text{calc.}} - c_{\text{found}}$
				found from v_c	mean found	calculated	
0°.00	5 1/2	0.80630	0.80629	54.23	54.23	54.24	+ 0.01
	4 1/2	0.80627 *)		54.24			
	4 1/2	0.80630 *)		54.23			
5°.00	4	0.79605 *)	0.79605	57.23	57.23	57.22	— 0.01
	5	0.79608		57.22			
	5	0.79603		57.24			
10°.00	4 1/2	0.78656 *)	0.78651	60.04	60.05	60.05	± 0.00
	5	0.78650		60.06			
	5 1/2	0.78646		60.07			
15°.00	4 1/2	0.77740 *)	0.77741	62.77	62.76	62.73	— 0.03
	5 1/2	0.77738		62.77			
	5 1/2	0.77745		62.75			
20°.00	4	0.76917 *)	0.76914	65.24	65.24	65.27	+ 0.03
	4	0.76916 *)		65.24			
	24	0.76910		65.26			
	4	0.76912 *)		65.25			
	48	0.76914		65.24			
25°.00	24	0.76123	0.76122	67.63	67.63	67.65	+ 0.02
	24	0.76118		67.64			
	5	0.76125 *)		67.62			
30°.00	24	0.75375	0.75374	69.90	69.90	69.89	— 0.01
	24	0.75377		69.89			
	5	0.75370 *)		69.91			
32°.00	24	0.75087	0.75090	70.78	70.77	70.74	— 0.03
	24	0.75090		70.77			
	24	0.75092		70.76			

*) signifies: starting from supersaturated solution.

50°00 C. so that the saturated solutions which were formed at the highest temperature investigated (48°) could never crystallize during the determination of their specific volume.

The equation of the curve $(v_c)_{50^{\circ}00} = f(c)$ was obtained by determining the specific volume at 50° of solutions which contained 15, 25, 35, 45, 55, and 75 % of salt respectively (sum = 100), and which had been prepared by weighing, as is described in par. 10. Table 3 contains the results of the determinations of the specific volume.

TABLE 3.
Specific Volume of Ammonium nitrate solutions of different concentrations.
Temp. 50°00 C.

Weight of salt in grms	Weight of solution in grms	Concentration grms of salt in 100 gr. of sol.	v_c found	v_c mean found	v_c calc.	v_c calc.-found $\times 10^5$
5.1247	34.1904	14.99	0.95527	0.95525	0.95532	+ 7
5.1247	34.1904	14.99	0.95522			
10.8391	43.3554	25.00	0.91826	0.91828	0.91822	— 6
10.8391	43.3554	25.00	0.91830			
15.1917	43.4148	34.99	0.88206	0.88207	0.88192	— 15
15.1917	43.4148	34.99	0.88208			
19.9609	44.3810	44.98	0.84626	0.84630	0.84631	+ 1
19.9609	44.3810	44.98	0.84634			
24.9593	45.3964	54.98	0.81123	0.81122	0.81136	+ 14
24.9593	45.3964	54.98	0.81120			
28.4039	43.7149	64.98	0.77708	0.77710	0.77708	— 2
28.4039	43.7149	64.98	0.77712			
32.1572	42.8859	74.99	0.74346	0.74348	0.74341	— 7
32.1572	42.8859	74.99	0.74350			

By means of the method of least squares we find:

$$(v_c)_{50^{\circ}00} = 1.01227 - 0.0038565c + 0.000003855c^2 - 0.00000000319c^3. \quad (5)$$

From columns 5, 6 and 7 of table 3 we see that the equation describes the experimental data.

13. We have also controlled the equations (3) and (5) mutually, by determining the specific volume of the solution, saturated at 32°.3, at that temperature as well as at 50°.00 C, and by deducing from it the concentration of the solution by means of the equations (3) and (5).

In this way we found from the determinations of the specific volume at 32°.3 C. the values 70.87

and 70.88

and from the determinations of the spec. vol. at 50°.00 C. the values 70.87
and 70.86,

in other words: complete agreement.

14. As regards the determinations of solubility of modification III itself may be observed that they were done in the very same way as those of modification IV. The results are found in table 4. By means of the method of least squares we find for $c_{III} = f(t)$:

$$c_{III} = 57.861 + 0.4384 t - 0.00111 t^2 \quad . \quad . \quad . \quad (6)$$

From columns 6, 7 and 8 of table 4 we see that this equation describes the observations.

C. Calculation of the Transition temperature.

15. The point of intersection of the curves, represented by the equations (4) and (6) gives for the transition temperature

$$t = 32°.27 \text{ C.}$$

while $c_{IV} = c_{III} = 70.85$.

So there is complete agreement between this result and the fact that COHEN and KOOP¹⁾ have found the temperature of transition IV \rightleftharpoons III at 32°.3 C. We wish, however, to observe that too great a value must not be attached to this agreement, as for $t = 31°.8$ or $32°.8$ the two equations give a difference in the solubility of only 0.025 per cent, a difference which lies within the errors of the measurements.

D. Calculation of $\left(\frac{dc}{dT}\right)_{IV}$ and $\left(\frac{dc}{dT}\right)_{III}$ at the Transition temperature.

16. If we call the values

$$\left(\frac{dc}{dT}\right) \text{ and } \left(\frac{dc'}{dT}\right), L \text{ and } L'$$

from LE CHATELIER's equation (see above par. 1) in our case, where they refer to the modifications IV and III of ammonium nitrate

$\left(\frac{dc}{dT}\right)_{IV}$ and $\left(\frac{dc}{dT}\right)_{III}$, respectively Q_{IV} and Q_{III} , we find:

¹⁾ These Proceedings 27, 65 (1924); Zeitschr. f. physik. Chemie 109, 81 (1924).

TABLE 4.
Solubility of Ammonium nitrate, Modification III, in water.

Temp.	Period of shaking in hours	v_c found	v_c mean	Solubility: gr. of salt per 100 gr. of solution			$c_{\text{calc.}} - c_{\text{found}}$
				c_{found} fr. v_c	c mean found	c calculated	
33°,00	15	0.75638 *)		71.11			
	18	0.75636	0.75636	71.12	71.12	71.12	± 0.00
	18	0.75635		71.12			
36°,00	12	0.75268 *)		72.22			
	18	0.75272	0.75271	72.20	72.21	72.20	$- 0.01$
	18	0.75272		72.20			
39°,00	12	0.74915 *)		73.27			
	18	0.74913	0.74914	73.28	73.27	73.27	± 0.00
	18	0.74913		73.28			
42°,00	12	0.74564 *)		74.32			
	18	0.74563	0.74563	74.32	74.32	74.32	± 0.00
	18	0.74562		74.33			
45°,00	4	0.74222 *)		75.35			
	5	0.74225	0.74223	75.34	75.34	75.34	± 0.00
	5	0.74223		75.34			
48°,00	12	0.73885 *)		76.36			
	24	0.73887	0.73886	76.35	76.35	76.34	$- 0.01$
	24	0.73887		76.35			

*) signifies: starting from supersaturated solution.

From equation (4):

$$\left(\frac{dc}{dT}\right)_{IV} = 0.6106 - 2 \times 0.00297 \times 32.27 = 0.4189 \frac{\text{weight } \%}{\text{degree}}.$$

From equation (6):

$$\left(\frac{dc}{dT}\right)_{III} = 0.4384 - 2 \times 0.00111 \times 32.27 = 0.3668 \frac{\text{weight } \%}{\text{degree}};$$

therefore

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} = \frac{0.4189}{0.3668} = 1.14^2.$$

E. Calculation of $\frac{Q_{IV}}{Q_{III}}$ at the Transition temperature.

17. By means of an adiabatic, electrical method for the intermediate heats of solution of modification IV and III at their point of transition ($32^{\circ}.3$) ERNST COHEN and W. D. HELDERMAN ¹⁾ have found:

$$(Q_i)_{IV} = -5910 + 83.057 c - 0.73476 c^2 + 0.00224 c^3. \quad (7)$$

and

$$(Q_i)_{III} = -5510 + 83.057 c_1 - 0.73476 c_1^2 + 0.00224 c_1^3. \quad (8)$$

in which c , respectively c_1 , represents the concentration of a solution of ammonium nitrate (sum = 100), in which one molecule of the modification in question is dissolved.

For the transition temperature ²⁾ $c = c_1 = 70.93$; by means of the equations (7) and (8) we then find:

$$Q_{IV} = -2917 \text{ gramcalories}$$

and

$$Q_{III} = -2517 \text{ gramcalories}$$

so:

$$\frac{Q_{IV}}{Q_{III}} = \frac{2917}{2517} = 1.15^9.$$

F. Experimental proof of the relation of LE CHATELIER.

18. Whereas in par. 16 was found:

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} = 1.14^2$$

we find in par. 17

$$\frac{Q_{IV}}{Q_{III}} = 1.15^9$$

which proves experimentally the exactness of LE CHATELIER's relation.

¹⁾ These Proceedings 28, 1 (1924); Zeitschr. f. physik. Chemie 113, 145 (1924).

²⁾ We take here $32^{\circ}.27$ C., the point of intersection of the curves of solubility, therefore the value which was found in par. 15, instead of $32^{\circ}.3$, the value determined by COHEN and KOOY by dilatometric way.

G. MONDAIN MONVAL's investigation.

1. The solubility determinations.

19. The results of his solubility determinations are given in table 5

TABLE 5.
Solubility of NH_4NO_3 at different temperatures (MONDAIN MONVAL).

Temperature	Gr. NH_4NO_3 in 100 gr. of water	Molecular concentration C. (sum = 1)
26°.7	215.0	0.3257
28.6	223.6	0.3344
29.4	227.1	0.3379
30.4	232.5	0.3431
30.8	234.5	0.3450
32.2	241.2	0.3515
32.9	244.4	0.3544
33.8	248.3	0.3581
35.3	255.6	0.3648
36.0	259.0	0.3679
39.2	274.5	0.3814

By means of these experimental results, which give a point of intersection of the solubility curves of modification IV and III at $31^\circ.8$ MONDAIN MONVAL calculates (without further explanation) for the quotient

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} \text{ the value of } 1.17, \text{ at the temperature mentioned.}$$

By means of the method of least squares we find, however, from columns 1 and 3 in table 5:

$$c_{IV} = 0.3354 + 0.00472(t - 28.8) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$c_{III} = 0.3664 + 0.00429(t - 35.7) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Table 6 proves that the equations (9) and (10) are in very close agreement with the results of MONDAIN MONVAL.

TABLE 6.

Temperature	c_{found}	$c_{\text{calculated}}$	$(c_{\text{calc.}} - c_{\text{found}}) \times 10^4$
26°.7	0.3257	0.3255	— 2
28.6	0.3344	0.3345	+ 1
29.4	0.3379	0.3382	+ 3
30.4	0.3431	0.3430	— 1
30.8	0.3450	0.3448	— 2
31.8	0.3500	0.3496	— 4
32.2	0.3515	0.3514	— 1
32.9	0.3544	0.3544	\pm 0
33.8	0.3581	0.3582	+ 1
35.3	0.3648	0.3647	— 1
36.0	0.3679	0.3677	— 2
39.2	0.3814	0.3815	+ 1

The point of intersection of the curves (9) and (10) is 31°.8, while, by means of these equations we find:

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} = \frac{0.00472}{0.00429} = 1.10$$

and *not* 1.17, which figure is given by MONDAIN MONVAL.

20. We are of opinion that it is superfluous to trace the reason which has led to such a great divergence from the figure (1.14) found by us. We only wish to observe that MONDAIN MONVAL finds values for the solubility at all the temperatures investigated by him, which lie far below ours, and as we have always attained equilibrium of solution with highly different periods of shaking, from above as well as from below, at which we found identical values, whereas he, with far shorter periods of shaking (during which the temperature was but a short time above the temperature of equilibrium) thought to have reached equilibrium, it is very probable that in his investigations this has not been the case.

The way in which MONDAIN MONVAL prepares the saturated solutions for analysis (filtering the excess of salt through a previously heated funnel, during which crystallisation is not excluded) may also have been one of the causes of his too low results. Then he has been experimenting

within too small ranges of temperature, so that the values of $\left(\frac{dc}{dT}\right)_{IV}$ and $\left(\frac{dc}{dT}\right)_{III}$ are doubtful.

2. *Determination of the fictitious heats of solution Q_{IV} and Q_{III} .*

21. Now that we have obtained our results we will not enter into a discussion of the particulars of MONDAIN MONVAL's method to find $\frac{Q_{IV}}{Q_{III}}$, and only wish to observe, that the way, in which he has measured the intermediate heats of solution of the two modifications in solutions of different concentrations, has been a rather rough one. COHEN and HELDERMAN¹⁾ have determined those values by means of a highly perfected, calorimetric method, with an accuracy of 0.3 per cent. Tables 7 and 8 show that the divergencies between the values of MONDAIN MONVAL and those of COHEN and HELDERMAN are not inconsiderable.

MONDAIN MONVAL calculates the quotient $\frac{Q_{IV}}{Q_{III}}$ by means of the values found by him $Q_{IV} = -2.93$ and $Q_{III} = -2.53$, whereas the investigation by COHEN and HELDERMAN has given the values -2.91^7 and -2.51^7 .

The value of $\frac{Q_{IV}}{Q_{III}}$, calculated by MONDAIN MONVAL happens to be the same as the value furnished by the much more accurate figures of COHEN and HELDERMAN, viz. 1.16.

TABLE 7.

Intermediate heats of solution of Ammonium nitrate, Modification IV, according to MONDAIN MONVAL and according to COHEN and HELDERMAN, at 28° and 32°, 3 respectively.

Experiment	Initial conc. in gr. p. 100 gr. of solut.	Final conc. in gr. p. 100 gr. of solut.	Mean conc. in gr. p. 100 gr. of solut.	Intermed. heat of solution in Kgr. cal. per mol.		Difference
				MONDAIN MONVAL	COHEN— HELDERMAN	
1	0	2.23	1.11	— 5.90	— 5.819	+ 0.08
2	20	22.03	21.01	— 4.62	— 4.468	+ 0.15
3	50	50.91	50.46	— 3.33	— 3.302	+ 0.03
4	56.9	57.53	57.22	— 3.19	— 3.144	+ 0.05
5	66.6	67.18	66.89	— 3.02	— 2.972	+ 0.05

¹⁾ These Proceedings 28, 1 (1924); Zeitschr. f. physik. Chemie 113, 145 (1924).

TABLE 8.

Intermediate heats of solution of Ammonium nitrate, Modification III, according to MONDAIN MONVAL and according to COHEN and HELDERMAN, at 36° and 32°. 3 respectively.

Experiment	Initial conc. in gr. p. 100 gr. of solut.	Final conc. in gr. p. 100 gr. of solut.	Mean conc. in gr. p. 100 gr. of solut.	Intermed. heat of solution in Kgr. cal. per mol.		Difference
				MONDAIN MONVAL	COHEN— HELDERMAN	
1	0	2.57	1.28	— 5.35	— 5.405	— 0.06
2	34.8	35.94	35.37	— 3.44	— 3.392	+ 0.05
3	57.0	57.71	57.36	— 2.86	— 2.741	+ 0.12
4	70.0	70.37	70.19	— 2.54	— 2.525	— 0.01

22. From the investigation of MONDAIN MONVAL results:

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} = 1.10 \quad \text{en} \quad \frac{Q_{IV}}{Q_{III}} = 1.16.$$

A satisfactory experimental testing of the "law of tangents" is therefore out of the question.

Summary.

In the above paper was shown that the experimental testing of the "Law of Tangents" of LE CHATELIER by MONDAIN MONVAL has led to unsatisfactory results, in consequence of insufficient accuracy of the data necessary for such a proof. An agreement between theory and experiment, satisfactory in every respect, was found by employing more accurate methods.

Utrecht, April 1925.

VAN 'T HOFF Laboratory.

Geology. — "*The Palaeothermal Problem in the Light of the Giant and Dwarf Theory of Stellar Evolution*". By Prof. EUG. DUBOIS.

(Communicated at the meeting of May 30, 1925).

In all geographical formations with well characterized faunas or floras, starting with the Cambrium, these up to the upper division of the Tertiary give evidence of a hotter climate than at present, pliothermal conditions, at high geographical latitude. Though the distribution over the Earth was never perfectly uniform, it is not until the beginning of the Tertiary era, and then at first locally restricted, gradually more circum-polarly, that palaeontologic witnesses appear, testifying to gradual and progressing cooling, till at last in the Plistocene period evidence is found of the present distribution of heat.

Some of the surest palaeontological proofs of a hotter climate at high geographical latitude and more uniform distribution of heat over the Earth may be mentioned here, with a view to defining the palaeothermal problem.

In the Cambrian reef-building corals, which anthozoa now-a-days scarcely reach further than beyond the 28th degree of latitude at a single point, because they are physiologically-chemically restricted to hot seas, the secretion of lime being actually a function of the temperature, are met with up to $76^{\circ} \frac{1}{2}$ N. lat. in the New-Siberian Islands, and as far as beyond the Antarctic circle in Antarctica (Weddell-Sea).

Especially in the Upper Silurian formation coral reefs are known of all latitudes; in the extreme North, of the peninsula of Kanin, at 68° N. lat., and of the New-Siberian Islands and the Arctic-American Island of North-Devon, at 75° N. lat. The general hot climate throughout the period appears moreover from the cosmopolitan character of the faunas. In the Southern Hemisphere the Graptoliths in the South-Orkney Islands, found at 61° S. lat., bear witness to the same fact.

Also in the Devonian formation reef corals are found inside the Arctic circle. The Upper Devonian floras of Ellesmere Land as well as of Bear Island at 78° N. lat. give evidence of the great uniformity of the vegetable world of the time. Likewise the marine Devonian fauna of the Falkland Islands and the Cape show the more uniform distribution of heat.

That the luxuriant Carboniferous flora, which is very uniformly of character over the whole Earth, must be considered as a lowland flora of a moist warm, i.e. tropical climate, appears beyond all doubt. In Spitsbergen reef corals are found in the Upper Carboniferous (chronologically equivalent to our

coal-measures), and in the Lower Carboniferous of this group of islands and of Greenland, here even at 81° N. lat., the same flora as was widely spread at much lower latitude.

The Permo-Carboniferous *Glossopteris* flora of the Southern continents and India, which was found at 51° S. lat. as far as the Falkland islands, and in the Antarctic continent at 85° S. lat., i.e. five degrees from the pole, but also in Mongolia and China, and mixed with the northernhemispheric Permian flora, in Siberia and North Russia (at 61° N. lat.), had likewise the character of a flora of a hot and humid climate, as was recently set forth by GOTHAN¹⁾. This may also be derived from the fact that it occurs mixed with the *Lepidodendron* flora in South America and South Africa.

In the Triassic formation of Alaska the same fauna of reef-corals occurs at 60° N. lat. as in California at 41° 1/2° N. lat., and in the Alps up to 45° N. lat.

Among the most reliable palaeontological evidences of a tropical climate are large forms of Reptiles. As cold-blooded animals the Reptiles are entirely dependent on the temperature of their surroundings as regards metabolism and consequently in all their functions. For this reason their life is minimum in our winter; in recent times only small forms, which can hibernate hidden, can exist at high geographical latitude. The general presence at high geographical latitudes of large Theromorpha in the Upper Carboniferous, the Permian and the Triassic formation, of large Dinosauria throughout the Mesozoic era, from the Triassic up to the upper Cretaceous formation, prove with perfect certainty that the climate there was without any winter, i.e. tropical.

In the Permian period there lived in Russia, at 61° N. lat., large Theromorpha (*Pareiasaurus*, *Inostranzewia* and others) which were closely related to South African forms, belonging to a widely-spread fauna found also in India, Europe and North America up to the Triassic period.

To a hot climate at high geographical latitude point also the large Stegocephalic Amphibia in the Triassic formation of Spitsbergen.

Already in the Triassic period there existed large forms of Dinosauria in North America up to at least 43° N. lat., in Europe up to at least 53° N. lat., in South Africa, India, Australia. Large Dinosauria also occur in the Jurassic formation of North America, Europe, South Africa. The time at which these landreptiles really flourished is, however, the Cretaceous period. From the beginning till the end of this period there existed the rich fauna of gigantic Dinosauria in North America and East Africa, in India, Central Asia, and Europe, as well as in South America and Australia. We know it of 51° N. lat. in Canada, of 70° N. lat. in Greenland, of 51° N. lat. in Belgium, of 45° N. lat. in Mongolia, and of 39° S. lat. in North Patagonia. That of East Africa (Tendagu-

¹⁾ W. GOTHAN, *Palaeobiologische Betrachtungen über die fossile Pflanzenwelt*. Berlin 1924.

ru), at 10° S. lat., presents close resemblance to the famous fauna of the Como beds of North America. Compare Kentrurosaurus with Stegosaurus!.

The flora of the Jurassic is more uniform than that of any other period. On the east coast of Greenland, at 70° N. lat., it had the same tropical or sub-tropical character as in England at 54° N. lat., and of the species of Ferns, Equisetaceae and Cycadeae found in West Antarctica at 63° 15' S. lat., at least as many occurred also in Europe as in India.

Also the angiospermian Cretaceous flora of the west coast of Greenland had a sub-tropical character at 70° 1/2 N. lat.; it shows to be allied to the Dakota-flora of western North America known to beyond 56° N. lat., which for the greater part resembled the hot-temperate angiospermian Cretaceous flora of South Patagonia at 51° S. lat.

Coral reefs of the Jurassic period are known in Europe up to 52° N. lat., in North America to 38° N. lat., and in South America to 40° S. lat. Those of the Cretaceous formation reach 47° 1/2 N. lat. in Europe.

Important indications of a formerly hot climate are also given by fossil Palms. The general boundary lines of the present palm zone do not extend further than 38° N. lat. and 32° S. lat.; only a single palm species in the Pacific islands is found as far as 45° distant from the equator. The Middle Eocene flora of South England at 51° N. lat. contains a number of palm species. This flora presented on the whole, according to GARDNER, the appearance of the forests in the Malay Archipelago and tropical South America. The Middle Eocene flora of North America at the same latitude gives evidence of a much less hot climate than there. It contains but few palms, a deviation of the same nature as in the present temperatures of those places. At present the average temperature there in North America is in January 15° C. and in July 6° lower than in South England. The Eocene nummulites, which bear witness to the presence of hot sea-water, reached Zeeland in Holland, South England and even Bremen (53° N. lat.). The Eocene marine flora of Alaska (at about ten degrees higher latitude) was, indeed, only subtropical. In the Oligocene period coral reefs lay off the north and the south borders of the Alps, and as late as the Lower Miocene the tree flora of Europe contains some palm species by the side of a diminished number of other tropical forms to beyond 50° N. lat.

On the Pacific coast of North America, from Oregon northwards, only a cool-temperate climate prevailed in Miocene times. This difference in temperature between North America and Europe compared with the Arctic regions, which is constantly met with, corresponds to the present distribution of heat, and unless a consequence of a more America-ward position of the North Pole, it might be caused, just as at present, by hot North Atlantic ocean currents, which, undoubtedly, had preponderating influence in the Pliocene period.

The Arctic Tertiary floras, famous by the work of HEER, and now almost universally placed in the Eocene, have already long been considered of great significance for the palaeothermal problem. The most northern finding places are Grinnell land at $81^{\circ} 45' \text{ N. lat.}$ and Spitzbergen at $78^{\circ} 56' \text{ N. lat.}$ The richest finding-place lies on the west coast of Greenland, at $70^{\circ} \text{ N. lat.}$ Such floras of from uniformly temperate to a hot-temperate climatic character are now-a-days found 20 to 30 degrees more south. An equally mild climate as that of Greenland at $70^{\circ} \text{ N. lat.}$ must have been that in which existed the Eocene flora of Alaska between 55° and $62^{\circ} \text{ N. lat.}$ On the other hand, judging from the fossil flora, the Miocene climate of Japan, at about $33^{\circ} \text{ N. lat.}$, was slightly cooler than its present climate. But this seems to be compatible with a circumpolar hot condition, when by strengthening of the hot North Atlantic ocean-currents, the Arctic lowlands, especially in winter, were favoured, and Japan, in consequence of a more pronounced monsoon climate, in winter, was in a less favourable condition as regards heat.

In the Southern Hemisphere the fossil flora of Coronel in Chili, which is Lower Miocene or older according to Berry, bears the character at $37^{\circ} \text{ S. lat.}$ of a tropical rain-wood flora. At present the temperature is there on an average 15° C. in January and 10° C. in July. The Eocene flora of the northern island of New Zealand, at about the same latitude, is described as only temperately-subtropical. The present temperature is there almost 20° C. in January and 10° in July. The formerly more favourable thermal condition on the coast of Chili than in New Zealand may probably be explained by the at the time less cold polar current along this coast, as a necessary consequence of a general pliothermal condition. The so-called *Fagus* flora of the region round the Strait of Magellan, between 51° and $53^{\circ} 1/2 \text{ S. lat.}$, which was hesitatingly placed in the Lower Miocene by DUSÉN, suggests a formerly hot-temperate, and in opposition to the present, a humid climate. In our times it is much cooler there, the average temperatures being 10° C. in January and 5° C. in July. Of the highest southern latitude is the fossil flora of Seymour-island in West Antarctica, at $64^{\circ} 15' \text{ S.}$ a place now buried under ice, which flora was placed in the Tertiary by DUSÉN. It gives evidence of a subtropical climate. These South-American and Antarctic floras are considered as Pliocene by IRMSCHER¹⁾ in connection with the hypothetical place of the pole according to WEGENER. The subtropical Seymour flora then remains, however, at at least $50^{\circ} \text{ S. lat.}$ WEGENER himself places it at $45^{\circ} \text{ S. lat.}$ in the Upper Tertiary. If the indeed not sharp, but at any rate older estimations of the geological age of these floras by BERRY and DUSÉN are accepted, they fit into the frame of the Tertiary floras of the Northern Hemisphere, which bear witness to a hotter condition throughout the

¹⁾ E. IRMSCHER, Pflanzenverbreitung und Entwicklung der Kontinente. Hamburg 1922

Boreal Earth, with temperatures diminishing from the beginning to the end of the Tertiary era. Disturbances in the zonic climate system, as in Europe through hot ocean-currents, in Japan through the monsoon-climate could locally retard or accelerate the, on the whole gradual, cooling, in the former case cause the temperatures even to rise above the earlier ones, in the latter case cause them to fall below the present ones. To the latter the Miocene glacial deposits in Alaska seem also to testify.

Of the orders of Reptiles extant after the Mesozoic era large forms are now-a-days found only in hot climates, at low geographical latitude. In the Tertiary of Europe Crocodiles and large Tortoises — not seldom of genera identical with those living at present — and also large Snakes are met with at high latitude. Thus *Tomistoma*, the Malay Gavial, up to $48^{\circ}10'$ N. lat. in the Miocene of Lower Austria, a gigantic *Testudo* as far as $42^{\circ}1/2$ N. lat. in the Pliocene of South France, large *Pythonides* in the Eocene of England, Belgium, France, Switzerland. In North America, on the other hand, Alligator is found only 5 degrees more northern than at present, in the Lower Pliocene of Nebraska, a little above 40° N. lat.

In the Miocene of Central France (Allier) a Parrot was found of the present tropical African genus *Psittacus*.

Anthropoid Apes are found in the Miocene and earliest Pliocene of Europe. The best-known are the large *Dryopithecus* and the small *Pliopithecus*. *Dryopithecus* was found in the south and the south-east regions of France up to $45^{\circ}1/2$ N. lat., also in Spain, on the southside of the Pyrenees at $42^{\circ}20'$ N. lat., in Upper-Swabia at 48° N. lat. and with *Pliohylobates* in Rhine-Hessen at $49^{\circ}40'$ N. lat. *Pliopithecus* is known from south, south-east and central France up to 48° N. lat., from northern Switzerland ad $47^{\circ}1/2$ N. lat., from Upper-Swabia at $48^{\circ}1/2$ N. lat., from Styria at $47^{\circ}1/2$ N. lat., and from Silesia (Oppeln) at $50^{\circ}40'$ N. lat. As all present-day Anthropoid Apes are confined to the tropical rain-wood zone, the small forms (the *Hylobatides*) are met with only at a latitude 25° degrees lower in Burma, and the large forms in Sumatra, Borneo, and in Africa are found only to 5 degrees distant from the equator, it may be assumed that the Miocene and Old Pliocene climatic condition in the regions of Europe agreed with that in the present tropical rain-wood zone. Certainly the occurrence of a number of large Anthropoid Apes, among others *Dryopithecus*-species, in the Siwalik beds of the same time, to 33° N. lat., point to a climatic condition as is now-a-days to be found only at a few degrees' distance from the equator. The same may be said of the South African *Australopithecus*, which was found at a distance from the equator 23 degrees larger than the Gorilla and Chimpanzee of these times, to which this fossil, probably Lower Pliocene Anthropoid Ape is certainly closely allied.

Homunculus, an Ape of the family of the Cebidae, which family is

now-a-days confined to the tropical rain-wood zone of America, was found in the Upper Miocene of Patagonia, at 50° S. lat., hence its testimony goes to prove the same.

Of the family of the Cynopithecidae only a single species hardly reaches, under particularly favourable circumstances (in Japan), the 41^{st} degree of latitude, but in the Lower Plistocene (or Upper Pliocene) of Europe representatives of this family are found in different places of higher geographical latitude (in South France, Hungary, Wurtemberg, England). The most northern finding-places are the Heppenloch at Kirchheim in Wurtemberg, at $48^{\circ} 40'$ N. lat., and the Cromer Forest-Bed, at $52^{\circ} 1/2$ N. lat. In those times Hippopotamus in Europe was found to beyond the 50^{th} degree of latitude (Cromer, Tegelen), 20 degrees more to the north than it lived in historical times (in the Nile delta and the Jordan valley).

In the same way the Lower Interglacial fauna and flora of Tegelen, which may be referred to the upper Pliocene, at $51^{\circ} 20'$ N. lat., and the rich Megalonyx-fauna, which is met with in the Lowest-, Pliocene or Aftonian Interglacial of North America, to 41° N. lat., testify to warm-temperate, humid climates.

After this time it has never been considerably hotter anywhere at higher geographical latitude, than at present. It had generally become so much cooler here that with slight intermittant fall of the temperature, which also manifests itself in earlier formations, glacial periods could now begin to interchange with interglacial times. Before the Upper Pliocene, unless it be in the Miocene of Alaska and possibly Northeast Siberia, no traces of such an alternation of glacial and interglacial periods with comparatively small differences of temperature, are found, evidently because then it was still too hot on our planet for this.

To this short enumeration of some of the surest palaeontological proofs of a formerly warmer climate at high geographical latitude a geological testimony may be added, i.e. the occurrence in old formations of such products of weathering as laterite and beauxite. The Plistocene or older laterite in the Kalahari of South Africa, probably also the laterite of West Australia, the Cretaceous beauxite of South France, the Pliocene of the Vogelsberg in Germany and the Eocene of Antrim in Ireland testify, like the beauxite of Alabama in North America, to a former tropical climate.

Of equally great significance in the palaeothermal problem as the palaeontological proofs of former hotter conditions at high geographical latitude are the geological proofs of former cold conditions at comparatively low geographical latitude, the palaeozoic and proterozoic ground moraines or tillites. We know most about the Permo-Carboniferous "Ice Age", the glaciation of South Africa, India, Australia, and South America which took place at the transition of the Carboniferous in the Permian period. This glaciation has been proved with as much certainty — especially through polished and striated rocks under the tillites which, shown

by MOLENGRAAFF in South Africa for the first time with certainty, have now been found everywhere — as the Plistocene glaciation of Europe and North America, South America, Australia, Tasmania and New-Zealand. In some places viz. in New South Wales and West Australia, in North India and South West Africa, glacial deposits were formed in the sea by floating ice.

In South Africa the traces of this Permo-Carboniferous "Ice Age" are found from $33^{\circ} \frac{1}{2}$ S. lat., in Cape Colony, to 8° S. lat., in Katanga ¹⁾; in India from 20° N. lat., in Central India, to $32^{\circ} \frac{1}{2}$ N. lat., in the Salt Range; in Australia from 21° S. lat., in Queensland, to 43° S. lat., in Tasmania; in South America from 23° S. lat., in Brazil, to 52° S. lat., in the Falkland Islands.

The great prevalence of its ground-moraines does *not* distinguish the Permo-Carboniferous glaciation from the Plistocene, for this extended in the Cordilleras of South and Central America over 70 degrees of latitude and in fact over all the continents at the same time. But in contrast to the Plistocene the Permo-Carboniferous glaciation seems to have no *bipolar character*, for in the Northern Hemisphere unmistakable and extensive Permo-Carboniferous traces of ice have not been found except at comparatively low latitude, only in and near India. At any rate the extension in the Northern Hemisphere was comparatively restricted. Nor is a shift of the pole conceivable with the present situation of the continents, through which bipolarity of the known Permo-Carboniferous ice-traces would be obtained. Besides the general direction of the movement of the ice-sheets in South Africa is towards the South pole, in Australia and India away from the pole, hence at least partly *independent* also of the South pole, even if its position had been different.

It is further in contrast to the Plistocene glaciation that most traces of the Permo-Carboniferous ice age occur at comparatively low latitude; even the marine glacial deposits are found at only about 33° , in India north of the equator and in Australia south of the equator, and at 27° S. also in South Africa.

Still in another respect does the Permo-Carboniferous glaciation greatly differ from the Plistocene, i.e. in this that the climatic character of the fossil flora immediately under and above the tillite and where two successive ground-moraines are found, in New South Wales, also that of the interglacial flora, presents more or less a tropical hot, not only temperate or at most hot temperate

¹⁾ It has not been established beyond doubt that the tillite of Katanga is equivalent to the Dwyka tillite, possibly it is older. There is still less certainty about the age of the tillite found by KOERT in Togo, at 7° N. lat. That discovered by BALL and SHALER in the upper river basin of the Kongo, between 3° and 5° S. lat. is without doubt Triassic. Possibly some of the tillites found at very low latitude are the ground-moraines of local old glaciers. (Cf. E. HENNIG in: Geologische Rundschau, Band VI, p. 154, (Leipzig 1915)).

character. Evidently the glaciation in the Permo-Carboniferous period cannot have been the consequence of a few degrees' lowering of the general temperature, as in the Plistocene period.

From the fact that everywhere the *Glossopteris* flora appears after the Permo-Carboniferous glaciation, while in Australia and South Africa the Carboniferous *Lepidodendron* flora preceded this glacial period, it was, indeed, inferred that the new flora arose under the influence of the cold, and being adapted to cold, replaced the thermophile *Lepidodendron* flora. But this view must be relinquished now that the *Glossopteris* flora has been found in South Africa also under, even in the Dwyka tillite, and immediately above this Permo-Carboniferous ground-moraine, just as immediately above the Orleans tillite of South America (Brazil), a mixed *Glossopteris*-*Lepidodendron* flora. A fact of the same significance is the mixture of the *Glossopteris* flora with the flora of the Siberian and North Russian Upper Permian testifying to heat, together with which flora large Theromorphous reptiles lived. Nor have traces of ice been found there anywhere. Besides the plants of the *Glossopteris* flora are partly huge trees, partly large-leaved herbs; with GOTHAN it may be assumed that this flora physiognomically certainly did not present any differences worth mentioning from the Permo-Carboniferous flora of the Northern Hemisphere. Hence the *Glossopteris* flora did evidently not arise under the influence of glacial cold; on the contrary, it required heat, like the *Lepidodendron* flora.

But while these latter lowland floras existed under high temperatures, the immense ice-masses which transported the material of the Permo-Carboniferous tillites, were accumulated in the mountains.

There have been found convincing proofs of some glacial periods older than the Permo-Carboniferous one. In South Africa the existence of a lower Devonian tillite at Griquatown at 29° S.lat., and of a Silurian or Cambrian (perhaps even Algonkian) tillite at Clanwilliam at 32° S.lat., and at Capetown at 34° S.lat., established by ROGERS and others. According to HOLTEDAHL the tillite discovered by REUSCH at 70° N.lat. on the Varangerfjord, in the most northern part of Norway, is Lower Silurian and was probably supplied by a local glacier. The Arctic seas of the whole Silurian period were, however, undoubtedly hot. Upper Algonkian tillites have been found in China on the Jangtsekiang at 31° N.lat. by BAILEY WILLIS, and in South Australia at Adelaide at 35° S.lat. by HOWCHIN. The very extensive tillites in the Canadian province of Ontario between 46° and 50° N.lat. discovered by COLEMAN are dated in the Middle Algonkian period. Still perhaps somewhat doubtful is the Permo-Carboniferous glaciation discovered by WEIDMAN in Oklahoma at about 34° 1/2 N. lat. Also the Permo-Carboniferous tillite of Boston at 1/2 42° N.lat., described by SAYLES.

Of a more local character is probably the Triassic tillite discovered by BALL and SHALER in Central Africa, between 3° and 5° S.lat.

On the ground of all this evidence it may be assumed that during the Proterozoic and Palaeozoic eras, which judging from the lead-content of uranium minerals may be estimated at from three to four times the whole later geological time, at least now and then the conditions were present for extensive accumulation of ice in the mountains, which conditions were absent thereafter. In view of the space of time they occupy, these events constitute a very important side of our problem, which might make us inclined to consider the condition in that long space of time as "normal" and miothermal (less hot), just as the present and Plistocene condition, in contrast to the Mesozoic-Tertiary "abnormal" and pliothermal (hotter) interval, in which no extensive glacial traces were found. We might also think of such very long pliothermal times as the latter, occupying from a fourth to a third of the whole space of time, in the Proterozoic and Palaeozoic eras, interglacial periods of the highest order, which have alternated with the glacial periods proper. Judging from the best documented of these latter, the Permo-Carboniferous glacial period, pliothermal conditions were, however, present also then even in the neighbourhood of the ice. The circumstances that have led to ice accumulation in the Permo-Carboniferous period must at all events had been entirely different from those in the Plistocene-period. This renders it impracticable to continue the line from those earliest climatic conditions to the present times.

But still many geologists see no essential difference between the Permo-Carboniferous and the Plistocene glaciation. Both events are considered to be caused by an extension of a niveous polar climate on to the rainy region of a temperate zone, in consequence of an only slight temporary lowering of the temperatures during a miothermal condition already existing over the whole Earth. WILHELM RAMSAY¹⁾ and others have rendered it plausible that miothermal times are periods of vigorous mountain formation, in which extensive parts of the Earth's crust are raised to a considerable height, which then cause the mean temperature on the Earth to fall through stronger loss of heat by radiation, lively vertical circulation in the atmosphere and increased condensation of water vapour. Such a miothermal period is the time in which we live. Anorogenetic periods, as the whole Mesozoic era, with lower and levelled continents and mountains, were, on the contrary, pliothermal times. Then glacial deposits were formed nowhere, not even at high latitude.

However the variations of the assumed conditions of heat on the Earth and those of its relief do not always run parallel. The climatic mechanism described by W. RAMSAY can, evidently, be suppressed by more powerful factors than an elevated or low relief of the Earth. In an "anorogenetic phase" the Lower Silurian tillite on the Varangerfjord was deposited, the Lower Devonian in South Africa, the Triassic in

¹⁾ WILHELM RAMSAY, *Orogenesis und Klima*. Helsingfors 1910.

Central Africa. On the other hand the orogenetic Tertiary period was not miothermal, and it is inconceivable that millions of years of orogenesis were required for the development of the Pliocene miothermal effect. Besides, if there is a foundation of truth in the contraction theory, which is too much neglected at present, the relation between orogenesis and climate may possibly be opposite to what RAMSAY and others suppose it to be, and the long Mesozoic anorogenic phase may be the result of the universally acknowledged pliothermal condition of that time.

Apart from the "generally hotter or less hot conditions" on the Earth, we have apparently only to do with another localisation of the same climatic types as those existing at present. In fact the characteristics of these are absent in none of the geological formations considered here, — with the exception of glacial deposits in the Jurassic, the Cretaceous, and the greater part of the Tertiary periods. Besides the characteristics of a hot climate at high latitude and of accumulation of ice at comparatively low latitude, also those of the dry regions are found in the different formations; deposits of rock-salt, gypsum, desert sand, far from the places where they are found in recent times. They are all geographically distributed quite differently from the present distribution.

Was this distribution in every geological formation, not quite irregular, after all, and possibly analogous to the present distribution of the types of climate?

A priori it seems that the answer to this question can only be affirmative. In virtue of the spheroidal shape of the Earth the heat received from the Sun by any point of its surface must always have been function of the geographical latitude. Hence not even in the hottest geological period can a perfectly uniform climate have prevailed over the whole Earth. There must always have existed a system of climatic zones analogous to the present one with anomalies of a corresponding nature as in the present climatic system, which are to be attributed to the distribution of water and land, the height of the land, and the presence of meridional mountain-chains. In this the Sun, practically the only source of heat of the Earth's surface, is assumed to be invariable. To account for the constantly modified localisation of the climate types it is then natural to assume displacement of the equator and the poles during the whole geological past. Under for the rest equal telluric circumstances, as considered by RAMSAY, and taken in general, the climatic zones must have been distinguished from each other then in the same degree and the irregularities of the zonic system must have been comparatively as small as they are at present.

W. KÖPPEN and A. WEGENER¹⁾ see the climatic conditions of the geological past from this point of view, considering them in the light of WEGENER's hypothesis of the continental drift. On the maps of the

¹⁾ W. KÖPPEN and A. WEGENER, *Die Klimate der geologischen Vorzeit*. Berlin 1924.

world giving the different geological formations constructed by WEGENER, are indicated in the first place the two dry climatic zones, necessarily to be expected at about 30° then northern and southern latitude, from the deposits of rock-salt, gypsum, and desert sand, and between them the large circle of the equator is traced, along which the coal is situated of the equatorial rainy zone. Outside the dry regions are found the rainy regions of the temperate zone equally characterized by coal deposits. The ground-moraines of a niveous polar climate are often absent. A glacial period can certainly, in KÖPPEN and WEGENER's opinion, be suppressed by extensive transgressions in the polar region. It may, however, be stated, that for a continent as Antarctica with the earlier annexes the required extensive covering with water is always improbable. Besides they assume the polar climate to have been comparatively mild during the Mesozoic and Eocene time. This, like other "disturbances" in the climatic system of their maps is chiefly ascribed by them to the varying distribution of land and water, and the ocean- and air-currents dependent on them. They now see the situation of these climatic zones, which have been thus empirically determined, change from formation to formation. The poles have, therefore, shifted, though only within certain narrow limits, and the continents have drifted. Hence the history of the climate of a place is very nearly the history of its position with regard to the pole and the equator.

KÖPPEN and WEGENER consider that in this way they have shown systems of climatic zones, in main lines equal to the present system and with irregularities of the same nature, for all formations from the Carboniferous to the Plistocene. For the Quaternary period the shift of the poles accounts for the Ice Age, but they ascribe the alternation of glacial and interglacial periods to the secular variations of the eccentricity, the perihelium, and the obliqueness of the Earth's orbit, with which the solar radiation received by the Earth varies and in consequence the summer heat.

They consider the Sun itself as a source of heat constant throughout the whole geological past up to the present time. Already on account of an earlier greater "solar constant" their explanation of the varying distribution of the climatic types would call for a modification, in as much as disproportionately more heat than at present was transported from low to high latitudes with the then greater atmospheric circulation and sea currents. But when besides the greater energy of solar radiation had another spectrum maximum, the heat received by the Earth might have been distributed more uniformly or less uniformly over its surface than at present on account of the different behaviour of the atmosphere and the hydrosphere of our planet towards solar radiation of different wave length. Then also the difference of temperature between high and low might have been smaller or greater, and the "disturbances" might in general have been comparatively smaller or more important than at

present. Moreover with very considerable apparent size of the Sun, the heat directly received at any place of the Earth will, according to BLANDET's hypothesis, have been less dependent on the geographical latitude.

Under certain states of evolution of the Sun, in which it possibly may have been in the geological past, the climatic zonic system may, therefore, have been less pronounced, and there may have been disturbances of more importance than at present. If the Sun's radiation itself has changed during the Earth's past, the history of the climate of a place is *not* chiefly the history of its situation with respect to the equator and the pole, plants and animals of a hot climate may have lived at comparatively short distance from a former pole and also from highlands covered with ice, and ice may have been accumulated at comparatively low latitude, isolated, and without polar connection.

Actually the following floras and faunas testifying to a hot climate existed at high latitudes on KÖPPEN and WEGENER's maps, also when there was ice at those places:

The prae-, inter-, and postglacial Permo-Carboniferous flora in South Africa at 70° to 80° S. lat., in Australia at 70° S. lat., in South America, in the Falkland-Islands, and in the Antarctic continent between 60° and 70° S. (*Gangamopteris* was also found in the Dwyka tillite).

The Permian large Theromorphous reptiles: *Pareiasaurus*, *Dicynodon* and others in South Africa at 55° to 60° S. lat. (Their nearest relations lived at 30° N. lat. in Northern Russia, like other Theromorpha: *Dime-trodon*, *Naosaurus* and others in Texas. The fresh-water reptile *Mesosaurus*, which is indeed only 70 cm. long, is found immediately on the Dwyka tillite).

The Triassic reef corals in California and Oregon near and beyond 60° N. lat. to Alaska at 75° N. lat.¹⁾

The Triassic large Theromorpha: *Cynognathus* and others in South Africa at 60° S.

The Lower Jurassic large Dinosauria in South Africa at 60° S. lat.

The Jurassic flora in West Antarctica at 68° S. lat.

The large Dinosauria of the Lower Cretaceous Tendaguru fauna in East Africa at 53° S. lat.²⁾ and the closely allied Como fauna of the same time, and also the Upper Cretaceous large Dinosauria in North America at about 45° to 50° N. lat.

The Upper or Middle Cretaceous large Dinosauria in North Patagonia at 60° to 70° S. lat.

The Under Cretaceous flora of Uitenhage in South Africa at 67° S. lat. and the Upper Cretaceous flora in South Patagonia at about 65° S. lat.

The Eocene hot-temperate leaf-tree flora in Alaska at 60° to 70° N. lat.

The probably Tertiary hot-temperate *Fagus* flora of the region about

1) In KÖPPEN and WEGENER's text p. 63, Triassic coral reefs in Oregon erroneously at "fast 40°".

2) In KÖPPEN and WEGENER's text p. 92 "damals 35° S.," probably printer's error.

the Strait of Magellan at 60° to 70° S. lat. (if however Plistocene at only about 30° S. lat.) and the probably Tertiary subtropical flora in Seymour island at 70° to 75° S. lat. (if Plistocene yet higher than 50° S. lat.).

The Eocene nummulites in the northern part of Madagascar to 67° S. lat. on the west coast.

The Miocene and Lower Pliocene Anthropoid Apes in Europe: *Dryopithecus* and *Pliohylobates* to about 37° N. and *Pliopithecus* to about 38° N.

The Upper Miocene Santa-Cruz fauna in Patagonia with *Homunculus* and *Nesodon* and others at at least 50° S. lat.

The Pliocene (or Lower Plistocene?) marine warm-water fauna of Nome in Alaska at at least 67° N. lat.

The Upper Pliocene (= Lower Plistocene) flora and fauna of Tegelen at 57° N. lat. and the simultaneous fauna of Cromer at 59° N. lat.

The Upper Pliocene (= Lower Plistocene) *Megalonyx* fauna in North America to 65° N. lat.

This palaeontological evidence, which might easily be added to, may suffice to prove that the shift of the poles and the drift of continents alone are not sufficient to solve the palaeontological problem. KÖPPEN and WEGENER acknowledge this for the Mesozoic and Eocene periods, but it applies equally well to the Palaeozoic and the Neogene period.

At comparatively low latitudes of KÖPPEN and WEGENER's maps ice is actually found accumulated outside polar connection. The Triassic tillite discovered in Central Africa between 3° and 5° S. lat. lies, on their map, at 38° S. lat., i.e. at a greater distance from the Triassic pole and too much isolated to have arisen through polar cold climate. The same thing holds for the Boston- and Oklahoma tillites, which however perhaps somewhat dubious, lie at about 15° N. lat. and 22° N. lat. with regard to the Permo-Carboniferous north pole. Nor do the directions of movement of the Permo-Carboniferous ice-sheets in South Africa, which are independent of the hypothetical Permo-Carboniferous (and the present) south pole, testify to polar glaciation. If circum-polarly glacial, the Upper Algonkian tillites on the Jangtsekiang would require much greater displacement of the pole than KÖPPEN and WEGENER assume from the present to the Carboniferous period. From the Cretaceous to the Carboniferous period, this point always was under or close to the equator of their maps.

However meritorious in details, the hypothesis of the shift of the poles and the drift of the continents, therefore, leaves the palaeothermal problem at bottom for the greater part unsolved. As further all the other attempts at telluric explanations have proved inadequate, as far as the essential part of the problem is concerned, the solution apparently must be found in the changes indicated above, of the quantity and the quality of the energy radiated by the Sun, in its evolution, to our planet, during the geological time. The successive genesis of the geological formations

and the development of the vegetable and the animal world on the Earth must then have kept pace with this evolution.

According to the giant and dwarf theory of stellar evolution drawn up by HENRY NORRIS RUSSELL in 1914, the principle of which had already been acknowledged by EJNAR HERTZSPRUNG in 1905, who also introduced the names of "giants" and "dwarfs", our Sun at first was in the state of a giant star of great dimensions but slight density, of rising temperature and with a maximum of the energy of radiation and colour shifting from red to yellow and further in the spectrum. After a certain maximum of temperature and certain smallest wave-length of maximum energy of radiation in the spectrum had been reached, the Sun entered the phase of a shrunken but dense dwarf star of descending temperature. The maximum of the energy of radiation in the spectrum and the colour now shifted in the opposite direction, towards the red, so that our yellow dwarf sun has passed its present temperature and spectral stage already once, viz. as a giant star. In the giant stage the dimensions gradually diminished, but at the same time the temperature rose so that the total intensity of radiation remained the same throughout this whole phase. In the dwarf stage, on the other hand, the Sun became smaller with descending temperature, so that the total intensity of radiation steadily diminished.

The highest temperature reached in the giant phase and the smallest wave-length of the maximum of radiation in the spectrum reached corresponding to it, depends on the mass of the star. The maximum temperature is comparatively low in a scarcely middle-sized star like the Sun, and the displacement of the maximum energy of radiation in the spectrum from the red, has been comparatively small. At present the Sun is in the condition of a yellow dwarf star, in the middle of the *G*-class of the Harvard-classification, and its effective temperature is about 5900° abs. The temperature maximum at the transition from the giant- to the dwarf phase was calculated at 6600° abs. by EDDINGTON (1922). It may have been still less high. At such a maximum temperature the Sun as giant star has probably never reached the stage of the *F*-class. With the Harvard classes *A* and *B* following in the ascending series of the temperatures, this belongs already to the First class, of the "White Stars", according to the earlier classification of SECCHI. During its giant phase the Sun first belonged to the *M*-class, corresponding to the Third class, of the "Red Stars" of SECCHI, then to the reddish yellow *K*-stars, which with the *G*-stars constitute the Second class, of the "Yellow Stars" in the earlier classification, and to all the transitions between the *M*- and the *K*-stage and between the *K*- and the *G*-stage, till the highest point of the giant phase above the *G*-stage was reached. According to WIEN's law a displacement of the maximum of energy in the spectrum to a wave-length about 0.9 times the value from about $570 \mu\mu$ in the yellow to $510 \mu\mu$ in the green corresponds

to a change of temperature from 5900° to 6600° , and according to STEFAN's radiation law a total intensity of radiation almost one and a half times the value ¹⁾. But these are probably extremes. If the maximum of the temperature in the Sun's evolution curve lay close above the *G*-points, the total intensity of radiation in the giant phase was not much greater than in the present condition of the Sun, and the spectral radiation has changed only little since the highest temperature had been reached.

The views about the sources of the stellar energy of radiation and the cause of the change of the giant phase into the dwarf phase, hence about the internal nature of stellar evolution, have undergone important modifications and extension since the new theory was drawn up, especially of late years, through the work of EDDINGTON, JEANS and others, and chiefly in connection with the results of modern physics. These views themselves are still in a state of evolution, but to all probability the conception of the course of stellar evolution, which we owe to HERTZSPRUNG and RUSSELL, will remain unaffected.

For the Sun's evolution ages are calculated hundreds of times greater than the geological past considered here. It seems, therefore, to be entirely inadmissible to connect this evolution with the palaeothermal events discussed in this communication. But in the calculations of the Sun's age there is still so much uncertainty, chiefly on account of insufficient knowledge of the internal nature of stellar evolution, that the possibility at least remains that the whole or a large part of the giant phase of the Sun and the part of its dwarf phase passed through up to now, coincide with the geological time ²⁾. This possibility becomes probability when we consider the palaeothermal problem in the light of the giant and dwarf theory.

If it is an established fact that the Sun was still a giant star comparatively shortly ago, it must have passed the greater part of its past as a reddish yellow giant star of the *M*- and *K*-classes. The total radiation was then greater, just as in the whole giant stage, but not very much greater than the present radiation, but the maximum of energy lay in or near the red, and on the whole the radiation was of greater wavelength than at present. Besides the volume was really gigantic, especially in the *M*-stage, and the apparent size very considerable.

The long time of the Sun's past as much less hot red or reddish giant star, or at least a large part of it, may be considered in connection

¹⁾ According to the same law about 35° C. (against 3° C. now) is found for the Earth's mean effective temperature under the hottest sun, *ceteris paribus*. The calculated temperature at the surface of the Earth would have been still higher. The real temperatures must have remained far below this on account of the much greater albedo.

²⁾ Cf. the end of J. H. JEANS's article: On the Masses, Luminosities, and Surface-Temperatures of the Stars. Monthly Notices R. Astron. Soc. Vol. 85, January 1925, p. 211.

with the long Protero- and Palaeozoic time, in which "Ice Ages" occurred more than once. Then the Earth received, indeed, more solar radiation than at present, but of lower temperature, and also of another quality as regards its relation to the atmosphere and the hydrosphere. It should be remembered that the atmosphere acts in two ways on the solar radiation that passed through it. First through its water-vapour and carbonic acid it absorbs all the solar radiation and also the dark radiation emitted again by the heated Earth at certain places in the red part of the spectrum and far beyond it: *selective absorption*. Secondly it absorbs more or less of the energy of the whole radiation, on account of internal reflections at the air-molecules and other small particles which scatter them in all directions. This makes the atmosphere itself source of light and heat, the great significance of which has only been realised quite recently. The "diffuse daylight" and "the blue shy light" is at the same time radiation of heat. Lord RAYLEIGH has shown that *this diffuse reflection* is in inverse ratio to the fourth power of the wave-length; hence it is slight for red and yellow, great for blue and violet rays. Also in water the short-wave rays undergo strong dispersion, and return to the atmosphere for the greater part, the red and ultra-red rays, on the other hand, are absorbed. Thus the energy of radiation of short wave-length is chiefly communicated to the high atmospheric layers, those of great wave-length, on the contrary, to the lower atmospheric layers, which are rich in water-vapour and carbonic acid, and to the hydrosphere.

It is, therefore, easy to see that where in the Protero- and Palaeozoic eras there were extensive highlands even at comparatively low latitudes, as there certainly were at the end of the latter period in the Southern Hemisphere, large ice-masses must have accumulated on the strongly radiating highlands in the badly heated upper air, more isolated also on mountains of the lowest latitude; we see the latter even as late as the Triassic period. The lowlands and the sea being well heated, there was strong vertical circulation in the atmosphere, consequently sufficient supply of water-vapour towards the highlands for accumulation of snow-ice. For the rest the niveous circuit is many thousands of times slower than the pluvial circuit, and large ice-sheets can already be formed with slight snowfall during thousands of years (examples of this are Antarctica and Greenland). In the lowlands and in the sea, which were hot to the highest latitudes on account of the strong currents, caused by the high "solar constant" and the strong absorption of the red radiation, hot-climate plants and animals could live, even near the ice-covered highlands. Possibly the considerable apparent size of the then giant sun also contributed to making the climate hot at high latitude.

As the different conditions of the Sun's development gradually passed into each other, just as the geological formations do, this long first period

cannot be sharply defined in either way. Probably it was much longer than the whole period succeeding it, for the temperature rose to double its value in the giant phase from the *M*-stage to the *G*-stage, and after it to the highest point of the giant phase only still about a tenth. In this respect the Mesozoic period may probably be brought in connection with the *G*-giant stage to the maximum of the Sun's evolution. With an intensity of radiation or "solar constant" of the same value the distribution of energy over the spectrum was the same in the *G*-stage as at present. Further with maximum of energy shifted still more away from the red, the wave-lengths of the spectrum were on the whole at the highest temperature smaller than ever before or after. In this period the rays of short wave-lengths obtained more and more importance compared with the long-wave ones, ultimately even more than they have in the present condition of the Sun. The upper atmospheric layers were more heated at the time than before, and air masses charged with great quantities of entropy in equatorial regions and capable of radiation were now carried to high latitudes by the general circulation of the atmosphere operating especially powerfully in winter; they thus contributed greatly to the more uniform distribution of the heat over the earth, in the way as has been shown for the present time especially by EMBDEN. This mechanism must have been more powerful than at present on account of the greater "solar constant", in consequence of which a much more uniform climate must have prevailed over the whole Earth, at the same time the differences of temperature between high and low were much smaller than before, and in general the highlands could not become sufficiently cold for accumulation of ice.

But in the dwarf phase the temperature fell and the maximum of energy in the spectrum was displaced in the direction towards the greater wave-lengths. At the same time the total intensity of radiation, the "solar constant", decreased, and ultimately the present condition of a dwarf star which is in the middle of its *G*-stage, was reached. At this maximum of the giant phase a new epoch in the Sun's life does, therefore, really start. The effect of the low temperature on the intensity of radiation has no longer been cancelled since then by certain (insufficiently known) factors, which kept the intensity of radiation equal in the giant phase, and this while the heating of the upper atmospheric layers and the diminution of the want of uniformity in the distribution of the heat over the Earth caused by it, decreases. If this dwarf period is assumed to run parallel with the Neozoic period, it becomes comprehensible that climatic zones began to take definite form, and that at last the whole Earth got into a really miothermal condition with real general glacial periods.

When this view is held, great revolutions in the biosphere, the causes of which remain else perfectly unaccountable, are still more easily accounted for than in the light of the earlier views about the evolution

of the Sun. Already shortly after the beginning of the Cretaceous period, i.e., according to the synchronism assumed, still before the turning-point in this evolution, the new epoch of the vegetable world sets in, in which the Angiospermal leaf trees predominate, which in contrast to the Mesozoic Gymnospermal flora, which was then for the greater part dying out, possess a very great total leaf-surface. This great revolution in the vegetable world may now be considered as an adaptation to the quantity of red radiation, which was then becoming minimum. For it is this radiation, to which the principal absorption band of the chlorophyl corresponds, that chiefly brings about the carbonic acid assimilation at the slight light intensity under which the leaf operates according to WIESNER's researches. It is also available already in the early morning and still late in the evening. The chlorophyl of this time is evidently the same green colouring matter as in the oldest carbonic-acid assimilating plants.

The greatest revolution in the animal world occurs somewhat later. The largest forms of the class of Reptiles, a number of orders, die out at the end of the Mesozoic era. This is accompanied at the beginning of the Neozoic era by the rapid and rich development of the class of Mammals, which was only represented by a few small, scarcely changing forms from the Triassic period to the end of the Cretaceous period. In fact the predominance in the animal world passes from the Reptiles to the Mammals. The Neozoic period is the Age of Mammals, as the Mesozoic period was the Age of Reptiles. It is natural to seek a connection between this revolution and the general diminution of heat in the high latitudes starting at the turning-point of the Sun's evolution. Large Reptiles, being animals entirely dependent on the heat of their surroundings, could no longer in general exist then at high latitude. Mammals, on the other hand are in a high degree independent of the temperature of their surroundings on account of their own heat. This class could, therefore, not but occupy the places in the biosphere left vacant by the extinct Reptiles, as we actually see in many convergent developments.

The new stellar evolution-theory thus throws a clear light on some of the most important problems met with in the investigation of the Earth's crust.

May the discussed, well established geological facts contribute to the further development of this theory!

Microbiology. — "*The catalytic transference of hydrogen as the basis of the chemistry of dissimilation processes.*" By A. J. KLUYVER and H. J. L. DONKER. (Communicated by Prof. G. VAN ITERSON Jr.).

(Communicated at the meeting of February 28, 1925).

§ 1. *Introduction.*

As far back as 1876 PASTEUR¹⁾ expressed the opinion, that the fermentation processes of anaerobic organisms must be considered as a substitute for the respiratory process of aerobic organisms. Later researches have convincingly proved the correctness of this view. It appeared from these researches that the significance of both fermentation and respiration lies in the fulfilment of the energetic requirements of the living cell, for which reason both processes can be collected under the general term: dissimilation processes. In addition it was shown, that the similarity in physiological function expressed itself also in the chemical reactions brought about. Numerous investigations have made it in a high degree probable, that when sugar functions as substrate of respiration, with aerobic organisms, both animal and vegetable, as a rule the free oxygen intervenes only after the sugar has undergone an anaerobic transformation.²⁾

Although the discovery of the anaerobic phase in the respiration process has removed the contrast between the processes of oxidative and fermentative dissimilation of sugar to a remarkable extent, still this does not take away the gulf still existing between these two ways of providing energy, as long as the final phases apparently differ so much.

Here and there in more recent literature some remarks are already to be found which also point to the similarity of certain partial changes in the *aerobic* phase of respiration and some reactions occurring in fermentation. It is the aim of this communication to demonstrate that in reality the same chemical process lies at the basis of both aerobic and anaerobic respiration processes.

§ 2. *The chemistry of the oxidation processes in aerobic respiration.*

With a view to subsequent considerations it is desirable first of all to

¹⁾ L. PASTEUR, Etudes sur la bière, Paris 1876, pag. 229 et seq.

²⁾ Reference may be made in this connection to: O. MEYERHOF, Ueber den Zusammenhang von Atmung und Gärung, Die Naturwissenschaften vol. 7, p. 253, (1919); also: O. MEYERHOF, Chemical Dynamics of Life Phenomena, Philadelphia, 1924, Chapter III and to: S. KOSTYTSCHEW, Pflanzenatmung, Berlin, 1924.

study more closely the chemistry of the oxidation processes occurring in aerobic respiration. As is well known, these are oxidations which do not proceed of their own accord at ordinary temperatures and which take place in the organism under the catalytic influence of the living protoplasm of the cells. It is obvious that biologists have tried to get a better insight into the mechanism of this catalysis. A number of investigators are of the opinion that the action of the living cell consists before all of an activation of the oxygen necessary for combustion. Opposed to this, a theory has been put forward by H. WIELAND, according to which the catalytic action of the protoplasm will depend on an activation — eventually after a preliminary hydration — of hydrogen atoms present in the substrate, which atoms in this active state are then able to combine with the oxygen.¹⁾

WIELAND finds strong support for this opinion in his researches on the catalytic oxidation of organic compounds under the influence of inorganic catalysts such as palladium black. With the aid of this catalyst WIELAND was able to oxidise alcohol to acetaldehyde and the latter in the presence of moisture to acetic acid. That we have to do here firstly with a hydrogen removing action of the catalyst, is made very acceptable, because the oxygen used for the oxidation can be quite successfully replaced by other so-called hydrogen acceptors such as methylene blue or quinone. Besides this the hydrogen activating action of the catalyst is especially evident from the fact that in the absence of any hydrogen acceptor the splitting off of hydrogen can be established without doubt. By showing that acetic acid bacteria are able to oxidise alcohol to acetic acid by making use of methylene blue instead of oxygen, WIELAND extended his dehydrogenation theory to the chemistry of biological oxidations.

In the meantime O. WARBURG has advanced quite another theory on the chemistry of the oxidation processes in aerobic respiration based upon an extensive series of extremely important experiments.²⁾ In these investigations WARBURG showed that traces of iron present in an unknown organic combination are able to transfer catalytically free oxygen to a number of substances, amongst which several biochemical oxidation substrates are to be found. It is easily to be understood that WARBURG wants also to ascribe the catalytic action in the respiratory process to iron, which element is always present in the living cell. A further proof of the correctness of this view is seen by WARBURG in the fact that hydrocyanic acid inactivates the oxidative action both of the „carbon

¹⁾ See: H. WIELAND, *Ergebnisse der Physiologie*, vol. 20, pag. 477, (1922); *idem* *Ber.* vol. 55, p. 639, (1922) and also WIELAND's Synopsis in OPPENHEIMER's „*Handbuch der Biochemie*“ 2nd Ed., Jena, 1923, vol. II, p. 252.

²⁾ Compare: O. WARBURG, *Biochem. Zeitschr.* vol. 119, p. 134, (1921); *ibid.* vol. 136, p. 266, (1923); *ibid.* vol. 142, p. 518, (1924); *ibid.* vol. 145, p. 461, (1924); *ibid.* vol. 152, pag. 479, (1924).

model" and of the living cell in stoichiometric relation to the iron present.

WARBURG criticizes WIELAND's theory of hydrogen activation very strongly, as may appear from his statement: „Da es keinen Versuch gibt, der die Theorie begründet und keine Konsequenz der Theorie die zutrifft, so soll sie in der Folge nicht mehr berücksichtigt werden."

Lack of space forbids us here to enter into the polemics carried on in various places by WARBURG and WIELAND. We will content ourselves by giving as our opinion that both theories in their present mode of representation are untenable, yet on the other hand both contain elements with the help of which the observed phenomena can be explained in a completely satisfactory way.¹⁾ The experiments of WARBURG make it most highly probable that in biological oxidations molecular oxygen is intermediately attached to an organic iron compound by which means the oxygen is converted into an active state.²⁾ However, the opinion of WARBURG, that oxygen taken up by the iron compound should be able to oxidise the oxidation substrate straight away and that the catalytically acting iron compounds should be the only agents acting in respiration, is not in agreement with the facts.

Against this, among many arguments, is the replaceability of molecular oxygen by reducible substances like methylene blue or quinone, in which case the living cell is likewise indispensable as a catalyst and the catalysis is possible without the cooperation of an iron compound, since the process is insensible to cyanides. Further the selective action of the living cell towards different oxidation substrates cannot be easily brought in agreement with WARBURG's theory.

On the other hand, if we assume with WIELAND that the action of living protoplasm as a catalyst in the respiratory process consists of a dehydrogenation of the respiration substrate and a transference of the activated hydrogen to a hydrogen acceptor, then the observed phenomena find an easy explanation, if we also introduce the secondary hypothesis, that in opposition with other acceptors, free oxygen can only act as a hydrogen acceptor after combination with iron.

The theory of the hydrogen activating action of protoplasm finds its strongest support in the fact, that — as will be seen below — it puts us in a position to obtain an insight into the chemistry of anaerobic dissimilation processes, by which the apparently essential difference in the chemistry of aerobic and anaerobic dissimilation processes is reduced to a gradual one.

1) After this communication was in the press, it came to our notice that this opinion was expressed earlier and made probable on experimental grounds by A. V. SCENT-GYÖRGYI. See: Biochem. Zeitschr. vol. 150, p. 195, (1924). [Note added during correction].

2) The earlier well-known researches of ENGLER and WEISZBERG on the autoxidation of various organic substances, in which it was shown conclusively that molecular oxygen reacts in the first instance only with the formation of moloxides, supports this view.

§ 3. *The chemistry of fermentative dissimilation processes.*

As we have set forth in a previous communication¹⁾, it appears that on closer examination the fermentative sugar dissimilation processes of microbes may be reduced to a number of coupled dehydrogenation and hydrogenation reactions along with intramolecular changes and condensation reactions.

We will now fix our attention on the first mentioned type of reaction which can be brought back to a catalytic transference of hydrogen.

In the paper mentioned above we were satisfied in giving a representation as if the dehydrogenation simply existed in the formation of a compound of protoplasm and hydrogen from which the protoplasm was regenerated either spontaneously or by the transference of the hydrogen to other compounds (hydrogenation). Meanwhile this conception is too simple and it is necessary to consider this catalytic process more particularly.

We may suppose, that during the first part of the catalysis: the dehydrogenation, the protoplasm exerts an influence on the substrate, leading to an alteration in the latter substance, which is termed by BÖESEKEN in his discussions on catalysis²⁾ as "dislocation".

The consequence of this alteration is, that one or more hydrogen atoms present in the substrate become less firmly bound, or in other words: become activated.

This dislocation is undoubtedly a result of the chemical affinity of the catalyst for the dehydrogenation substrate or more precisely for the atoms present in this substrate.³⁾ Since a portion of the affinities of these atoms is saturated by the affinities of the catalyst the bonds between the atoms in the molecule are weakened.

We now have to consider how this dislocation leads in certain cases to an activation of hydrogen. Therefore it should be pointed out, that undoubtedly the affinity of the protoplasm for the dehydrogenation substrate may be brought back more especially to the affinity of the protoplasm for the hydrogen and oxygen atoms of the substrate. It must be understood that the affinities for hydrogen and oxygen are not independent properties, but that these properties are so connected that a large affinity for oxygen always means a small affinity for hydrogen and vice versa, as is also shown in the behaviour of metals towards these elements.

That an affinity of the protoplasm for hydrogen can give rise to an activation of the hydrogen atoms present in the substrate can be illustrated as follows. The saturation of a part of the affinity of the hydrogen by that of the catalyst, which in itself is unsaturated, will have in con-

¹⁾ These Proceedings vol. 28, p. 297, (1925).

²⁾ Compare e. g.: J. BÖESEKEN, These Proceedings, vol. 25, p. 210, (1922).

³⁾ Compare also: H. J. PRINS, *Bijdrage tot de kennis der katalyse*, Proefschrift Delft 1912 and „Over het verband tusschen katalyse en affiniteit“, *Chemisch Weekblad*, vol. 14, p. 63, (1917).

sequence, that the hydrogen remains bound to the substrate rest with a smaller affinity and so this rest will be brought to a state of unsaturation. Meanwhile this condition has the immediate result that the affinity set free tries to neutralize itself somewhere else in the molecule. As this tendency is more or less fully satisfied, or in other words in proportion as more definite translation of atoms in the molecule occurs, the hydrogen will remain bound with a smaller affinity to the rest of the molecule, which means activation. In the extreme case this will lead to the transformation of the remainder of the molecule into a completely saturated compound whereby the hydrogen will be completely liberated by this remainder. In this connection it is to be borne in mind that the amount of hydrogen activation is at the same time dependent on the affinity with which the protoplasm combines with the hydrogen. If this last mentioned affinity is too small only a small activation of hydrogen will occur because the hydrogen remains too firmly attached to the rest of the molecule; if the affinity in question is too big, there is neither an optimum activation, because the hydrogen is now fixed firmly, it is true no longer to the rest of the molecule, but to the protoplasm. In this case, as PRINS remarks, the catalyst as a catalyst exceeds its aim.

Hence it is obvious that the optimum hydrogen activation in different substrates will be smaller in proportion as the hydrogen, which is activated, was bound more firmly in the substrate, while, to obtain the optimum activation a greater affinity of protoplasm for hydrogen is necessary. On the other hand this brings along with it, that a protoplasm with relatively small affinity for hydrogen will be able to activate hydrogen only from dehydrogenation substrates with relatively weakly bound hydrogen, and yet in that case the resulting activation will be much larger than in the case of hydrogen activation from such a substrate under the influence of a protoplasm with a greater affinity for hydrogen.

Meanwhile not only can the activation of hydrogen be the result of a predominant affinity of protoplasm for hydrogen, but the affinity of protoplasm for oxygen may similarly give rise to hydrogen activation. This can be illustrated as follows. Let us consider firstly those dehydrogenation substrates in which the activated hydrogen is in a hydroxyl group. In this case, on the grounds of similar considerations as set forth above, it will be seen that saturation of a portion of the affinity of the oxygen of the hydroxyl group by that of the unsaturated catalyst, will have the consequence, that the oxygen is combined with hydrogen with a smaller affinity, or in other words, the hydrogen will be activated. If now the extreme case occurs, where the remainder of the molecule completely releases the hydrogen atom, these atoms of hydrogen are set free and combine to gaseous hydrogen, in contrary to what is the case if the activation is caused by the affinity of protoplasm for hydrogen.

Now it still remains for us to explain how the affinity of the protoplasm for oxygen can lead to the result that in oxygen containing dehydrogenation substrates other hydrogen atoms than those, which are situated in hydroxyl groups, are activated. As the protoplasm grasps a part of the affinity of the oxygen there will be a weakening of the bond between the oxygen and the remainder of the molecule, and so the atom of this remainder to which the oxygen is bound will become unsaturated and will try to compensate the loss by taking up affinity from some other part of the molecule. In consequence of this there can be activation of hydrogen somewhere else in the molecule ¹⁾.

It will be clear that, at any rate in oxygen containing dehydrogenation substrates, the activation of hydrogen will always be the result of both the affinity of the protoplasm for hydrogen and that for oxygen. Both influences will act supplementary; yet since a large affinity for hydrogen always brings along with it a small affinity for oxygen and vice versa, as a rule one will have to do only with one of these factors ²⁾.

Considering now the second part of the process of the catalytic transference of hydrogen, evidently only these substances lend themselves to act as hydrogen acceptors which are more or less easily reducible. It will be quite clear that the protoplasm will also take up (partially) affinities of the hydrogen or oxygen atoms of the molecule acting as a hydrogen acceptor. As a sequence, centres of unsaturation will be produced in the part of the molecule which binds these atoms, leading to an activation of the acceptor, which increases the tendency for hydrogenation.

If, and with what velocity, a particular hydrogen transference will take place, is exclusively dependent on the reduction tendency of the activated hydrogen acceptor, and on the degree of hydrogen activation in the dehydrogenation substrate, which activation — as we saw above — is in its turn a function of the strength of the bond between the hydrogen to be activated and the dehydrogenation substrate, and of the degree of affinity of the protoplasm for hydrogen and oxygen respectively.

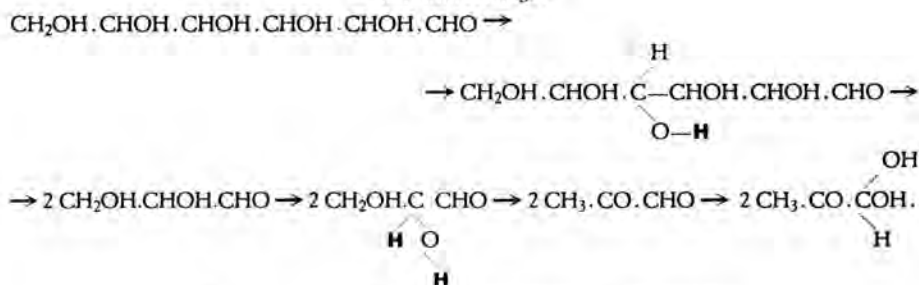
Let us now direct attention to the intramolecular changes and condensation reactions mentioned at the beginning of this paragraph. A closer examination shows that also these parts of the chemistry of fermentative dissimilation processes are in reality nothing but changes in which hydrogen is catalytically transferred. To elucidate this view we may refer in the first place to the following scheme.

¹⁾ This idea is in agreement with the views of H. J. PRINS, who describes in his study „The Mechanism of Reduction“ *Rec. trav. chim.* vol. 42. p. 473, (1923), how the affinity of a catalyst for oxygen can lead to the activation of hydrogen. Compare also § 4 p. 617 of this communication.

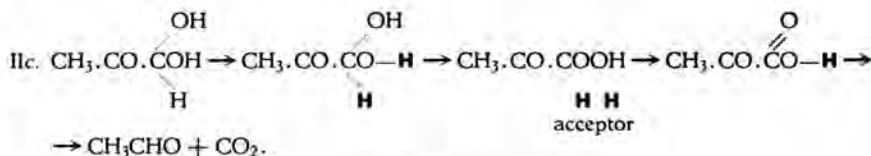
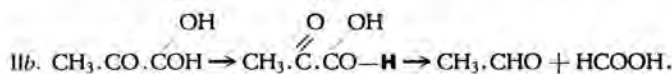
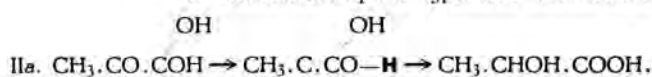
²⁾ An analogy of this situation is found in the hydrolysis of esters which is accelerated by both hydrogen ions and hydroxyl ions. In an acid medium only the action of the former ions, in an alkaline medium only that of the latter ions, is of practical importance.

SCHEME 1)

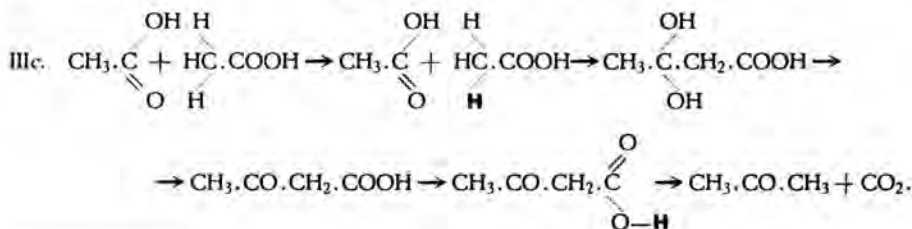
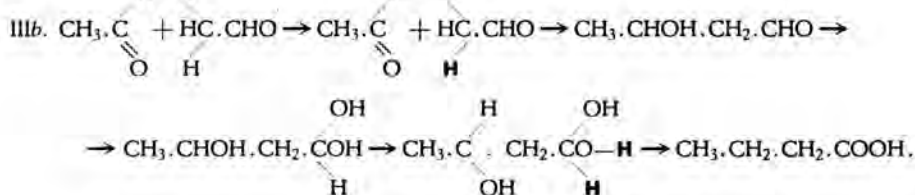
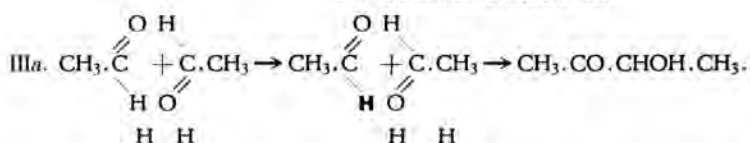
I. Initial change.



II. Conversions of the hypothetical intermediate product.



III. Condensation reactions.



1) This scheme gives the reactions taken under the same headings in Table II of our paper cited previously. Only it must be pointed out, that the reaction given under IIc has been newly added, which has to do with note 4 p. 306 of the previous paper.

An **H** printed in heavy type denotes an activated hydrogen atom.

As follows directly from this the particular intramolecular transformations are to be explained by assuming that the protoplasm exerts an activating influence on hydrogen atoms in the reacting substances. This dislocation of the molecule brings in its train a displacement of the affinities in the remaining part of the molecule, leading to the formation of a centre of unsaturation elsewhere in this molecule.

This centre will have the inclination to attract the activated hydrogen to itself or in other words to act as a hydrogen acceptor. In most cases when the hydrogen is transferred in this way, it leads to a rupture of the molecule and in others only to the transmigration of hydrogen and to consequent further changes of affinity within the molecule.

The peculiarity of this type of coupled dehydrogenation and hydrogenation is found in the fact that it is in a much less degree sensitive to an alteration in the affinity of the protoplasm for hydrogen or oxygen respectively. While in intermolecular transference of hydrogen a greater affinity of the protoplasm than the optimum has an adverse effect on the catalysis, as set out above, this is the case to a much smaller extent in intramolecular transference of hydrogen, because a protoplasm with greater affinity certainly fixes hydrogen to itself more firmly, yet on the other hand this stronger combination also brings along with it a more intensive unsaturation of the remainder of the molecule, which in this particular type of reactions itself acts as hydrogen acceptor, or in other words: simultaneous powerful activation of the acceptor takes place.

Finally it appears from the scheme given that also the condensation reactions can be reduced to the catalytic transference of hydrogen. Here the activated hydrogen is accepted by a second molecule of the same substance, which always contains an unsaturated group, while the affinities set free in such a molecule lead to the production of a new C—C bond.

Though we have limited ourselves here to a consideration of the fermentative sugar dissimilation processes of microbes, we will now indicate that the catalytic transference of hydrogen apparently also is at the basis of the chemistry of the fermentative sugar dissimilation processes of higher organisms. Also it is found again in dissimilation processes in which substances other than sugars form the substrate.¹⁾

§ 4. *The aerobic and anaerobic dissimilation processes as a function of the affinity of the living protoplasm for hydrogen.*

While it appears from the previous paragraph that the catalytic trans-

¹⁾ In this connection it may be pointed out in particular, that the process of fermentative dissimilation of amino acids by bacteria of the *Proteus*-group elucidated by NAWIASKY readily fits into the framework of the catalytic transference of hydrogen. See: Archiv für Hygiene, vol. 66, p. 209, (1908).

ference of hydrogen forms the nucleus of all fermentative dissimilation processes, we saw in § 2, that the oxidation processes which form the characteristic element of aerobic respiration, can also be made understandable with the assumption of such a transference. Considering the incontestable fact of the activation of hydrogen in a number of anaerobic dissimilation processes (evolution of gaseous hydrogen), the corresponding explanation of aerobic dissimilation processes finds its most powerful support in the unmistakable gradual passage of aerobic and anaerobic modes of life in each other. We will only refer here to the extremely numerous micro-organisms which in the absence of free oxygen provide for their energy requirements by a fermentation process, yet which in the presence of free oxygen derive the necessary energy from oxidative processes, which proceed with the absorption of oxygen.

We then come to the conclusion that the whole of the dissimilation processes of aerobic as well as anaerobic organisms in all their diversity may be brought back to the catalytic transference of hydrogen under the influence of the protoplasm present in these organisms ¹⁾. In this way then the observed diversity in dissimilation reactions is only a consequence, following logically from the laws of chemical catalysis, of the gradual variation in affinity of the different kinds of protoplasm for hydrogen.

We shall elucidate this view further below, where we limit ourselves however to a very short discussion of those dissimilation processes in which a hexose occurs as a substrate.

I. Aerobic organisms with strong oxidative powers.

Examples: several kinds of moulds and acetic acid bacteria. The protoplasm of these organisms is characterised by a very great affinity for hydrogen. When oxygen is present as a hydrogen acceptor, glucose undergoes a direct dehydrogenation and gluconic acid is formed. Under optimum conditions gluconic acid as a rule is not found as a metabolism product but following on this change there takes place a whole series of further dehydrogenations and finally water and carbonic acid are produced.

Besides oxygen only such other powerful hydrogen acceptors as methylene blue (WIELAND) appear to be effective.

II. Aerobic organisms with weaker oxidative powers.

Examples: higher plants, (muscular tissue of the) higher animals, many aerobic spore forming bacteria. The hydrogen affinity here is so much

¹⁾ In this connection it is well to remember a statement of T. THUNBERG (see for example: *Die Naturwissenschaften*, vol. 10, p. 417, 1922), who concluded after a closer discussion of aerobic respiration processes that „der Wasserstoff als das elementare, gemeinsame Brennmateriale der Zellen zu betrachten ist“.

smaller than the direct dehydrogenation of glucose with oxygen as hydrogen acceptor is not possible, yet instead of this intra-molecular dehydrogenation and hydrogenation occurs, which causes the sugar to break down into compounds of the C_3 -type. In the presence of sufficient oxygen the methylglyoxal formed will be dehydrogenated. Under anaerobic conditions the methylglyoxal is converted by muscular tissue of higher animals into lactic acid by an intramolecular change. The lactic acid can undergo further dehydrogenation if oxygen is re-introduced ¹⁾.

More or less the same situation is met with in the higher plants, in which however methylglyoxal, under anaerobic conditions, is converted chiefly in the same direction as in alcoholic fermentation.

Although in this group of organisms the affinity for hydrogen is already reduced so far that fermentative dissimilation under anaerobic conditions is very noticeable, the changes brought about do not quantitatively provide for the need of energy, which need is normally met with by the larger energetic effect of the transference of hydrogen to oxygen.

III. Organisms which cause alcoholic fermentation.

Examples: alcohol yeasts, moulds such as *Mucor racemosus*. The affinity for hydrogen of these organisms is again smaller, so that all the methylglyoxal can be dehydrogenated to pyruvic acid with relatively weaker hydrogen acceptors. The pyruvic acid produced then undergoes an intramolecular change into carbonic acid and acetaldehyde and the latter then acts further as a hydrogen acceptor in the process of the dehydrogenation of methylglyoxal ²⁾.

In all the groups discussed below, the affinity for hydrogen is too small to make a dehydrogenation of methylglyoxal to pyruvic acid possible with the relatively weak acceptors formed by the splitting up of the sugar. In the place of this change an intramolecular rearrangement takes place in which methylglyoxal is converted into formic acid and

¹⁾ The fact that glycogen is converted into lactic acid by muscular contraction, and that this acid again disappears on the restoration of the oxygen supply, (see for example O. MEYERHOF, *Die Energieumwandlungen im Muskel. Die Naturwissenschaften*, vol. 12., p. 181, 1924) may not be considered as a proof of the idea — as many others including MEYERHOF are inclined to do — that also in the „Ruheatmung“ i.e. under conditions of more complete aeration, lactic acid will be produced intermediately from glycogen. On the contrary under these conditions, in all probability, direct dehydrogenation with oxygen as the acceptor will occur for the greater part with the methylglyoxal or with one of the other preceding intermediate products in the formation of lactic acid under anaerobic conditions.

²⁾ Meanwhile, as long as acetaldehyde is not yet formed, this view requires an introductory acceptor. Free oxygen will occur as such in most cases. Herein we see an explanation of the fact that yeast — contrary to the organisms treated below — is unable to lead a perfectly anaerobic existence, a feature, which is always taken into account in all fermentation industries, as appears from the preliminary aeration of the mash before fermentation.

acetaldehyde. Along with this there always remains the possibility of the conversion of methylglyoxal into lactic acid. Both intramolecular dehydrogenations and hydrogenations are, because of reasons given previously, to a large extent insensitive to a decrease in the hydrogen affinity of the protoplasm.

IV. The bacteria of the colon-group.

The hydrogen affinity is again smaller than in group III and decreases in the order of the three sub-groups considered.

a. Sub-group of *B. typhosum*. Lactic acid, formic acid and acetaldehyde are formed in the way indicated above. The hydrogen affinity is too large, however, to allow of the formic acid being decomposed catalytically without an acceptor. The acetaldehyde is not suitable for this purpose, because it itself undergoes a powerful dehydrogenation, in which hydrogen is transferred to a second molecule, which leads to the formation of alcohol and acetic acid.

b. Sub-group of *B. coli*. In many respects the situation here is the same; only the somewhat smaller affinity for hydrogen makes the catalytic decomposition of formic acid into carbon dioxide and free hydrogen possible. Besides the acetaldehyde is dehydrogenated to a smaller extent, so that this substance can act more or less as a hydrogen acceptor in the dehydrogenation of formic acid. Also the dehydrogenation of acetic to succinic acid occurs to some extent.

c. Sub-group of *B. aerogenes*. The formation of lactic acid is here pushed into the background, which doubtless depends on the effective way in which the acetaldehyde disappears from the fermentation medium. This is a consequence of a still smaller affinity for hydrogen, which certainly brings along with it a less rapid dehydrogenation to acetic acid, but which is just the optimum for the incomplete dehydrogenation of the acetaldehyde, which leads to the formation of acetylmethylcarbinol. Both this carbinol and a portion of the acetaldehyde then act as acceptors for the more activated hydrogen formed in the catalytic decomposition of formic acid, which situation leads to the formation of 2:3 butylene glycol and ethyl alcohol.

V. The group of true lactic acid bacteria.

The affinity for hydrogen is again smaller than with the organisms of the foregoing group. While in the previous groups the hydrogen affinity was always so large that the corresponding oxygen affinity, although increasing from group to group, was of no account as regards the activation of hydrogen, the hydrogen affinity in the true lactic acid bacteria is so much smaller that in this case the oxygen affinity is also of importance for the activation of hydrogen. We consider that a clear indication of this may be seen in the fact, that with this group we meet

for the first time with organisms which, contrary to all¹⁾ organisms belonging to the previous groups, lack the power of bringing about the catalytic decomposition of hydrogen peroxide into water and free oxygen. This decomposition of hydrogen peroxide is, as WIELAND also remarks, undoubtedly due to a catalytic transference of hydrogen from one molecule to a second molecule. While now this investigator similarly accepts the general opinion, that the reaction in question proceeds under the influence of an independent enzyme: catalase, we must point out here that there is every reason for seeing in the reaction in question only a special manifestation of the general agent bringing about dissimilation. With the so-called catalase-negative organisms the catalytic decomposition of hydrogen peroxide will not take place for the simple reason that in this case the oxygen of the hydrogen peroxide remains fixed on the protoplasm. That the protoplasm in these organisms does indeed possess a noticeable affinity for oxygen, appears conclusively from the fact that all these organisms are characterised by a smaller or greater sensitivity towards free oxygen, which sensitivity in catalase-positive organisms is entirely lacking.

a. Sub-group of the heterofermentative lactic acid bacteria. The considerably decreased hydrogen affinity on the one hand and the relatively small oxygen affinity on the other hand, cause even easily dehydrogenated compounds as formic acid and acetaldehyde to be dislocated to only a small degree. This appears from the fact that free hydrogen is scarcely if at all met with among the dissimilation products and that the hydrogen from the compounds mentioned above is only transferred to acceptors. In the fermentation of glucose acetaldehyde functions especially as acceptor, while in the fermentation of laevulose this substrate itself is a good acceptor. Without doubt this depends on the activation of the laevulose caused by the noticeable oxygen affinity. The small power of dehydrogenation leads further to the pronounced occurrence of lactic acid formation, because the hydrogen of the methylglyoxal is insufficiently activated to bring about the rapid fission into formic acid and acetaldehyde.

b. Sub-group of the homofermentative lactic acid bacteria. In this group the dehydrogenation powers are still smaller, so that here practically only lactic acid is formed.

VI. The group of propionic acid bacteria.²⁾

The hydrogen affinity is again smaller than in the previous group and

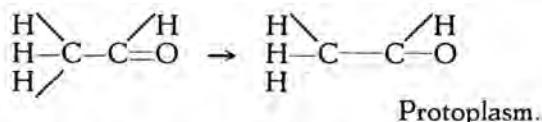
¹⁾ After the above had been printed a species of acetic acid bacteria was isolated which so far appears to be unable to bring about the catalytic decomposition of hydrogen peroxide. Also in the meantime a paper by KNORR [Münchener medizin. Wochenschrift p. 1381, (1923)] reached us, according to which the "echte Ruhrbazillen" which are generally assigned to the *Colongroup*, are quite catalase negative. On account of this a closer investigation will be instituted on the exceptions of a rule which appears to hold in hundreds of cases.

²⁾ It must be stated that the placing of the propionic acid bacteria between our groups

consequently the oxygen affinity becomes more pronounced. On the one side this again leads to a somewhat increased dehydrogenating power which among many things is evident from the reoccurrence of the dehydrogenation of acetic acid to succinic acid. On the other hand the oxygen affinity gives rise to a noticeably more powerful acceptor activation, even to such a degree that lactic acid functions as an acceptor and is converted into propionic acid.

VII. *The group of butyl alcohol and butyric acid bacteria.*

a. Sub-group of butyl alcohol bacteria. The hydrogen affinity has now become so small that it has no longer any significance for hydrogen activation. Meanwhile the dehydrogenating action has again become considerably greater on account of the considerably increased oxygen affinity, which also brings along with it a powerful activation of the acceptor. The considerable affinity for oxygen shows itself very strikingly in the great sensitivity towards free oxygen, small quantities of which, as a rule, cause the death of the organism. The particular nature of the hydrogen activation caused by an affinity for oxygen appears from the fact that both in acetaldehyde and in acetic acid it is notably a hydrogen atom from the CH_3 -group which is especially activated. This leads to the condensations previously mentioned. The schematic representation below illustrates this for acetaldehyde:



The particularly powerful acceptor activation is evident from the power of reducing products such as butyric and propionic acids, which are only reduced with great difficulty in the ordinary ways.

b. Sub-group of butyric acid bacteria. This sub-group differs from the foregoing only because the oxygen affinity is somewhat greater, which leads to a still greater sensitivity towards oxygen. Consequently also the hydrogen activation is again somewhat greater. The reason, that practically all transference of hydrogen on acids as acceptor remains in abeyance, is the greater acid-sensitivity, which causes the organisms to die off before the concentration of the acceptors is sufficiently high to cause any appreciable transference of hydrogen. These reasons combined lead to the result that only carbon dioxide, hydrogen, acetic acid and butyric acid occur as chief dissimilation products.

V and VII is at first quite speculative and is based only on the incomplete data which can be found regarding this group of bacteria in literature. If the observation of SHERMAN [Journal of Bacteriology Vol. 6, p. 379, (1921)], according to which the propionic acid bacteria he examined showed a strong catalase reaction, is confirmed, a revision of this grouping will be necessary.

§ 5. *Final considerations.*

While in the previous section we have limited ourselves to showing how by the help of the theory of activation and the catalytic transference of hydrogen, an insight may be obtained into the various dissimilation processes in which a sugar functions as substrate, it may be pointed out that this is equally the case for all other dissimilation processes. In this connexion we mention only the dissimilation of denitrifying, sulphate reducing, methane producing and amino acid fermenting microbes.

A logical consequence of our theory is that it is no longer necessary to have recourse to the assumption of a large number of separate enzymes to explain the partial reactions of the dissimilation process. In the light of the foregoing discussion it will be obvious that the changes which are ascribed to separate enzymes such as catalase¹⁾, reductase, zymase, lactozymase, alcoholoxidase, carboxylase, carboligase, glyoxalase, aldehydomutase, SCHARDINGER's enzyme etc., are actually only manifestations of a definite degree of affinity of the protoplasm for hydrogen. The question as to how far one will think of the affinity of protoplasm itself for hydrogen or of the action of a single hydrogen transferring enzyme, has no significance here.

Finally let it be expressly stated that while, in the previous sections, we have represented the affinity for hydrogen of the protoplasm of a definite organism as constant, this affinity in reality varies to a certain extent with the hydrogen ion concentration in the protoplasm. From a number of concordant examples we are of the opinion that we may conclude, that within the region of hydrogen ion concentrations, which are harmless for the organism, a decrease of the concentration brings about a decrease in the affinity of the protoplasm for hydrogen. In connexion with the fact that every dissimilation of sugar practically always goes parallel with the formation of acid, and on the other hand every dissimilation of the hydrolytic decomposition products of proteins gives rise to ammonia, organisms, which are more adapted to action on carbohydrates, have a region of development situated at higher hydrogen ion concentrations than organisms more suited for acting on protein decomposition products. From all this we may conclude, that the dissimilation of every living cell is determined only by the limits of the allowable hydrogen ion concentrations on the one hand and the affinity of the protoplasm for hydrogen within these limits on the other.

We intend to return to the above considerations elsewhere in greater detail.

Delft, February 1925.

¹⁾ Here we mean only the insoluble catalase, the so called α -catalase of LÖW.

Ophthalmology. — *"On Enlargement of the "Optic Foramen".* By
Prof. J. VAN DER HOEVE.

(Communicated at the meeting of April 25, 1925).

In normal persons the size of the optic foramen shows only very little individual variations. WHITE's anatomic research showed that the diameters of the canalis opticus ranged from 4—6.5 m.m. GOALWIN's averages varied from 4.26 to 4.5 m.m.

My own observations are chiefly based on röntgenograms of the foramen.

The method of photographing the foramen opticum by Röntgen rays has first been suggested by RHESE. This author, who tried to find and actually did find in his method an excellent means to photograph the the accessory nasal cavities, did not realise himself the significance of his invention. It was A. DE KLEYN who pointed to the great use of this procedure for ophthalmology. In collaboration with STENVERS he slightly modified RHESE's method, so that the optic foramen and the fissura orbitalis superior could be observed more distinctly and these authors showed that in cases of accident: fractures, fissures and later on callus formation could be found in the bony environment of these holes.

Since the first announcement of their experience, nine years ago, I had Röntgen photos taken of the foramen opticum as often as opportunity offered. From the results of my rather extensive experience I learnt that at a distance of 75 c.m. from the Röntgentube to the photographic plate the diameter of the foramen varied from 4—6 m.m. A foramen of 6 m.m. looks a bit suspicious, one of more than 6 m.m. I consider to be decidedly too large.

The form of the foramen on the röntgenogram is perfectly circular, oval, or slightly angular. GOALWIN considers them as quadrants.

What we really see on the photographic plate, is not the foramen opticum, but a projection of the lumen of the canalis opticus. Obviously a wrong position of the patient's head may give a projection that is too small but not one that is too large. For this reason greater precaution should be exercised in diagnosing too small a foramen than an abnormally dilated one. If an abnormally large image is found on the röntgenogram, the foramen is certainly too large.

Of late I have given special attention to the possibility of an enlargement of the optic foramen, being convinced that it might occur just as well as an enlargement of the meatus auditivus internus sometimes will occur. Like the optic foramen the meatus is also an opening encircled

on all sides by bone which affords a passage for a nerve; tumours of the auditory nerve or its environment may enlarge this hole. The study of this enlargement on the röntgenogram is of great significance for the identification of these tumours.

The enlargement of the meatus auditivus internus is occasionally observed in RECKLINGHAUSEN's disease, in which pontile tumours (occurring most often bilaterally in this disease) may occasion deafness and dilatation of the inner auditory canal.

Now considering that this disease may also be attended with blindness or weak eyesight caused by atrophy of the optic nerve, I suspected that this blindness in some case might be attributed to tumours similar to those occurring along the auditory nerve or to diffuse neurofibromatosis of the optic nerve itself. Both processes might possibly engender dilatation of the optic nerve canal to such an extent, that it might be imaged on the röntgenogram.

The first patient that I examined to ascertain this, was blind at the right eye and had a markedly reduced visual acuity at the left eye. The application of Röntgen rays proved that the right optic foramen was far wider than normal, while the left optic foramen was much wider still. (See fig. *b*¹ and *b*² as compared with the normal optic foramen *a*).

An acute deterioration of the eyesight necessitated operation. It was performed by Prof. ZÄYER. We then observed that there were no definitely marked tumors in the foramen opticum, but that the two optic nerves were much thicker than normal, which was presumably owing to neurofibromatosis.

Prof. ZÄYER removed the roof of the optic canal and slit the dura mater, so that the optic nerve was relieved of pressure. The result was very satisfactory: visual acuity and field of vision improved considerably, and at the present time, two years after the operation, patient still enjoys a fairly good eyesight.

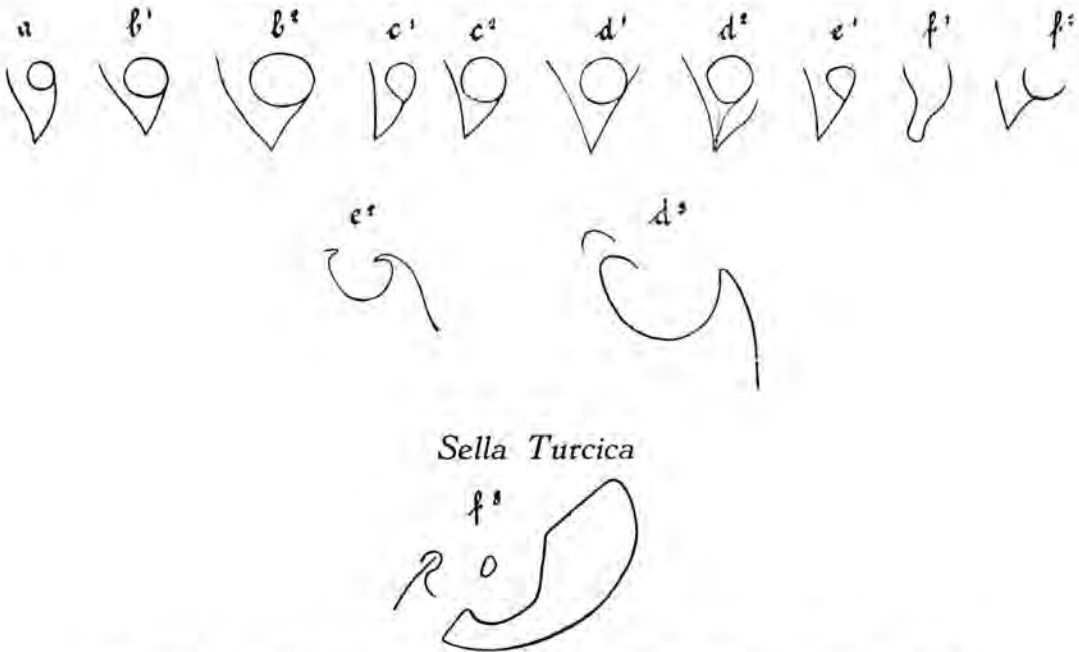
This, then, went to show that a long-continued swelling of the optic nerve can induce a marked widening of the foramina.

In another patient the widening was generated by a tumour growing out from the orbit towards the cranial cavity. When two years old this patient had been brought to me for glioma retinae of the right eye. At the time the parents objected to having the eye enucleated immediately. After ten months the child was brought to me again in a sorry plight; the eye was blind, excessively dilated, while it gave an impression as if there was tumourous mass also in the orbit. Being convinced that the optic nerve was affected, I had photos taken of the foramina. It appeared now that the diameter of the foramen at the diseased side equalled about twice that at the healthy side (fig. *c*¹ and *c*²). Besides this a small portion of the wall of the enlarged foramen opticum had been corroded.

After the whole orbit had been evacuated, it appeared that the optic

nerve had thickened considerably, so that the area of the section equalled about four times the normal surface. This goes to show that in young individuals a thickening of the optic nerve, which has originated from

Röntgen pictures of the Optic Foramen.



a. normal; b. enlargement by neurofibromatosis diffusa; c¹ normal and c² diseased side in glioma retinae. d. dilatations in hydrocephalus. e. normal condition in hydrocephalus; f. dilatation and destruction in glioma of the chiasm, all on the same scale.

a tumourous growth, can give rise to enormous dilatation of the optic foramen.

A third case tended to show that also tumours growing out from the cranial cavity towards the orbit can expand and affect the optic foramen. A female patient was brought to me from the neurological ward, because she had lost the visual acuity of both eyes in a short time. The left eye was still slightly sensible to light.

From the ophthalmoscopic picture I learnt that we had to do here with primary atrophy of the optic nerve as well as with choked disk. This led me to make the presumptive diagnosis glioma of the chiasm and the optic nerves, as recently described by MARTIN and CUSHING. In this case I expected a change of the sella turcica and incidentally also of the foramen opticum. As will be seen the röntgenogram really revealed a marked dilatation and an almost complete destruction of the sella turcica (fig. f³), while on the side of the eye that had still retained some perceptive power, the foramen opticum had merged into the fissura orbitalis superior (fig. f¹), and at the blind eye only the lower part of

the wall of the enlarged optic foramen was still present (fig. f^2). The line of the base of the skull was almost completely destroyed, which could also be seen on stereoscopic röntgenograms. During the printing of this article I observed a quite similar case in a less advanced stade.

Since it has been proved by the above that tumours, developed along the optic nerve, can induce dilatation of the foramen opticum, I suspected that mere overpressure in the fluid of the cranial cavity might generate also this dilatation; with a view to this I examined various cases of hydrocephalus.

One of them concerned a patient of 10 years of age. In this case I observed the dilatation, the sella turcica being considerably enlarged (d^3). Figs. d^1 and d^2 illustrate the enlargement of the foramen opticum, while the wall remained smooth.

Figs. e^1 and e^2 present a foramen and sella turcica of normal size in a child of 8 years, also with hydrocephalus. Further investigation will perhaps settle the question in what cases of hydrocephalus enlargement of the foramen opticum occurs and in what cases it does not.

It has been seen that the expansion is easily brought about in young patients. So long as the causative agent is confined to the sheaths of the optic nerve, the wall will retain its smoothness; as soon as the tumour affects also the environment of the optic nerve, there is a chance of the walls of the optic nerve-canal being corroded, as was shown in the cases of glioma retinae and glioma of the chiasm.

Various problems still remain unsolved, i.e. if the enlargement of the foramen opticum will also occur with other affections that cause overpressure in the skull of young patients, e.g. microcephalus through premature closure of the cranial sutures.

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Chemistry. — "On a Qualitative Resemblance between the Velocity of Hydration of Acid Anhydrides and the Velocity of Hydrolysis of Diacylperoxides". By Prof. J. BÖESEKEN and H. GELISSEN.

(Communicated at the meeting of May 30, 1925).

BRODIE ¹⁾, the discoverer of the organic peroxides, or more in particular of the acylperoxides (which are derivatives of H₂O₂ in which one or both H atoms have been replaced by an acyl rest) already found that they are decomposed by water into free acid and oxygen.

A considerable time later v. PECHMANN and VANINO ²⁾ observed that phtalylperoxide was comparatively rapidly changed into phtalic acid and hydrogen peroxide by alkalies and their carbonates.

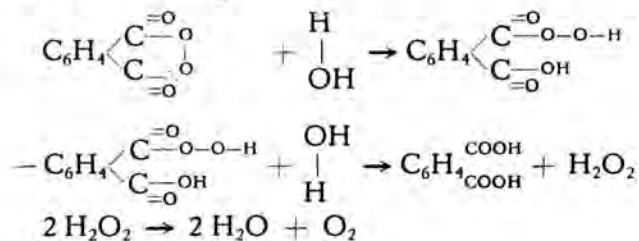
Neither BRODIE nor v. PECHMANN and VANINO entered any further into the mechanism of this decomposition.

VON BAEYER and VILLIGER ³⁾ found that phtalylperoxide, on careful treatment with alkali-hydroxides in the cold, first changes into the alkali-salt of phtalylmonoperacid. These investigators also observed that the two-sided substituted H₂O₂-derivatives by no means act rapidly oxidizing, but only become active when they have been converted into the one-sided substituted derivatives by hydrolysis ⁴⁾.

The difference in velocity of hydrolysis between acetylbenzoyl-, diacetyl-, and dibenzoyl-peroxide observed by these investigators, was no further accounted for by them.

From the fact that VON BAEYER observed the formation of hydrogen peroxide when the phtalylperoxide was heated with alkali-hydroxide, in connection with what precedes, follows the course of the reaction between diacylperoxides and water.

The reactions that take place when H₂O acts on phtalylperoxide, are in our opinion the following:



¹⁾ An. 1863. III Supl. 211.

²⁾ Ber. 27, 1511, 1894.

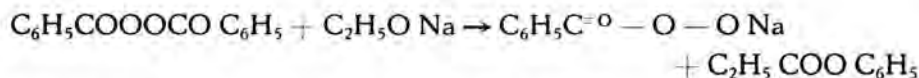
³⁾ Ber. 34, 765, 1901.

⁴⁾ The action of dibenzoyl- and acetylbenzoyl-peroxide on a solution of indigo-blue (disulphonic acid-indigo dissolved in H₂O is discoloured with formation of isatine) or on a KI solution is ascribed by v. BAEYER (Ber. 33, 1569, 1900) to the action of the peracid formed intermediately.

(Remark. The structure formula of the phthalylperoxide given here, was proved by us (see Chem. Weekblad 22, 187, 1925); we also point out at once that the splitting up takes place in the bond C—O and not in the bond O—O—).

VON BAEYER¹⁾ succeeded in converting benzoylperoxide, which can resist cold alkali, into benzoyl hydroperacid-Na and benzoic acid ethylester through careful saponification with sodium ethylate.

The reaction:



shows that on hydrolysis of the diacyl peroxides *not* the —O—O—bond is broken, but the —C^O=O bond, since in C₂H₅ONa not the —ONa group combines with a C₆H₅COO—part, but the Na combines with the C₆H₅COOO—part of the benzoyl peroxide-molecule, as one of us will show more in detail.

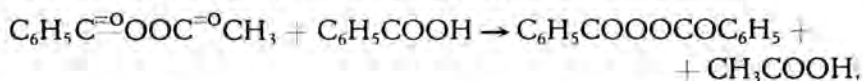
Through an aqueous alkali-solution VON BAEYER could change diacetyl peroxide into aceto peracid and acetic acid.

We shall see presently that the difference between benzoyl peroxide and acetyl peroxide towards aqueous alkalies consists simply in a difference in velocity of hydrolysis.

FREER and NOVY²⁾, who examined the oxidizing action and the behaviour towards certain bacteria of benzoyl acetyl- and of diacetyl peroxide, agreed with VON BAEYER that benzoylacetyl peroxide as such is no direct oxidizing substance.

They write: "Pure benzoylacetyl peroxid is not an oxidising substance, nor has it any odor, a fact which was also observed by BAEYER".

These investigators found further that on hydrolysis of benzoylacetyl peroxide in aqueous solution a precipitate of dibenzoylperoxide is formed, which they represent by the following equation:



(in other words the primary product of hydrolysis C₆H₅COOH of the benzoyl acetylperoxide acts on unchanged benzoylacetyl peroxide).

Also these investigators observed the insensibility of dibenzoylperoxide to water; for they write: "On the other hand, benzoylperoxid is difficultly soluble, does not undergo hydrolysis, has no oxidising action, and is wholly without effect upon bacteria".

Accordingly FREER and NOVY have entered again somewhat more deeply into the process of hydrolysis of the diacylperoxides, and on the ground of this they could furnish the proof that symmetrical acylperoxi-

¹⁾ Ber. 33, 1569, 1900.

²⁾ Am. 27, 161, 1901.

des are inert towards definite bacteria, whereas the peracids are strong poisons to these same bacteria.

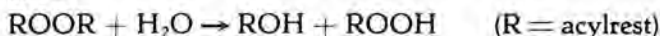
The hydrolysis of the diacylperoxides has been most successfully studied by CLOVER and RICHMOND ¹⁾.

These investigators came to the following conclusions:

1. Diacylperoxides are completely hydrolysed into acid and peracid by water.

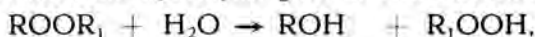
The duration of the reaction is dependent on the solubility in water and on the nature of the peroxide.

The reaction:



is *not* reversible according to these investigators, and proceeds therefore quantitatively in the direction towards the right.

In mixed peroxides the hydrolysis goes in two directions:



or



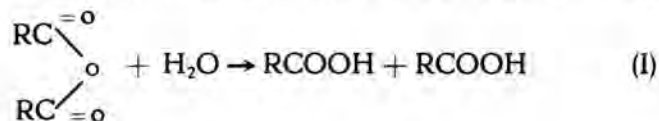
2. Peracids hydrolyse into acid and hydrogen peroxide.

According to CLOVER and RICHMOND this reaction is *not* reversible either; it proceeds more slowly than the hydrolysis of the diacylperoxides and is accelerated by acids.

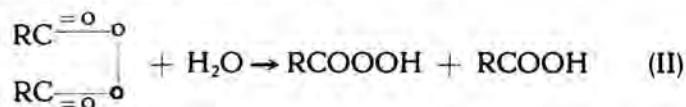
They found that a 5% solution of diacylperoxide was completely hydrolysed according to equation 1 in 24 hours, that buteric acid peroxide, and also crotonic acid peroxide, hydrolysed much more slowly, and that "with benzoic peroxide it is so slow as to be scarcely detected in the course of several days".

We shall discuss this difference in velocity of hydrolysis of these diacylperoxides more in detail later on, and only state now that C. and R. do not enter any further into this matter.

When we compare the reaction of hydration of the acid anhydrides ²⁾



and the reaction of hydrolysis of the diacylperoxides,



we observe:

¹⁾ Am. 29, 180, 1903.

²⁾ According to VERKADE (Diss. Delft) the two successive reactions for fatty acidanhydrides are;

Anhydride + H₂O → addition product;
addition product → 2 mol. acid.

1. that in both cases a C—O-bond is broken up through the action of the water,

2. that the reaction products are two acids in both cases,

3. that both I and II are accelerated through alkali hydroxides, carbonates, and bicarbonates, as was found by ORTON and JONES¹⁾ for the hydration of acid anhydrides, and by VON BAEYER (loc. cit.) for the hydrolysis of the diacylperoxides.

4. that both reactions are catalytically affected by acids, which was observed by CLOVER and RICHMOND (loc. cit. p. 184) for the diacylperoxides, and by ORTON and JONES (loc. cit. and Dissertatie VERKADE p. 17) for the hydration of the anhydrides.

These facts have led us:

I to consider the diacylperoxides as anhydrides of peracids and acids;

II to draw up the rule:

Diacylperoxides derived from acid anhydrides which have a small hydration constant, do not hydrolyse, or they hydrolyse exceedingly slowly.

This rule, which expresses a qualitative relation between the velocity of hydration of the acid anhydrides, and the velocity of hydrolysis of the diacylperoxides, enables us therefore to derive the properties of the diacylperoxide from those of the corresponding anhydride, in which it appears that the velocity of hydrolysis of the diacylperoxide is always smaller than that of the corresponding anhydride, which follows from a comparison of the reaction constants in question.

VERKADE (Diss. Delft, p. 56) found that the hydration reaction of the lower acid anhydrides (up to C₅) satisfies the equation of a mono-molecular reaction (excess of H₂O), and CLOVER and RICHMOND observed that the hydrolysis of the diacylperoxides likewise takes place according to the equation:

$$K = \frac{1}{t} \log. \frac{a}{a-x} \text{ hence also as a reaction of the first order.}$$

VERKADE observed that the velocity of hydration of the anhydrides of acetic acid, propionic acid, and butyric acid decreased from the left towards the right; it may be concluded from CLOVER and RICHMOND's investigations that the velocity of hydration of the peroxides of acetic acid, propionic acid, and butyric acid likewise greatly decreases from the left towards the right.

CLOVER and RICHMOND found two peroxides that do not hydrolyse at all, viz. crotonic acid peroxide and benzoylperoxide. About crotonic acidperoxide they say (loc. cit. p. 196). "The slowness with which it hydrolyses, however, renders it suitable for such study", and about benzoylperoxide "with benzoic peroxide it (i.e. the hydrolysis) is so slow as to be scarcely detected in the course of several days".

¹⁾ J. Chem. Soc. **101**, 1708, 1917.

Striking is the agreement in the behaviour of the corresponding acid anhydrides in question towards water resp. towards hydrolysing agents.

Of benzoic acid anhydride we find stated (V. MEYER and JACOBSON II 547). "Es ist sehr beständig gegen Wasser und wässrige Natronlauge", while VANINO (Handbuch II, 612) says that it "selbst gegen heisse Soda-lösung mäßig beständig ist", and it moreover follows from CLOVER and RICHMOND's researches that crotonic acid anhydride is *not* converted to crotonic acid by soda solution (p. 194 loc. cit.). We see from this that this agreement in velocity of hydration of the two anhydrides that are insensible to water corresponds to the velocity of hydrolysis of the peroxides that are likewise insensible to water: both velocities are very small. As was stated above, the velocity of hydrolysis of the diacylperoxides is smaller than the velocity of hydration of the anhydrides.

In order to show this agreement in velocity of hydration further we have made a few new diacyl peroxides, derived from acids whose anhydrides are insensible to water. These peroxides appeared likewise insensible to the action of water.

They are:

Cinnamoylperoxide. Melting point 144° C. (fine needles from acetone).

Phenylpropionic acid peroxide. Melting point $38^{\circ}.5$ (shiny leaflets from diluted alcohol).

Trichloracrylic acid peroxide. Melting point 49° C. (fine leaflets from ethylalcohol).

These peroxides are all as insensible to water as the corresponding anhydrides of the acids.

Inversely it is found that the diacylperoxides, in which the corresponding acid anhydrides are more easily hydrolysed than the acetic acid anhydride, become more and more sensible to water in the same succession.

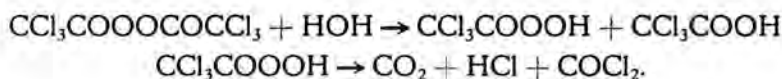
Acetic acid anhydride hydrates rapidly, the anhydrides of the chlorine substituted acetic acids are more sensible to water according as more chlorine has been substituted. Thus BUCKNEY and THORNSON¹⁾ say of trichloroacetic acid anhydride "der Körper geht bei Anwesenheit der geringsten Spur von Feuchtigkeit in die Säure über".

The analogy to the corresponding diacylperoxides is again great. The acetylperoxide is again completely hydrolysed in aqueous solution within 24 hours (CLOVER and RICHMOND loc. cit.). The monochloroacetylperoxide prepared by VANINO and UHLFELDE²⁾ is already decomposed when exposed to moist air; while trichloroacetylperoxide, which FICHTER³⁾ had fruitlessly tried to find, and which we had succeeded in preparing by the application of an artifice, lasts only a few minutes, and when exposed contrivance to air is among others converted to phosgene, probably according to the following reactions:

¹⁾ Ber. 10, 698, 1877.

²⁾ Ber. 33, 1043.

³⁾ Helv. 1923, 503.



The agreement found by us does not only hold for the diacylperoxides of the carbonic acids, but also for those of the sulphonic acids, at least for the only one known, benzene sulphonic acid peroxide.

This peroxide ¹⁾ is very unstable, does not dissolve in cold water, on account of which it can be washed in ice-water, but it gives a separation of iodine in a neutral iodine-iodine potassium solution, as a sign that it is rapidly hydrolysed.

Benzene sulphonic acid anhydride ²⁾ is likewise insoluble in water, but is very rapidly hydrolysed in aqueous solvents and by moist air.

As it is stated of some substituted sulphonic acid anhydrides, that they are very stable, this might be attributed to their exceedingly small solubility in water. If it should, however, appear that their velocity of hydrolysis is much smaller than that of the non-substituted sulphonic acid anhydride, a corresponding small velocity of reaction is to be expected in the substituted sulphonic acid peroxides.

Delft, May 1925.

¹⁾ WEINLAND and LEWKOWITZ. Ber. 36, 2702, 1903.

²⁾ MEYER and SCHLEGL. Monatshefte 34, 561, 1913.

Chemistry. — "*Contribution to the Knowledge of the Higher Fatty Acids of Peanut Oil*". By W. D. COHEN. (Communicated by Prof. BÖESEKEN).

(Communicated at the meeting of May 30, 1925).

Introduction. The constitution of the fatty acids from peanut oil has already repeatedly been studied¹⁾, and for this reason there would perhaps have been no occasion to return to this subject, if it had not appeared from a publication by EHRENSTEIN and STUEWER²⁾ that there still prevails diversity of opinion about the constitution of the higher fatty acids.

Till the appearance of the communication of these last-mentioned investigators it had been considered as proved that the higher fatty acids (i.e. the acids above C-18) from peanut oil consisted of a mixture of arachidic acid, i.e. the normal C-20 acid and the so-called lignoceric acid, i.e. a C-24 acid considered by MEYER and his collaborators — in my opinion on debatable grounds — as an iso-acid, while other investigators (JAMIESON c.s.) do not pronounce an opinion about the structure, but confine themselves to the proof that we have to do here with a C-24 acid. The quantity of each of these two acids would amount to 2–4 % of the total quantity of fatty acids.

Totally discrepant conclusions are arrived at by EHRENSTEIN and STUEWER²⁾, who had been struck with the fact that the methyl- and ethyl ester of arachidic acid separated out of peanuts, would not fit into the series of melting points of the esters of palmitic acid, stearic acid, behenic acid, lignoceric acid. The same irregularity would apply to the alcohol made from this arachidic acid with respect to the alcohols C-16, C-18, C-22, and C-24. By means of KOH-melt of erucic acid they prepared the unquestionably "genuine" arachidic acid, which really yielded esters and corresponding alcohols of the expected melting point.

EHRENSTEIN and STUEWER prepared their "arachidic acid" by isolating it from the peanut oil via the methyl ester. In what way this had been done, is not clearly stated. It may, however, be assumed that fractionated

¹⁾ SCHWEIZER. *Ar.* 222, 757 (1884).

MEYER and BEER. *Sitz. ber. K. Akad. der Wiss. (Wien)* 122, 2B, 567 (1913).

MEYER, BROD, SOYKA. *ibid.* p. 485 (1912).

HEIDUSCHKA and FELZER. *Z. Unt. Nahr. u. Genussm.* 38, 241 (1919).

JAMIESON, BAUGHMAN, BRAUNS. *Journ. Am. Chem. Soc.* 43, 1372 (1921).

²⁾ EHRENSTEIN and STUEWER. *J. pr. N.F.* 105, 199 (1923).

distillation of the esters under reduced pressure has been applied. Now it has been proved with great certainty among others from still unpublished observations in our laboratory that the separation of a natural fatty acid mixture by means of fractionated distillation of the methyl or ethyl esters of the fatty acids with the usual moderate vacuum of the wet air-pump is exceedingly difficult, and that this method practically yields results only for the lower fatty acids (to C-14 inclusive) from cocoanut fat and palmkernel fat. A proper separation of the higher fatty acids is hardly possible¹⁾, and there is a great chance of getting a constant-boiling mixture of two different esters, which on analysis makes the impression of being a simple substance. EHRENSTEIN and STUEWER have undoubtedly been victims to this misconception, and it is owing to this that they consider the natural arachidic acid as a C-22 acid, not identical with the behenic acid, hence of another configuration.

They have tried to support this conception by a comparison with a synthetic acid, in which it appeared that the melting points corresponded. Particularly with regard to the higher fatty acids, however, the determination of the melting point has comparatively little value, because traces of impurities undetectable by analysis, can considerably affect the melting point, which MEYER has already pointed out. Moreover, the presence of acids with branched chain is very improbable in the natural fats, and the occurrence of iso-acids has, strictly speaking, never been proved as yet with certainty (not by MEYER either for lignoceric acid; this cannot be discussed in detail here).

The investigation described below shows, in my opinion, once more that the fatty acids separated from peanut oil following after stearic acid are C-20 and C-24 acid, C-22 acid being absent, or at most can be present in a quantity so exceedingly small that its presence escapes observation. Of the separated C-20 acid the normal structure has been proved, while the general properties of the C-24 acid render the normal structure the most probable.

I stated above that the usual vacuumdistillation with moderate rarefaction of the air is not adapted to effect an efficient separation for the esters of the higher fatty acids. Fortunately, however, the distillation on extreme vacuum appeared to present an entirely different image, and leads very easily to the end in view, at least in the case in question.

Experimental part. The fatty acids are separated out of 2 kg. of peanut oil, dissolved in 2 litres of 96% alcohol, and left alone for a long time at about 6°. The crystals that had separated, were sucked off, washed on the funnel with about 200 cm³ of alcohol, and then twice recrystallized out of the just sufficient quantity of alcohol. Thus were

¹⁾ For this reason not much value can be attached to the experimental data of JAMIESON c.s. though there is no doubt that their conclusions are right, and in perfect agreement with mine.

obtained: 80 grammes of fatty acid, melting point 70° , iodine value: 1, average Mol. Weight 337¹⁾).

These fatty acids were esterized by boiling for 12 hours with 300 cm³ abs. ethylalcohol, in which 3% HCl had been dissolved. On cooling the esters crystallized for the greater part. They were twice remelted with water after sucking off and then twice recrystallized out of little alcohol; they practically contained no free fatty acids any more. Quantity 83 grammes.

The esters were distilled in a simple distillation flask, in which however all the connections were effected by the aid of ground pieces. Between distilling apparatus and pump (make: "Pompe double à Palettes" of Gaiffe-Gallot et Pilon at Paris) there was placed a vessel in a vacuum glass filled with liquid air. With this arrangement a vacuum could be reached and maintained, which always remained under 0,001 mm. Hg.

The distillation (or rather sublimation, for practically no phenomenon of boiling is observed) yielded the following results:

Temp. airbath $210-215^{\circ}$	Quantity	Melting point
Fraction I temp. $< 165^{\circ}$	21.5 gr.	41°
" II " $< 181^{\circ}$	25.0 "	45°
" III " $< 187^{\circ}$ (then the distillation suddenly stopped)	11.0 "	48°
" IV Residue	24.0 "	52°

It was first tried to determine the saponification values of these fractions; of the higher fatty acids, however, the potassium salts are so strongly hydrolytically split up, that a clear change of colour is not to be observed; for this reason the Mol. Weights of the separated fatty acids were determined by titration in alcoholic solution with alcoholic potassium hydroxyde.

Thus the following values were found:

Mol. Weight acids from fraction I:	315,0
" " " " " II:	331,7
" " " " " III:	353,8
" " " " " IV:	367,8

This so far favourable result was an inducement to continue the fractionated distillation.

¹⁾ When left for a long time at 0° a good deal still crystallizes out from the collected mother-liquids; part of the crystals were centrifuged off, and dried on filter paper. Melting point 52° . Average mol. w. 274. This is probably a mixture of about equal parts of palmitic acid and stearic acid, which are present in pretty large quantities (compare HEIDUSCHKA loc. cit. and JAMIESON c.s. loc. cit.).

Fraction II and III together distilled again:

	Quantity	Melting point
Fraction Ia boiling point $< 165^{\circ}$	11.0 gr.	41°
.. IIa $< 175^{\circ}$	21.0 ..	47°
.. IIIa Residue	10.0 ..	52°

Fraction IIa rectified anew:

	Quantity	Melting point
Fraction Ib boiling point 155°	4.0 gr.	41°
.. IIb $< 175^{\circ}$	11.0 ..	46°
.. IIIb Residue	5.0 ..	51°

The middle fraction was rectified a few times more (in a smaller and smaller apparatus), thus practically splitting up into two fractions, of which one distilled up to about 155° , melting point 41° , while as residue a substance remained behind with a melting point of $51-52^{\circ}$. Of these two fractions about equal quantities were obtained and combined with the fractions I and Ia etc. resp. with the residues (fractions A and B).

The fatty acids were liberated out of both, and then recrystallized many times out of alcohol, at last out of petroleum ether, till the melting points changed no more. At first the C-24 acid showed an entirely different crystalline form, but after it had once been recrystallized with addition of a small quantity of "Norit", the crystalline form characteristic of this series of acids, shiny leaflets, presented itself.

Fraction A gave an acid with the following properties:

glistening crystal leaflets (outwardly perfectly the same as palmitic and stearic acid). Melting point $74.5-75^{\circ}$.

Melting point of the ethyl ester: 42.5° .

Mol. Weight calculated for C-20: 312.3; found 313.1.

C calculated: 76.85 %; found: 76.80 and 76.89 %.

H calculated: 12.90 %; found: 13.01 and 13.10 %.

Through KOH melt of erucic acid I obtained, in excellent yield, an acid with a melting point of 75° , the ethyl ester obtained from it melting at 42.5° . Mixture with the preparations from fraction A did not bring about a change of the melting points. Recently ADAM and DYER ¹⁾ have synthesized arachidic acid by building it up out of stearic acid, they

¹⁾ ADAM and DYER. Soc. 127. 70. (1925).

found melting point 75–75.5°, melting point of the ethyl ester 42.5°, which is, therefore, in excellent harmony with my values.

Fraction B, shiny crystal leaflets (outwardly not to be distinguished from the preceding acid). Melting point 80–80.5°.

Melting point of the ethyl ester 53.5–54°.

Mol. Weight calculated for C-24: 368.4; found: 367.7.

C calculated: 78.18 %; found: 78.10 and 77.98 %.

H calculated: 13.14 %; found: 13.20 and 13.25 %.

Collecting the values found for the melting points of the two acids and ethyl esters in a table, to which the most probable values are added for palmitic acid, stearic acid, and behenic acid (from the hydrogenated ethyl ester of erucic acid, with the corresponding ethyl ester, we see:

Acid	Melting point acid	Difference	Melting point ethyl ester	Difference
C-16	62.6	7	24	9.3
C-18	69.6	4.9	33.7	8.8
C-20	74.5	5.0	42.5	6.0
C-22	79.5	1.0	48.5	5.0
C-24	80.5		53.5	

It is seen from this that the course of the melting points of the homologous acids and the corresponding esters, with the exception of the too low melting point of the C-24 acid, is perfectly regular; the differences in melting point become smaller and smaller when we ascend in the series.

MEYER, BROD, and SOYKA ¹⁾ have built up the normal C-24 acid with the aid of the malonester synthesis from the C-22-iodide. The observation that this acid showed a melting point some degrees higher than the natural acid, renders the conclusion that we should have to do with another isomer, by no means justified. The observation of these investigators themselves on p. 500 of their above cited treatise admonishes to great caution, and makes the value of their melting point diagrams exceedingly dubious ²⁾.

Now that the normal structure of the C-20 acid has been ascertained, it is for the present the most consistent assumption to assign the normal

¹⁾ Loc. cit.

²⁾ The presence of iso-acids in the natural fats is after all as improbable as the presence of acids with an odd number of carbon atoms. All the communications to this effect, which now and then crop up in the literature, have been refuted with certainty. Compare in this connection the very instructive publication of HEIDUSCHKA and FELZER, which investigators prove that the supposed C-17 acid from peanut oil was nothing but an equimolecular mixture of palmitic acid and stearic acid.

structure also to the C-24 acid from peanut oil. I hope however to return to this point on a future occasion.

Summary.

The higher (saturated) fatty acids from peanut oil contain:

1. a. a C-20 acid.
b. a C-24 acid.
2. the quantity of each of them is 3—4 % of the total quantity of fatty acids.
3. C-22 acid is absent.
4. the C-20 acid is the normal acid and identical with the arachidic acid described so far in the literature.
5. the general properties of the C-24 acid present render it probable that this likewise belongs to the same homologous series of fatty acids.

Delft, May 1925.

*Laboratory for Organic Chemistry of the
Technical University.*

Physiology. — "*Concerning the supposed Influence of Fructose and the Action of Mg-salts on the Coagulation of Citrate- and Phosphate-blood.*"¹⁾ By Miss E. SLUITER. (Communicated by Prof. G. VAN RIJNBERK).

(Communicated at the meeting of May 30, 1925).

When blood has been made incoagulable by receiving it in a solution of sodium-citrate, it will coagulate after the addition of fructose. The same obtains with citrate-plasma. So for instance

1 cc. citrate blood	+	1 cc. fructosesol. 10 ⁰ / ₀	causes coagulation after 10 min.
2 " " "	+	" " " "	15 "
3 " " "	+	" " " "	15 "
4 " " "	+	" " " "	15 "
5 " " "	+	" " " "	20 "
6 " " "	+	" " " "	25 "
7 " " "	+	" " " "	25 "
9 " " "	+	" " " "	25 "
1 " " "	+	" 1 ⁰ / ₀	did not produce coagulation

after 45 minutes: but after addition of one more c.c. fructose-solution 1⁰/₀ coagulation appeared after 2 minutes.

My experiments with citrate-plasma yielded the following data:

1 cc. citrate-plasma	+	1 cc. fructosesol. 20 ⁰ / ₀	gave coagulation after 15 min.
2 " " "	+	" " " "	15 "
3 " " "	+	" " " "	15 "
4 " " "	+	" " " "	30 "
5 " " "	+	" " " "	100 "
6 " " "	+	" " " "	4 hrs.

Blood that has been made incoagulable by receiving it in oxalate, Mg sulphate, or by defibrination, does not clot after the addition of fructose²⁾. Neither can the phenomenon be evoked by any other sort of sugar, for which I examined glucose, lactose, maltose, and saccharose.

¹⁾ From experiments in the Laboratory for Physiology at the Amsterdam University.

²⁾ Commercial fructose contains traces of calcium: determination by DE WAARD's method made out that 1 cc. 10⁰/₀ fructose contained 0.014 mgrs. Ca; 1 cc. 20⁰/₀ fructose contained 0.027 mgrs. Ca. (the average Ca-content of 1 cc. of bloodserum is 0.1 mgr.). This calcium is not responsible for the coagulation, for when an equivalent quantity of CaCl₂-sol., or an equivalent quantity of CaCl₂, is added to another sort of sugar, no clotting ensues. Occasionally I also worked with a fructose-solution, to which first a quantity of oxalate, sufficient to bind the calcium had been added, after which the Ca-oxalate had been centrifugalised.

Citrate is one of the few salts that does not precipitate the calcium of the blood, but combines with it in one way or other, a combination thus far only partially known. According to SABBATANI ¹⁾ the anti-clotting action of Na-metaphosphate is due to such a combination. From chemistry we know, in fact, that citrates and alkaline metaphosphates inhibit the precipitation of calcium through the action of oxalates, or render it less complete ²⁾. This naturally induced us to find out the coagulative action of fructose on phosphatic blood. It thereby appeared that after about half an hour 1 c.c. fructose-solution 20 % produced coagulation in 2 c.c. phosphatic blood or plasma (100 mgrs of metaphosphate to 100 c.c. of blood).

When trying to find an explanation for this phenomenon, I simplified the experimental conditions by making a fibrinogen-solution with which I made the following solutions:

1	fibrinogensol. in distilled water + fructose	} thrombi- nogen;
2	" in Ringer sol. + citrate + fructose	
3	" in Ringer sol.	
4	" in Ringer sol. + citrate	
5	" in Ca-free Ringer sol. + fructose	
6	" in Ca-free Ringer sol.	

a few drops of oxalate plasma were added as thrombinogen.

After a short interval clotting ensued in the tubes 2 and 3, while the contents of the other tubes were still liquid after 30 hours. The assumption is warranted, therefore, that the fructose liberates the Ca from the calcium-citrate compound. We know different fructose-calcium compounds; the most probable in this case seemed to be the combination $C_6H_{12}O_6CaO$

or $CH_2OH(CHOH)_3O \begin{array}{c} \text{Ca} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{C} \end{array} CH_2OH$, in accordance with the place

where oxidation of fructose with $HgO + \text{baryta-water}$ occurs.

When adding first a little fructose and then some oxalate to a mixture of $CaCl_2 + Na\text{-Citrate}$, or $CaCl_2 + \text{metaphosphate}$, which does not give a Ca-reaction with oxalate, a precipitate will be observed after some time, which appears to be calcium. Control solutions were an equal quantity of fructose solution and the Ca-citrate or Ca-phosphate mixture, both with as much oxalate as the Ca-citrate-fructose mixture contained. This, then, seems to show that through the action of fructose on the complex calcium-compound Ca-ions have entered into the solution. Some time afterwards I came upon chemically pure, beautifully crystallized fructose (made by KAHLBAUM from inulin). A solution of this preparation did not produce any coagulation, neither in citrate-, nor in phosphate-blood, nor in plasma.

¹⁾ Arch. ital. de Biologie T. 39. 1903.

²⁾ Vide FRESSENIUS: Quantit. Analyse Bd. I. e. 157. 6 Aufl.

There were two possibilities: either the behaviour of fructose prepared from inulin is other than the behaviour of the commercial fructose prepared from saccharose or, besides the Ca, whose quantity had proved to be insufficient for coagulation, the fructose contains still another impurity influencing the clotting.

The plausibility of the first assumption is supported by the researches of KARRER, of IRVINE and of HAWORTH¹⁾. They derived the methyl-compound from disaccharid, and split it up. This process localized the methylgroup, consequently also the anhydrid compound, as these workers assume that the anhydrid from a disaccharid is the main constituent of a polysaccharid. This method showed HAWORTH that the fructose-residue in the canesugar molecule has another grouping of atoms than the fructose that can be isolated in a permanent form. Now according to IRVINE inulin is derived by polymerization from fructose anhydrid, which as so-called γ -fructose has the same structure as in cane-sugar. So it seems improbable that the permanent product from cane-sugar should be of a different grouping from that derived from inulin. Besides this the rotatory and reducing power of the two kinds of fructose is approximately alike.

As regards the possibility of another contamination of the fructose, e.g. by Ca, I wish to refer to the research by KARPMAN²⁾, who studied the effect on coagulation of citrateplasma of a series of organic substances, aliphatic as well as aromatic compounds, of various alkaloids and of some inorganic substances, without being able to demonstrate a clotting action of any of these bodies.

Now, an analysis of the ash of the commercial fructose (the pure fructose left no ash) yielded the singular result that the ash contained, besides an inappreciable quantity of Ca., also $MgCl_2$ in a quantity of 0.64 grms to 100 fructose (as $MgCl_2 + 6 \text{ aq. } 1.456 \text{ grms}$). Control-experiments showed that a solution of $MgCl_2$, to this amount really causes coagulation in citrate-blood and phosphate-blood, or-plasma, not however in oxalate-blood. $MgSO_4$ in a solution equivalent to that of $MgCl_2$ has a similar effect. Likewise the experiment with the Ca-Ci-mixture, as described in the experiment with fructose, yielded distinctly a positive result with $MgCl_2$: It appears that Mg liberates Ca from the combination Ca-Ci, which was indicated as such. Of the other alkaline earths Sr gives coagulation in citrate-, and phosphate-plasma, as well as in oxalate-plasma. So its action is similar to that of Ca. This is also borne out by the fact that, from a Sr-Ci mixture, which does not give a precipitate with oxalate, Sr can be expelled by means of $MgCl_2$, a precipitate of Sr-oxalate is obtained. For control-experiment I used a tube with Sr — Ci + water, and a tube with $MgCl_2$ + water with the amount of oxalate present in the Sr — Ci + $MgCl_2$ mixture. Such an

¹⁾ Journ. of the Chem. Soc. (London) 117, 118 (1920) 121, 122 (1922).

²⁾ Amer. Journ. of Physiol. 53. (1920).

experiment cannot be carried out with Ba, because the Ba-salt of citric acid is extremely insoluble. The clotting action which I ascribed to the power of fructose to liberate Ca from its complex combination, in the form of ions, appears to be based on a similar action of Mg-salts. This fact might furnish a small contribution to the solution of the problem as to in which form Ca is acting in the coagulation-process, but this paper does not bring forward any evidence regarding the phase in which it happens ¹⁾.

¹⁾ Concerning the origin of the abnormal quantity of MgCl_2 present in the fructose no explanation could be given by the factory of SCHERING at Berlin, where the fructose had been prepared.

Geology. — "*Tertiary Rocks from North-Western British Borneo and from Berau (E. Borneo)*". By L. RUTTEN.

(Communicated at the meeting of June 27, 1925).

In the last few months I was in a position to investigate a good number of partly fossiliferous tertiary rocks, collected by Dr. W. HOTZ at Basel, and by the late Dr. G. NIETHAMMER in the north-western part of British Borneo, and a larger collection made by Dr. F. WEBER in Berau (E. Borneo). A full description of these collections will be given elsewhere ¹⁾; what follows here are only some results of my investigation.

Rocks from British Borneo.

1. The clastic material occurring in the tertiary rocks is nearly always derived from "old" rocks: the chief component fragments are much worn quartzes and grains of red and green radiolarite, besides much scarcer pieces of slate and intensely weathered fragments of green igneous rocks. Only in two rocks did we find fresh, angular feldspars, implying the occurrence of a badly developed tertiary effusive period in this part of Borneo.

2. Tertiary limestones are scarce in British Borneo, however, they occur far into the interior: when we draw a line parallel to the west coast from the G. Kinabolu, which consists chiefly of an acid intrusive rock, we find localities of tertiary limestone to the north as well as to the south of the highest mountain of the island.

3. It is next to certain that the neogene limestones represent only the very oldest part of the Neogene, as is indicated as well by the total absence of Miogypsina as by the regular occurrence of large *Lepidocyclinae*.

4. In four domains of the Kudat- and Bengkoka peninsula old-neogene and eogene rocks occur intimately bound up with each other; the former with *Lepidocyclina*, the latter with *Orthophragmina*.

5. In three rocks from the peninsula of Kudat- and Bengkoka we could recognize distinctly *Orthophragmina* in association with *Lepidocyclina*, while in three other rocks this occurrence seemed very probable. Inquiries by VERBEEK, MARTIN, DOUVILLÉ, VAN DER VLERK and myself showed that in the Archipelago *Orthophragmina* rocks representing the Eocene, and *Lepidocyclina* rocks, representing the Oligocene and the Neogene, are as a rule completely separated, so that up to the present

¹⁾ For Br. N. Borneo see: Verh. Geol. Mijnb. Genootschap Nederl. en Kol. Geol. Serie VIII. 1925, p. 415—428.

nobody ever succeeded in finding the two subgenera of *Orbitoides* in one and the same rock. Stratigraphically the two genera are, as far as we can see, absolutely separated also in Europa. In America, where, indeed, the development of the tertiary Foraminiferal fauna differs in many respects from that in Europe and Asia, *Orthophragmina* and *Lepidocyclina* are found in association in one and the same rock. *Now this contrast is partly done away with by the discovery of Orthophragmina and Lepidocyclina in the same rock in British Borneo.* It might still be imagined that in the rocks of British Borneo perhaps only *Lepidocyclina* is autochthonous, and that *Orthophragmina* has been infused from older rocks. This supposition may be dismissed as highly improbable in virtue of various considerations. In the first place such an infusion could be probable only in a region, where a great many older limes occur, and where younger limestones occur in the neighbourhood of older, upheaved limestones. This might still be deemed possible for Kudat peninsula, where limestones are not exactly numerous, but not so very rare either. For the peninsula of Bengkoka, however, where limestones are very rare, such an infusion-hypothesis would require the assumption of too many fortuitous circumstances. Moreover, the assumption of such an infusion might concern one single case, but three occurrences have been demonstrated, and there are probably three more, where *Lepidocyclina* and *Orthophragmina* occur together. *We cannot but conclude, therefore, that there are in the Archipelago — though they may be ever so scant — transition strata from Eocene to Oligocene, characterized by the joint-occurrence of Lepidocyclina and Orthophragmina.*

Rocks from Berau. The rocks investigated are derived from North Sangkulirang, from the basin of the Kelai river between Muara Lasan and Tg. Redeb, from the basin of the Lasan river, and from the Sidoöng, Tambalang and Birang, tributary rivers of the Segah or Makam-river. Basing on the literature on Berau, and on the investigation of the rocks we are safe to conclude that tertiary deposits in Berau east of the line Sg. Lasan-Birang-Keburau lama (Bulongan) have a very wide distribution, whereas to the west of that line they are few and far between, and occur probably as relicts. Very likely the tertiary deposits have a thickness of several thousands of meters and can be arranged stratigraphically as follows:

Young Neogene. Limestones with *Orbiculina* and *Alveolinella Boscii* in the littoral zone of North-Sangkoelirang near Tg. Domaring; Limestones and lime-sandstones from P. Maratua; brown coal formation of P. Sepinang on the Berau river with carbon containing 30 % water (HOOZE).

Middle Neogene. Coal-sandstone-shale formation of the Lower Kelai- and Makam-rivers with c.a. 14 % water in the pitch-coal (HOOZE), probably occurring also on the Lower Birang (SPAAN), with few fossiliferous banks; on the Kelai river with *Miogypsina polymorpha* var. *spiralis*, *Lepidocyclina angulosa* and *Lep. Ferreroi*. It may be that limestones and marls of Tg. Domaring, found in the interior, belong to the same level of the Neogene.

Limestones from the Middle Sg. Birang are believed to be somewhat older. They contain beside numerous Miogypsinae (M. aff. Dehaartii) scanty remains of large Lepidocyclusinae.

Old Neogene. Limestone formation, characterized by the occurrence of large reef-like limestone hills (Lower Kelai), always with Lepidocyclusina formosa, most often with spiroclypoid Heterostegina, with small Lepidocyclusina, and numerous other littoral Foraminifera and Corallinaceae. Only once did we find Miogypsina in this formation (Lasan). Widely distributed; Basin Lasan, Lower Kelai, Sg. Sidoong, and the interior of North Sangkulirang. The limestones belonging to this level, often contain boulders of radiolarite and quartz, potassium feldspar, and plagioclase, which must have originated from young, acid tuffs. Rhyolite-, and Dacite-tuffs are perhaps somewhat older than the limestone-formation. Their crystals, as stated above, can often be recognized in the rocks of the lime-formation; they are found in situ in different localities in the basin of Lasan-river.

Young Eocene. Limestones with reticulate Nummulites, Alveolina s. str., Lepidocyclusina and large Operculinae occur in the Lasan territory and in the limestone hills to the south of Tg. Redeb (Kg. Lianglangup). There is apparently an intimate sedimentary relation between the old neogene limes, the most recent eocene limestones under consideration, and the somewhat older, but still young eocene limestones, which occur especially on the Upper Lasan, and which are characterized by the absence of Lepidocyclusina, and by the frequent occurrence of reticulate Nummulites, Alveolina s. str., large Operculinae and Sorites. Orthophragmina and Assilina are still entirely lacking in these deposits, so that they are to be referred to the young-Eocene.

This stratigraphical table suggests the following remarks. In the first place it strikes us that in North Sangkulirang, in the younger as well as in the older layers of the Neogene, limestones and marls have a wide distribution. We may even call the whole of North Sangkulirang a limestone-marl region, while in the parts of the inland round about Tg. Redeb the Young-, and the Middle-Neogene on the contrary is very poor in limestones, but rich in coal-layers, which seems to show that the facies has become more continental. I think it probable, though not at all a proved fact, that this phenomenon has a similar origin to that of the modifications of the facies in the Tertiary of North-East Kutai, where towards the peninsula of Sangkulirang we note a gradual increase of the marine character of the various sections of the Neogene from W. to E. ¹⁾).

There are a number of facts indicating that in Berau the condition is certainly more complicate than that along the coast of Kutai, where the tectonic of the tertiary littoral hills is always very simple, only poorly folded anticlines being found there, whereas towards the interior the folding becomes intenser, so that eocene deposits in Kutai begin to appear only far into the inland, and the Pre-tertiary still farther. Already at Tg. Mangkalihat eocene limestone occurs very near the coast, ²⁾ to the south of Sg. Pantei quartzite is known to occur before the coal-bearing Neogene of Tg. Redeb and before the calcareous Neogene of the zone of Lasan-Lower Kelai ³⁾. MOLENGRAAFF has pointed out that in

¹⁾ L. RUTTEN, This Proceedings 1916.

²⁾ L. RUTTEN, Samml. Geol. Reichsmus. Leiden. (I) X. 1915, p. 3—10.

³⁾ J. A. HOOZE, Jaarb. Mijnw. Ned. Indië. 1886. Techn. Adm. Ged.

some places the mesozoic radiolarites trend eastward from the Lower Sg. Kelai¹⁾; in the Sg. Galong Ketjil, a tributary of the Lasan river serpentine-breccia and diabase occur eastward from the zone of old-neogene limestones, and lastly also the eogene limestones from the mountain track of Sg. Binai in South Boulongan are located comparatively close to the coast.²⁾ It is evident, therefore, that in Berau there are undoubtedly no anticlines that are folded upwards gradually to greater depth, if one is proceeding to the interior. With the altered strike of the mountains — which is still N.N.E. in North Kutai, and becomes N.W. in Berau, as shown clearly by the topographical map,³⁾ the geological aspect has apparently entirely changed, the due importance of which cannot be assessed as yet. It is not impossible that the analogues of the less sharply folded littoral anticlines in Kutai are in part lying, in Berau and Bulongan, in the territory covered by the sea. Tarakan and P. Bunju with their oil fields, and incidentally the zone on which P. Maratua is situated, lend support to this view.

In the foregoing we have endeavoured to make up the stratigraphy from the data furnished by the investigation of the Foraminiferal fauna. We feel justified to ask whether we should not exercise special precaution in determining the boundaries on the basis of tertiary Foraminifera, since it becomes more and more evident that there are all sorts of transitions, never thought of before. This will be readily understood if we consider that *Lepidocyclina* and *Orthophragmina* have been recognized in British North Borneo in one and the same rock, that remains of *Lepidocyclina formosa* appear in rocks from Birang territory in typical *Miogypsina*-deposits, whereas conversely a limestone from the Lasan territory contains remains of *Miogypsina* together with numerous specimens of *Lep.-formosa*. It seems to me that the exceptions alluded to imply that the sedimentation in the Malay region — at all events in various localities — has been effected very evenly and uninterruptedly, but that they do not take away from the significance of the Foraminifera with reference to the stratigraphy of the Indian Tertiary. That the stratigraphical schemes produced by VERBEEK-FENNEMA, H. DOUVILLÉ, VAN DER VLERK and the present writer are usable, is indicated by the very fact that the "anomalous fossil-associations" appear as rare exceptions and that in most cases fossil-associations are met with that are in good adjustment with those schemes. As regards the Berau-territory, I think I may therefore be allowed to say that in view of the material examined, it is an established fact that the rocks represented comprise the Young-Eogene up to the Young-Neogene, and that all transitions probably occur within those limits.

It is remarkable that probably old-neogene effusiva occur in the region

¹⁾ G. MOLENGRAAFF, Verslagen Geol. Sectie Geol. Mijnb. Genootschap I. 1914, p. 175—179.

²⁾ L. RUTTEN, Samml. Geol. Reichsmus. Leiden (1). X. 1915, p. 3—10.

³⁾ See also P. KRÖKEL, Samml. Geol. Reichsmus. Leiden. (1). X. 1923, p. 141 etc.

under examination, and seem to have a wide distribution there: traces of them were found from Sg. Sidoöng as far as the Upper-Majung over a distance of above 40 km., from the Sg. Sidoöng as far as the interior of Sg. Domaring over a distance of above 100 km. In this connection it is interesting to state that also west of Sangkulirang-Bay rhyolite tuffs have been recognized ¹⁾, though it be in very thin layers. It is moreover possible that the more basic effusiva from Bulongan, as described by KRÖKEL (l. c.), have taken origin in the same period.

In fine I wish to call attention to one thing more. In many tertiary rocks of Berau pebbles or sandy grains of radiolarite have been found. Exactly the same can be stated for numerous tertiary rocks from British North Borneo. Now, from a recent publication by WANNER ²⁾ we gather that W. HOTZ refers the radiolarites of British North Borneo in part to the Old-tertiary. This induced WANNER to discuss the genesis of the radiolaria-bearing deposits. Concerning this problem the material investigated does not yield conclusive evidence. However, I am inclined to think that the fact that the earliest known fossiliferous tertiary sediments in Borneo invariably contain rounded radiolarite, implies that the folding of radiolaria-bearing rocks must have taken place in the Pretertiary, and that it is not very likely that the radiolarites should still have developed in Borneo in the Tertiary. This can be assumed only if the radiolarian deposits may be considered as sediments in a shallow sea, the upheaval of the seabottom, necessary to bring the radiolarites to the surface, then having been only very inconsiderable, and perhaps only local, so that they could be re-deposited in a rounded condition a little further. If, however, we agree with MOLENGRAAFF and WANNER that the radiolarites are pure deepsea formations, so that they can be deposited again as clastic rocks only after due folding, it will be hard to deny the necessity of assigning to the radiolarites of Borneo a pretertiary age. In that case it is of great interest that according to HOTZ an "ultra-alpine tectonic" must be assumed for British North Borneo.

Utrecht, June 1925.

¹⁾ L. RUTTEN. These Proceedings, 1916.

²⁾ J. WANNER. N. J. f. Miner. Beil. Bd. 45. 1921. p. 149—213.

Geology. — "*Concerning some Erratics of Southern origin in the Dutch Diluvium*". By J. H. DRUIF. (Communicated by Prof. L. RUTTEN).

(Communicated at the meeting of June 27, 1925).

In his "Bijdrage tot de kennis der Zuidelijke Zwerfsteen in Nederland en omgeving" ¹⁾ CH. OOSTINGH reports the occurrence of ferruginous sandstone from the Upper Oligocene and of loose shells from the same formation (resp. p. 101 and 103).

A short time ago on my visit to the railway-cut near Mook I came by chance upon a ferruginous sandstone, which on closer inspection appeared to contain distinctly recognizable cores of *Pectunculus obovatus* Lamark. On further inquiry I was informed by the stationmaster that a few days previously a fragment of that rock, measuring about $40 \times 20 \times 15$ cm. had been found, and that it contained a good many similar impregnations. But, alas, the workmen, out of curiosity, had knocked it to pieces. The fragment I found was a part of this stone. It is now present in the collection of the Geological Institute of Utrecht. Similar fragments were often found there, as I was told, so that I asked my informant to preserve such finds in future and to communicate with me, which he promised.

On p. 89 of the publication referred to, the occurrence is discussed of the familiar siliceous oolites. To the number of localities mentioned there, I can add one more, viz. "de Stompert" near Amersfoort, where I found a specimen, small but clearly distinguishable, right at the top of the hill. A few days later Mr. R. IJZERMAN brought home more specimens from a visit to the railway-cut at Maarn.

Neither in Dr. OOSTINGH's publication, nor anywhere else to my knowledge, mention is made of an erratic block found in 1884 by LORIÉ near Zeddam, now present in the Utrecht collection. On re-examining that part of the collection, I was struck by a peculiar green mineral enclosed in it.

The rock under consideration is a common white dyke-quartz, coloured yellow here and there, while a grass-green mineral can be recognized, distributed in irregular aggregations, mostly in spots, sometimes more or less spherical, not in distinguishable crystals.

A chemical examination made out that it contained Cu and P, while on treatment with acid initially some CO₂ is emitted. On heating some

¹⁾ Mededeelingen der Landbouw Hoogeschool. Dl. XIX. Wageningen.

water is given off. It is highly probable, therefore, that we have to do here with one of the minerals from the Lunnite-group ¹⁾).

The habitus is most like Pseudo-Malachite.

The micro-chemical examination confirmed the presence of P.

Now, it is a known fact that in the basin of the Rhine such minerals consisting chiefly of copperphosphate, occur, namely at Ehl near Linz. We may safely conclude, therefore, that the rock originates from that district. Since nothing is known about the occurrence of similar rocks in the basin of the Meuse, we seem to have hit upon a new erratic block characteristic of the Rhine.

¹⁾ DOELTER: Mineralchemie III, 1, p. 437, 1918.

Palaeontology. — "*A Contribution to the knowledge of the Pleistocene Flora of the Netherlands*". By F. FLORSCHÜTZ. (Communicated by Prof. L. RUTTEN).

(Communicated at the meeting of June 27, 1925).

In the summer of 1924 a boring was performed for the waterworks of Velp, municipality of Rheden, in the vicinity of the pumpingstation. The bore-hole lies in the domain of the municipality of Rozendaal, 31.30 M. + O. D. (= New Amsterdam Ordnance Datum). On sheet 470 (Rozendaal, edition 1911) of the Government chromotopographical map $\frac{1}{25000}$ it is localized by the eastern intersection of two circles, drawn with radii of 36 and 25 m.m., respectively from the tower of the castle Rosendaal and the Rozendaal watercornmill.

The nature of the bored layers was discussed by Dr. J. F. STEENHUIS, geological adviser in the Government Office for the Drinking-water-supply, in a treatise entitled: „Eenige geologische opmerkingen over de in de winplaats der gemeentewaterleiding van Rheden verrichte diep-boring, benevens beschrijving der aangeboorde aardlagen" (Some geological observations on the deep-boring in the source of supply of the municipal waterworks of Rheden with a description of the bored layers), which treatise appeared as an annex to the „Rapport inzake de vergroting van het vermogen der waterwinplaats te Velp" (Report on the raised capacity of the source of water-supply at Velp), made in December 1924 for the municipal corporation of Rheden by the Director of the Office just mentioned.

Down to a depth of 7.80 M. — O. D. the layers consisted of more or less coarse-grained sand, mixed with fine or coarse gravel. Lower down the sand was generally finer, the gravel thinly scattered, while clay- and loamlayers appeared, containing from 28.50 to 28.80 M. — O. D. scales of dark brown peat. In the deepest deposit (85.50 to 90.45 M. — O. D.) Dr. STEENHUIS met with indeterminable shell-fragments, which according to him may indicate that the marine tertiary has been reached. This presumption may be confirmed by the fact that I found in the same layer numerous glauconite-grains and Foraminiferae (especially representatives of the Rotaliidae and of the Nummulinidae).

An examination of the clay revealed that the layer between 23.00 and 28.50 M. — O. D. contained plant-remains, of which I shall give an enumeration lower down as far as I could determine them. Besides the botanical remains I found a couple of fragments of the elytra of a beetle.

My former teacher Dr. ED. EVERTS of the Hague, whom I showed one of these fragments, kindly informed me that it had belonged to a beetle of the genus *Donacia*.

This fossiliferous layer, 5.50 M. thick, consists, according to the description by Dr. STEENHUIS, of a firm, darkgrey, faintly sandy to plastic, calciferous clay.

The outcome of a further inspection revealed that the clay was mixed with scales of a dark-brown, limeless, fibrous mass, turning black when moistened, and consisting chiefly of fragments of mosses.

The available clay with the fibrous scales was washed and sifted. In the vegetable residue I could demonstrate:

a. *Anthophyta*: a single or few seeds of *Polygonum*, *Batrachium*, *Comarum*(?), *Hippuris*, *Myriophyllum*, *Menyanthes*, *Potamogeton* and *Carex*;

b. *Archegoniatae*: a large quantity of parts of stems and branches with leaves and single leaves of *Musci*.

Since the latter appeared to have constituted the chief part of the vegetation, it may not be amiss to look at them more closely.

The first thing that struck me was the predominance of the genus *Drepanocladus* C. Müll. (syn. *Harpidium* Sulliv.), identifiable by the falcated tips of the stems and the branches, by the unidirectional leaves, most often curved in a similar way, and by the generally well-developed and differentiated angular cells.

The moss-rests had been so beautifully preserved that all particularities of the leaves, which are of systematic importance (e.g. size and form of the cells, notably of the angular cells), could be observed.

After more than a hundred separate preparations in canadabalsam had been made, the leaves of the stems and the branches being stripped off to increase their transparency, I could reasonably anticipate, in virtue of the marked differentiation of the shape and the size of the leaves, that I should succeed in identifying them with recent *Drepanocladi*. In fact, the presence of typical species, such as *Drepanocladus Sendtneri* (Schpr.) Warnst., could readily be established.

On further examination of this genus and the relative literature, however, I resolved for the present to stop my efforts in the determination of the single species, considering that, even if we have entire plants at our disposal, the determination of *Drepanocladi* entails great difficulties arising from the manifold morphological varieties. This will readily be understood, if we reflect that the leaves, which are the main criteria in systematization, may vary considerably in one and the same specimen, not only as regards form and dimensions, but also with reference to length and thickness of the nerve, the structure of the cells etc. Outward circumstances seem to be of great influence here.

So long as the students of the systematization of this genus confined themselves to the examination of herbarium-material, the number of

species and varieties increased ad infinitum, until their attention was given to the biological side of the problem. Experience in the study of the ecological factors called for a revision of the adopted system, but did not facilitate a general view of the whole genus. The new idea of collective species may perhaps obviate the difficulties. In face of these facts I think it safer to consider the fossil moss-flora as one whole and to confine myself to deducing a few conclusions from their general characteristics. Among these are in the first place the falcated tips of stems and branches, which seems to be typical of plants emerging partly above the water. Submerged specimens, e.g. of *Drepanocladus Kneiffi* (Schpr.) Warnst. and of *Drepanocladus fluitans* (L.) Warnst., lack that peculiarity. We may therefore presume with good reason that the mosses had been growing in a shallow bog. The presence of the above-mentioned Anthophyta does not go against that hypothesis.

Another characteristic is the absence of Sphagnaceae. When we correlate this with the lime-content of the clay, it points to what the German plantgeographers call a "Grünlandmoor", in contradistinction to a "Heide-moor", and what in Dutch would be designated by the name of "Laagveenmoeras".

However, peat-formation has apparently not been attained in this case. The pleistocene river soon covered up the plants with silt, subsequently buried them beneath a layer of sand and gravel and clay of about 50 M. thickness, where they remained hidden, until thirsty man disturbed their rest.

Velp (G.) (Holland), May 1925.

Physiology. — "*On Cathode-rays as Substitutes of Potassium*". By Prof. H. ZWAARDEMAKER and T. P. FEENSTRA.

(Communicated at the meeting of June 27, 1925.)

When the heart has been deprived of all the free, diffusible potassium and also of part of the permanent potassium, it comes to a standstill. The pulsations will recommence spontaneously as soon as potassium or any of its radio-active substitutes are administered. This result was achieved with rubidium, thorium, ionium, radium, emanation. Neither the kind of corpuscular radiation, nor its velocity causes any difference in the primary effect. The nature of the effect depends on the inherent physiological disposition of the organ, and further on the dosage, leaving aside a minor adventitious influence of previous condition and accessory circumstances.

Instead of the radio-activity of the radio-active elements added to Ringer's solution we may also apply external radiation. We managed to do this with mesothorium, radium, polonium. In this instance also the kind of radiation did not matter. The effect was the same in all cases examined. The dosis alone was of importance. Too small a dosis proved entirely ineffectual. At a given moment a certain threshold is passed and the effect is achieved. This cannot be attained before a certain latent period is gone through, in which a summation of radiation takes place. A prolonged radiation will again generate a standstill (super-radiation). When the source of radiation is removed an after-effect will be noticed. The speed of the corpuscle is of significance in so far as it determines the amount of radiation that penetrates the pericardium.

In the last few months we have tested the cathode-rays. We procured a cathode-tube with a Lenard window of aluminium, say $9\ \mu$ thick. The vacuum we allowed to range between 0,15 and 0,01 mm. Hg., and the current in the secondary circuit of our inductorium between 0,1 tot 0,5 mA. The primary current was drawn from a battery of 8 volts, and the voltage in the spark-gap that was employed as a shunt, may presumably have amounted to 700 volts. The inductorium was of an old construction and not very large, so that we could go on working without the risk of heating the cathode-tube too much. Of course, after some time the aluminium window was burnt through, but it was immediately replaced by a new one. The vacuum was maintained by a rot. Cenco hyvac pump. In the interval between two experiments the amount

of cathode-rays we worked with, was ascertained by roughly estimating their effect upon photographic paper. In the space of ten minutes a distinct blackening was obtained provided that the vacuum was kept lower than 0,03 mm. Hg.

A control experiment proved that a very powerful radiation, such as was used by W. E. PAULI and A. HARTMANN¹⁾, was completely negative. Not until we remained within the limits stated just now, did we obtain positive results. A current of 0,3 mA. in the secondary circuit and a vacuum of 0.03 mm. Hg. were the conditions we had in view.

At first frogs were the animals we experimented with but when the hot weather suddenly dried up the waters in the province of North-Holland, and fishermen found the frogs dead in their nets, we worked with eel's hearts. The smaller specimens served our purpose better than the larger ones, because with them weaker rays could be taken to penetrate to the nodus atrio-ventricularis.

The frog's heart was attached to a glass Kronecker cannula. After some time the rhythm is noted during 15 minutes' perfusion with normal Ringer's solution. The ligature that held the cannula in its place, was applied as near as possible to the sulcus atrio-ventricularis.

The eel's heart was attached to a simple, straight, glass cannula, held fast by a ligature on the junction between sinus and atrium. Again we waited for regular pulsations during 15 minutes' perfusion with Ringer's solution.

Next we proceeded to Ringer's solution, from which the 100 mgrs of potassium-chloride per liter that it contained at the beginning, had been left out. The water of these fluids had been freshly distilled in glass, and the chemicals had been tested for the absence of potassium (cobalt-nitrite-method). We now looked for the arrest of the cardiac action consequent on the deprival of potassium. Subsequently the organ was suspended at a distance of 6 m.m. from the aluminium window of the cathode-tube, so as to enable the pencil of rays to reach the atrio-ventricular junction in due time.

After a complete standstill of 15 minutes on an average the cathode-radiation was begun and we waited for the pulsations to recommence. If this did not happen within half an hour, the mechanical excitability was ascertained at different intervals. It seemed to us that it was chiefly the powerful rays (the kind that produced in 10 minutes a strong blackening on the photographic paper) that caused inexcitability for mechanical touch.

In a series of experiments with 15 hearts 4 negative cases occurred (the latter only when intense radiation was applied). The eleven positive results are given in the following table.

Even strong hearts cannot stand a long-continued potassium-free per-

¹⁾ W. E. PAULI und A. HARTMANN, Arch. f. mikrosk. Anat. Bd. 103, p. 95, 1924.

TABLE I.

Revival of the pulsations in a heart that is radiated while it is constantly perfused with potassium-free Ringer's solution.

Data	Animal	Previous standstill (min.)	Latent period until the 1st recovery (min.)	Vacuum m.m. Hg.	Recovery	After-effect	Particulars about the after-effect
8 May	frog	10	20		3 times	no	
20 "	"	10	18		2 "	"	
4 June	eel	48	18	0.08	1 time	yes	
8 "	"	5	17	0.09	1 "	"	in groups
8 "	"	6	3	0.08	1 "	no	
9 "	"	30	3	0.08	in groups	"	
10 "	"	7	15	0.09	1 time	yes	" "
10 "	"	30	3	0.09	1 "	"	
12 "	"	7	25	0.04	1 "	no	
13 "	"	7	3	0.02	1 "	yes	
15 "	"	5	9	0.02	1 "	"	" "
Average		15	12	0.07			

fusion. It would seem that a prolonged unbalanced condition $\frac{\text{Na} + \text{K}}{\text{Ca}}$ is inconsistent with a lasting automaticity. In order to ensure an indefinite space of time, between the beginning of the standstill and the cathode-radiation, about 50 mgrs. of Caesium-chloride per liter were added. Under the control of Prof. W. E. RINGER this caesium-chloride had been purified of the traces of a radio-active admixture present in the commercial preparation. In two years' time the inactivity of this salt had not changed at all. In 40 minutes the scale of the very sensitive quadrant-electrometer did not shift more than three division marks with 74 grms. of CsCl in a large flat ionization-chamber. So it can be considered to be absolutely inactive, and did not, of itself, make any heart resume its beating when it was added to potassium-free Ringer's solution.

Four hearts were subjected to these experiments. On an average 19 minutes were allowed to elapse between the complete arrest of the heart's action and the commencement of the cathode-radiation. Three hearts gave positive results, one negative. In all probability the radiation had been taken too weak in respect to the size of the heart.

Table II illustrates the positive cases:

TABLE 2.

Recovery of the pulsations in a heart that is radiated while it is constantly perfused with potassium-free Ringer's solution to which is added per liter 50 mgrms of purified, consequently non-radio-active caesium-chloride.

Data	Animal	Previous standstill (min.)	Latent period till 1st recovery	Vacuum mm. Hg.	Recovery	After-effect	Duration of cathode pulsations	After-effect	Particulars about after-effect
16 June	eel	6	10	0.03	in groups	yes	18	249	in groups
18	20	17	0.02	first continuous	..	195	66
19	30	17	0.02	continuous	..	51	150	continuous
Average		19	15	0.02			55	155	

The recovery of the heart-function generally appeared suddenly, without any previous intimation, after a latent period, in which a summation took place of averagely 12 min. in table I and 15 min. in table II.

After some time, however, the restored heart comes to a standstill (super-radiation). Then the cathode-radiation was discontinued and we waited. In half the cases an after-effect revealed itself, which was sometimes of short duration, but at other times could persist even for hours.

The type of recovery is not always the same. In Fig. 1 we have pictured a case of an eel's heart that has been deprived of potassium, and has subsequently been left alone for half an hour. After this long-continued absolute immobility it was exposed to cathode-rays, as above described, while at the same time the permanent potassium-free perfusion was continued. The vacuum measured 0,014 mm. Hg., the secondary current 0,15 mA. During the radiation the vacuum decreased to 0,022 mm. Hg., consequently the secondary current rose to 0,4 mA. After a latent period of 17 minutes, which was attended with a few spontaneous contractions, the latter were resumed very regularly, and gradually at first. These beats continued for 15 minutes. Then the current was interrupted and an after-effect remained, which was originally of a continuous nature, but eventually became grouped.

In Fig. 2 we give another type of recovery. On the left the gradually vanishing pulsations as a result of the deprival of potassium. After waiting 6 minutes the cathode rays were inserted. After 10 minutes the contractions were resumed, and continued, also after cessation of radiation, until far into the night. Meanwhile due care was taken to maintain a perfusion entirely free from potassium.

The penetrating power of the rays differed slightly. In table I the

vacuum averaged 0,08 mm. Hg., in table II 0,02 mm. Hg. We endeavoured to conform the penetrating power of the rays to the size of the heart, but we sometimes failed in our effort.



Fig. 1.

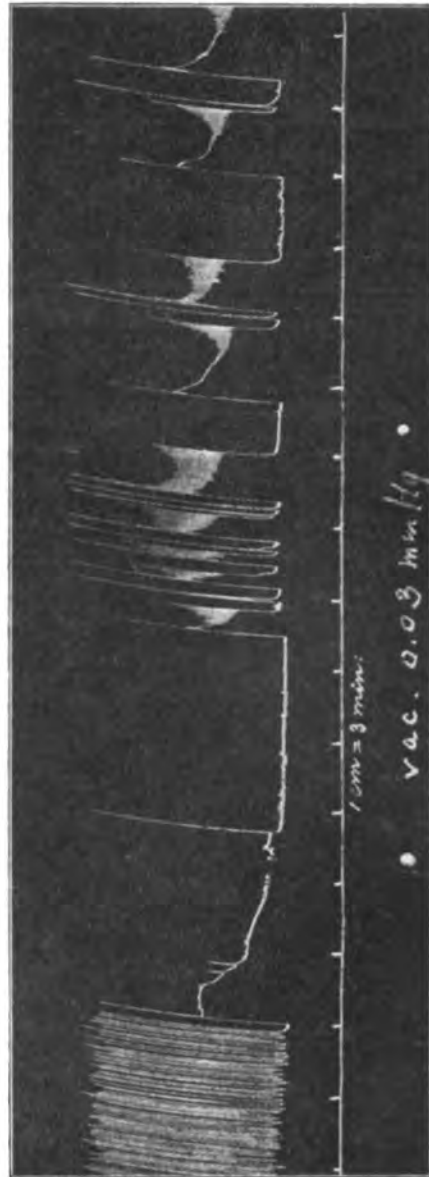


Fig. 2.

In spite of this uncertainty the result was positive in the large majority of cases (14). In the remaining 5 negative cases either the radiation

had been too penetrating and too profuse (3 cases), or the heart was covered by a layer of water (1 case), or the penetrating power was too weak in proportion to the size of the organ (1 case). The latter supposition proved to be true, when in a case that was negative at first, the heart (that had first been restored on normal Ringer's solution) was again brought to a standstill by deprival of potassium, and was finally restored again by a kind of rays of greater penetrating power.

We may, therefore, be justified in concluding that, provided that the circumstances are favourable, also cathode rays are competent to restore the automaticity of a heart that has been brought to a standstill by deprival of potassium.

So besides the mesothorium-, and the radium-rays, the cathode-rays are also to be considered as a physiological agent. The electrons emitted, though they vary as to speed (in the above series their penetrating power decreases $\frac{1}{2}$ c., $\frac{1}{2}$ c., $\frac{1}{15}$ c.), carry the same charge (1 unit). On the other hand polonium radiation has a smaller speed ($\frac{1}{10}$ c.) and a positive charge (2 units).

The manner of revival was in every case determined by the organ, not by the stimulant.

For the present we are unable to say to what amount the radiation reaches the nodus atrioventricularis.

EXPLANATION OF THE FIGURES.

Fig. 1. Recovery of the automatic movements by cathode-rays. Vacuum ranged between 0.014—0.022 mm. Hg. in second circuit 0.15 to 0.40 m.A.

Fig. 2. First standstill, then recovery by cathode-rays in the interval between the two white points.

Vacuum ranged between 0.01 and 0.05 mm. Hg.; in second circuit 0.3 m.A. After cessation of the radiation after-effect (continues until far into the night).

Physics. — "*Further experiments with liquid helium. X. On the electric resistance of pure metals, etc. XIV. Influence of elastic deformation on the supraconductivity of tin and indium*". (Comm. N^o. 174 from the Physical Laboratory at Leiden). By G. J. SIZOO and H. KAMERLINGH ONNES.

(Communicated at the meeting of June 27, 1925).

§ 1. *Introduction.*

As no satisfactory theoretical explanation of the supraconductive state of metals has been given yet, which might serve as a guide for further investigations, it seems desirable to try, by changing the external conditions, to discover the factors which play a roll in the appearing of the phenomenon. These considerations led to the institution of an inquiry into the influence which elastic deformation exerts on the appearing of the supraconductive state. The results of this investigation are published here.

In the first place the influence of the elastic extension on the "vanishing-point" was traced with tin, and then that of elastic compression with tin and indium.

A. *Extension.*

§ 2. *Method of the experiment.*

In the Heliumcryostat¹⁾ a tinwire (fig. 1. A) is placed, stretched vertically between two small tinblocks B and C. The lower one is kept in place by the glass tube D, which is fixed with sealing wax into the cap of the cryostat and the lower brim of which fits exactly in the circular incision in the tinblock. The upper block is carried by a small copper cylinder soldered to the glass tube E. This tube is suspended by means of a similar cylinder on the spiral F.

The length of the spiral, which is a measure of the applied tension, is read on a millimeter scale placed on the glass tube. In the tube D some holes are made so that the liquid may enclose the wire completely. The wire was made (drawn out) from "KAHLBAUM-tin".

The leads necessary for the resistance-measurements are soldered to the tinblocks. Two of them, isolated with glass tubes, pass through holes

¹⁾ Leiden Comm. N^o. 124c (1911) fig. 4.

in the tinblocks (for clearness these tubes are not shown in the figure).

The method of resistance-measurements was always that of the balancing of the potential at the ends of the unknown and the known resistance, with the aid of a compensation apparatus of DIESSELHORST, free from thermo-effects. Even below the "vanishing-point" the found potentials were calculated to resistances as if OHM's law held.

The vapour pressures of the heliumbath were read with a cathetometer on a closed mercury manometer. The temperatures were calculated therefrom by aid of the formula of Leiden Comm. N^o. 147b (1915) p. 33¹⁾.

For this purpose use was made of an accurately constructed curve which represents this formula in the temperature region required.

§ 3. The measurements.

The first measurements were made on March 28, 1924. As on the 4th of April following, it was possible to make a more complete series, the results of the first are not communicated here. They were however sufficient for it to be concluded that:

stretching of the tinwire was conducive to the appearing of the supraconductive state.

Namely, we repeatedly ascertained that at a temperature, below that at which the resistance begins to disappear, the resistance of the wire in the stretched was less than in the unstretched state.

On the 4th of April 1924 the measurement was repeated with a new wire of a length of 16.5 cm. and a diameter of 0.30 mm. The resistance of this wire at room-temperature was 0.30 Ω . The results of these measurements are given in table I, and represented by fig. 2.

The resistance-measurements were carried out in the order indicated by the Roman figures. Those indicated by II, III, IV, V, VI form a determination of the "vanishing point" of the unstretched wire; those by VI, VII, VIII, IX, X, XI, XII a similar determination of the stretched wire. The applied tension amounted to 197 grams, i.e. 2.52 k.g./mm².

After this the wire was stretched and unstretched alternately, at different temperatures and every time the resistance determined (XIII^b and XIII^a, XIV^a and XIV^b and c XV^b and XV^a and c).

In the measurement XV the current was maintained through the wire



Fig. 1.

¹⁾ See also Leiden Comm. N^o. 167a (1923) p. 4, note 1.

TABLE I. Measurements of April 4, 1924.

No.	Tension in G.	Tension in kg./mm ² .	P_{helium} in mm. Hg.	T	$W_{\text{Sn-1924 sp}}$
II	0	0	484.9	3.774 K.	0.000181 Ω
III	0	0	473.4	3.753	0.000176
IV	0	0	463.6	3.735	0.000072
V	0	0	453.6	3.716	0.000000
VI	0	0	442.6	3.696	0.000000
VII	179	2.52	442.6	3.696	0.000000
VIII	179	2.52	453.5	3.716	0.000000
IX	179	2.52	463.7	3.735	0.000029
X	179	2.52	467.9	3.743	0.000072
XI	179	2.52	473.3	3.753	0.000165
XII	179	2.52	483.4	3.771	0.000187
XIII ^a	179	2.52	477.6	3.760	0.000190
XIII ^b	0	0	477.6	3.760	0.000176
XIV ^a	0	0	473.7	3.753	0.000183
XIV ^b	179	2.52	473.7	3.753	0.000172
XIV ^c	207	2.92	473.7	3.753	0.000172
XV ^a	207	2.92	468.4	3.744	0.000090
XV ^b	0	0	468.4	3.744	0.000133
XV ^c	214	3.02	468.4	3.744	0.000086

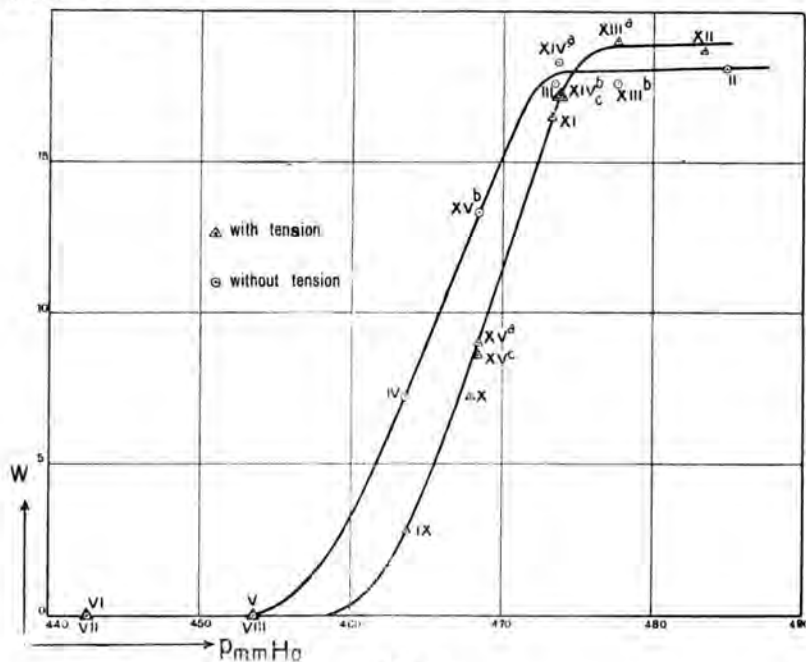
 $20 \times 10^{-5} \Omega$ 

Fig. 2.

during the stretching and unstretching, and the galvanometer was read. It was observed that the latter was displaced about 8 mm., namely during the stretching in the direction corresponding to the diminishing of the resistance, during the unstretching in the opposite direction.

Fig. 2 shows clearly how the "vanishing-curve" is displaced by the stretching of the wire to the side, of the higher temperatures. At the place where the resistance has half disappeared, the displacement amounts to 3.5 mm. Hg., corresponding to 0.007 degrees Kelvin.

In the region of normal conductivity a small increase of the resistance is to be observed.¹⁾

During these measurements the electrical current through the wire was always 13 mA. The highest tension with which was measured amounted to 3.02 k.g./mm². By trying to increase the tension still a little more, the wire broke. Thus the breaking load had been almost reached.

B. Compression.

§ 4. Method of the experiment.

The result, stated in § 3, gave rise to the supposition that compression of a tinwire would cause a displacement of the "vanishing-curve" to the side of the lower temperatures. To try this supposition an experiment was planned in which it would be possible to determine the "vanishing-point" of a tinwire, while this was subjected to a hydrostatic pressure. The amount of this pressure would, from the results found with the extension, have to be of the order of 200 kg/cm².

The experiment was arranged in the following way:

The resistance to be measured is wound round a small glass tube. The windings are separated from each other by silk thread. Round the resistance coil a second glass tube is slipped. The whole is placed in a copper cylinder (fig. 3. A)²⁾, with an inside diameter of 7 mm. and an outside one of 11 mm., closed at the bottom and at the top by a heavy head (screwed and soldered). Two german-silver capillaries pass through the upper. The first one serves for the admission of the helium gas and is connected with the compression apparatus. Through the second the copper wires, necessary for the resistance measurements are led. These wires leave the capillary outside the cryostat by a connecting-piece *D*, in which the packing has been replaced by a little ebonite block. The four little holes, through which the wires are led outside, are afterwards filled up with piceine.

In order to produce the required pressure on the resistance, the cylinder *A*, whilst under the liquid helium, and the leads are first filled from a cylinder with compressed helium to a pressure of about 60 atmospheres.

¹⁾ See however § 5.

²⁾ Compare also Leiden Comm. N^o. 132b (1912) fig. 1.

In the cylinder *A* and in a part of the capillaries liquid helium is formed then. After this, with the aid of a hydraulic press, the pressure is increased to the desired amount. This press is 8 filled with glycerine,

which, in two communicating pressureboxes, is separated by mercury from the heliumgas.

For the determination of the pressure two metal-manometers were used with ranges of measurement from 0—150 k.g/cm² and from 0—1500 atmospheres. Both were, after the measurements, calibrated with the small pressure-balance of the Physical Laboratory of Amsterdam. We wish to express our gratitude to Dr. A. MICHELS for his valuable help in this connection.

The resistance-measurements were made in the same way as set out in § 2. Also for the measurements of the vapour pressures and the determination of the temperatures reference may be made to § 2.

§ 5. The measurements with tin.

The measurements were made with the resistance Sn-1924-A, wound from a drawn tinwire of diameter 0.24 mm. The material used was "KAHLBAUM-tin". They were carried out on Oct. 24, Oct. 30, and Nov. 14, 1924. On the first two dates they had to be stopped, because

of the appearing of a leak in the joint-piece

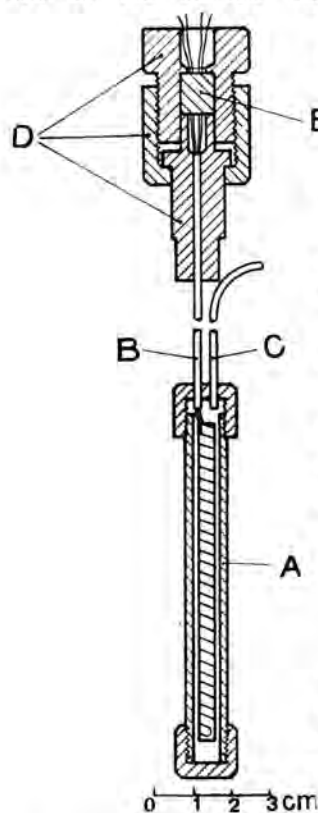


Fig. 3.

D (fig. 3). A pressure of 300 atmospheres seemed scarcely admissible for the pressure installation, especially for this joint-piece. The last time, however, the measurement could be carried out undisturbed. The current through the wire always amounted to 4 mA.

The results of the measurements are contained in the Tables II, III, IV. They contain determinations of the "vanishing-point" at 4, 95, 193 and 300 kg./cm² hydrostatic pressure. As it was not possible to give all the points in one figure, fig. 4 represents, as an example, the "vanishing-curve" at a pressure of 95 kg., whilst in fig. 5 the four curves are given, omitting the measured points.¹⁾

¹⁾ In constructing the graphs we always started from the idea that the line representing the disappearance of the resistance ("vanishing-curve") should be a continuous curve. Sometimes, however, by the position of the measured points the suspicion was raised that this supposition was wrong, and that the curve should show one or more discontinuities. To definitely settle down this question, however, a great number of measurements would have to be made and an exceedingly high constancy of the temperature of the heliumbath would be required.

TABLE II. Measurements of October 21, 1924.

Pressure in kg./cm ² .	p_{helium} in mm. Hg.	T	$W_{\text{Sn. 1924 A}}$
4	483.5	3.771 K.	0.00131 Ω
	474.3	3.754	0.00123
	468.4	3.744	0.00077
	464.4	3.736	0.00018
	466.6	3.740	0.00047
	458.5	3.725	0.00000
95	458.6	3.725	0.00000
	464.2	3.736	0.00039
	466.6	3.740	0.00078
	468.5	3.744	0.00097
	474.5	3.754	0.00126
	483.0	3.770	0.00131
193	494.0	3.790	0.00131
	466.4	3.740	0.00068
	474.6	3.754	0.00128
	468.6	3.744	0.00105
	466.5	3.740	0.00092
	464.0	3.735	0.00052

TABLE III. Measurements of October 30, 1924.

Pressure in kg./cm ² .	p_{helium} in mm. Hg.	T	$W_{\text{Sn. 1924 A}}$
4	760	4.2 K.	0.00132 Ω
	493.5	3.788	0.00131
	483.4	3.770	0.00131
	479.4	3.763	0.00130
	479.1	3.763	0.00129
	478.2	3.761	0.00129
	475.8	3.756	0.00126
	473.5	3.753	0.00116
	466.6	3.740	0.00045
	463.4	3.734	0.00008
	460.5	3.729	0.00000
	458.4	3.724	0.00000
95	494.4	3.790	0.00131
	484.4	3.772	0.00131
	473.7	3.753	0.00126
	468.2	3.743	0.00100
	464.8	3.737	0.00054
	461.0	3.730	0.00008

TABLE IV. Measurements of November 14, 1924.

Pressure in kg./cm ² .	P_{helium} in mm. Hg.	T	$W_{\text{Sn. 1924 A}}$
4	483.9	3.772 K.	0.00131 Ω
	473.7	3.753	0.00122
	467.8	3.742	0.00071
	463.3	3.734	0.00011
	462.0	3.732	0.00000
300	483.3	3.770	0.00131
	473.2	3.752	0.00127
	469.4	3.745	0.00110
	464.0	3.736	0.00056
	457.1	3.722	0.00000
193	484.5	3.773	0.00131
	473.8	3.753	0.00126
	469.7	3.746	0.00112
	466.4	3.740	0.00089
	463.1	3.734	0.00041
95	460.1	3.728	0.00007
	483.7	3.772	0.00130
	473.7	3.753	0.00126
	469.0	3.744	0.00108
	464.9	3.736	0.00050
4	460.6	3.729	0.00007
	473.9	3.753	0.00122
	468.8	3.740	0.00076
	464.3	3.736	0.00014

The measurements show the correctness of the supposition mentioned in § 4. The "vanishing-curve" is shifted by the application of the pressure to the side of the lower temperatures.

The displacement at the place where the resistance has half disappeared, for 300 kg./cm², amounts to 2.4 mm. Hg., corresponding to 0.005 degrees KELVIN. It is noteworthy that the displacement with increasing pressure soon seems to have reached a maximum value. The displacement, corresponding to an increase of the pressure from 193 to 300 kg. is scarcely outside the experimental error.

That the elastic limit is not exceeded by the application of the pressure, is clear from the return of the normal "vanishing-point" when the pressure is released. Also the resistance of the wire at 0° C., which was determined several times before, between, and after the measurements had not changed. It amounted to 2.0199 Ω .

It is noteworthy that in the region of normal conductivity no change

due to the pressure could be observed within the experimental accuracy. This is in agreement with what might be expected from the measurements of KAMERLINGH ONNES en BENGT BECKMANN¹⁾, who found only a small pressure effect at hydrogen temperatures, which, besides, diminished with temperature. It is understandable that this result has caused some doubts about the reality of the increase of the resistance in the region of normal conductivity found with stretching.

Perhaps this increase, which, besides, is only just outside the experimental error in this region, is to be ascribed to very small fractures in the wire, produced by the stretching.

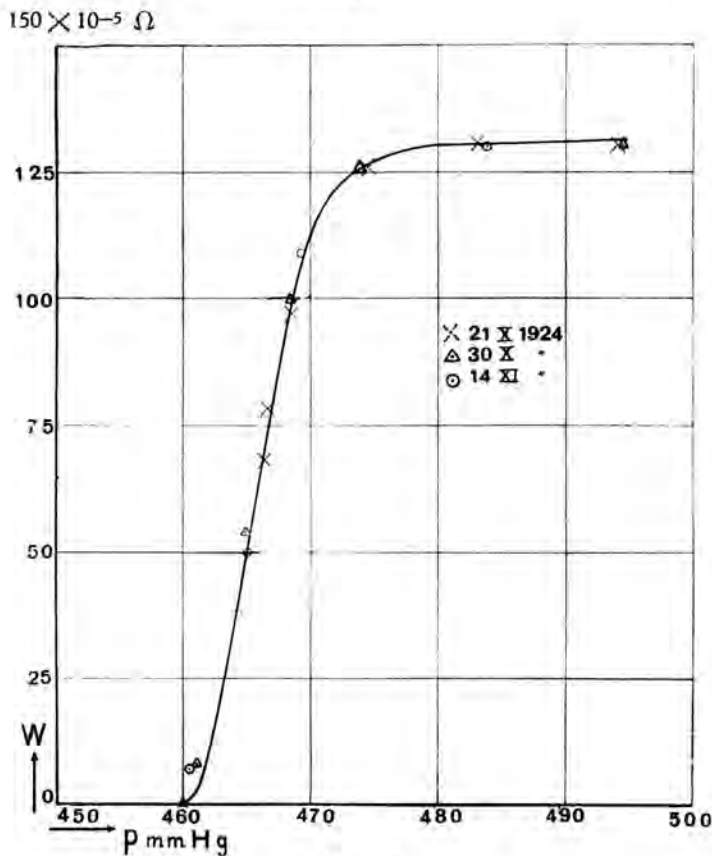


Fig. 4.

§ 6. The measurements with indium.

In order to decide the question whether the phenomenon mentioned above is to be regarded as a special property of tin rather than as a general property of the superconductors, it was considered desirable to repeat the experiment with at least one of the other superconductive metals. The most suitable for this purpose was indium, as it may be

¹⁾ Leiden Comm. N^o. 132b (1912).

drawn into wire (in opposition to mercury), as it does not oxidise too fast in the air (in opposition to thallium), whilst besides the situation of the "vanishing-point" is suitable (in opposition to lead).

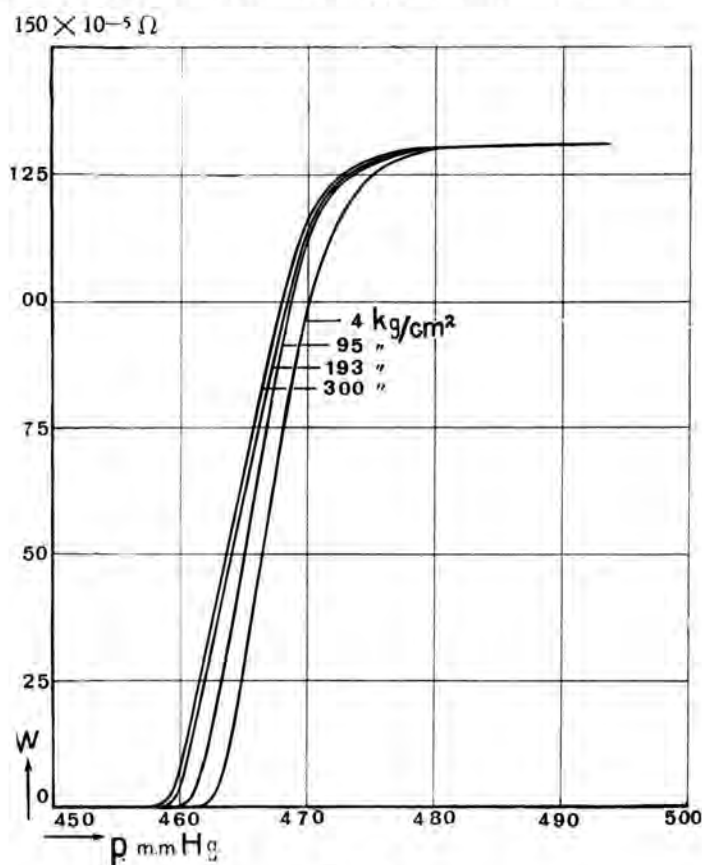


Fig. 5.

The resistance Ind.-1924-A, with which the measurements were carried out, was made of the same wire as that of the resistance Ind.-1922-A, used by W. TUYN ¹⁾. The resistance at 0° C. was 2.2862 Ω .

The measurements were performed in the same way as those with tin. Although the great value of the resistance at the temperatures of liquid helium favoured accurate measurements above the "vanishing-point", it hindered the measurements in the region of the great decrease of resistance; namely, very small temperature changes in the heliumbath cause then very considerable changes in the resistance to be measured. Therefore in this region the measurements were made with a current of only 0.4 mA; above the "vanishing-point" a current of 4 mA. was used. The results follow in the tables V and VI and are represented by fig. 6. The applied tensions were 4,100 and 200 k.g./cm.², respectively.

¹⁾ Diss. Leiden (1924) p. 29.

TABLE V. Measurements of December 12, 1924.

Pressure in kg./cm ² .	p_{helium} in mm. Hg.	T	$W_{\text{Ind. 1924 A}}$
4	760	4.2° K.	0.07668 Ω
	319.1	3.438	0.07647
	313.5	3.424	0.07647
	308.4	3.412	0.07584
	305.4	3.405	0.0042
	306.6	3.408	0.0338
	306.6	3.408	0.0375
	304.8	3.404	0.0000
100	319.5	3.439	0.07646
	313.2	3.423	0.07646
	308.0	3.411	0.07636
	307.5	3.410	0.07614
	307.8	3.411	0.0757
	305.9	3.406	0.0515
	305.0	3.404	0.022
	305.5	3.405	0.0520
	303.2	3.400	0.0000

TABLE VI. Measurements of December 19, 1924.

Pressure in kg./cm ² .	p_{helium} in mm. Hg.	T	$W_{\text{Ind. 1924 A}}$
200	317.9	3.434° K.	0.07648 Ω
	313.0	3.423	0.07627
	308.1	3.411	0.07608
	306.8	3.409	0.07592
	305.2	3.405	0.0732
	304.8	3.404	0.0643
	304.0	3.402	0.0050
	304.2	3.403	0.0206
	304.5	3.403	0.0284
	304.4	3.403	0.0248
	304.9	3.404	0.0543
	305.5	3.405	0.0704
	305.2	3.405	0.0637
	304.0	3.402	0.0034
	303.2	3.400	0.0000

The results show that the behaviour of indium is the same as that of tin. The displacement of the "vanishing-curve" at the point where the

resistance has half disappeared, for a pressure of 200 kg./cm² amounts to 2.1 mm. Hg., corresponding to 0.006 degrees KELVIN, thus only slightly different from that with tin.

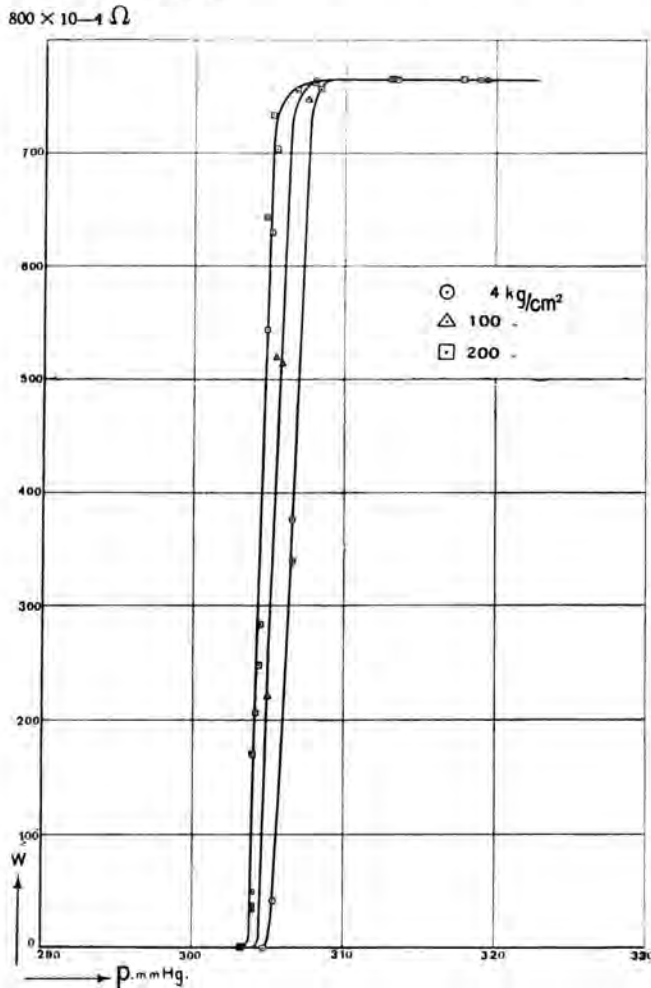


Fig. 6.

§ 7. Discussion.

If the extension and the compression of the supraconductive metal may be considered as equivalent to an increase and decrease respectively, of the distances between the atoms, then the results communicated above may be considered as supporting the hypothesis which has been stated in the report of KAMERLINGH ONNES to the IVth Conseil-Solvay, based on the drawings of Dr. H. A. KRAMERS contained therein; namely, that a relatively large space between the atoms is favourable for the appearing of the supraconductive state, when the further special conditions, shown only by the class of supraconductors, are present.

Physics. — "*On the measurement of very low temperatures.* XXXII. *The thermal expansion of Jena-glass, 16^{III}''.* By F. P. G. A. J. VAN AGT and H. KAMERLINGH ONNES. (Communication N^o. 176a from the Physical Laboratory at Leiden).

(Communicated at the meeting of June 27, 1925).

1. *Introduction.*

Some years ago KAMERLINGH ONNES and HEUSE (Comm. Leiden N^o. 85) and KAMERLINGH ONNES and CLAY (Comm. Leiden N^o. 95b) carried out measurements for determining the expansion of Jena-glass 16^{III} in the temperature domain from $+16^{\circ}$ to -182° C. As data of the behaviour of Jena-glass below this domain were missing, for the volume-determinations at lower temperatures, which were continuously necessary, the above-mentioned results had to be extrapolated to the temperature of liquid hydrogen with the aid of the relative measurements of LINDEMANN ¹⁾ of a rod of an unknown glass, assuming that these measurements would reproduce the character of the linear expansion of glass. As more accurate determinations of the thermal expansion of Jena-glass 16^{III}, of which for example all our gasthermometers are constructed, were necessary, they have been carried out by us to the temperature of liquid hydrogen.

Also, these new measurements are a beginning of a more extensive investigation of the thermal expansion of solid substances at very low temperatures, by which, for example, it should be possible to test the crystal theory of BORN ²⁾ and the law of DEBYE ³⁾ from the observations.

2. *Apparatus and method.*

The change of length was measured in the following manner. The inner wall of a vacuum tube, ± 1 M. long, was cooled to the boiling point of ethylene, oxygen, and hydrogen, respectively, the outer wall remaining at room temperature. The movement of the inner wall with regard to the outer wall could be measured accurately by observing, with a microscope, the alterations of position of the platinum points (C and C'), which were sealed into both the bottom and the top of the

¹⁾ CH. L. LINDEMANN, Ueber die Temperaturabhängigkeit des thermischen Ausdehnungs-coefficienten. Physik. Z. XII 1911 p. 1197 en XIII 1912 p. 737.

²⁾ M. BORN, Zur thermodynamik der Kristallgitter. Z. f. Physik. VII 1921, p. 217.

M. BORN, Ueber die Temperaturabhängigkeit der Pyro-electricität. Physik. Z. XXIII 1922, p. 125.

³⁾ DEBYE, Vortrag auf dem Wolfskehl-Kongress. Göttingen 1913 (B. G. TEUBNER, Leipzig 1913).

inner and outer walls. The observations were made through the plane glass windows (B and B'). The tubes and the microscopes were fixed

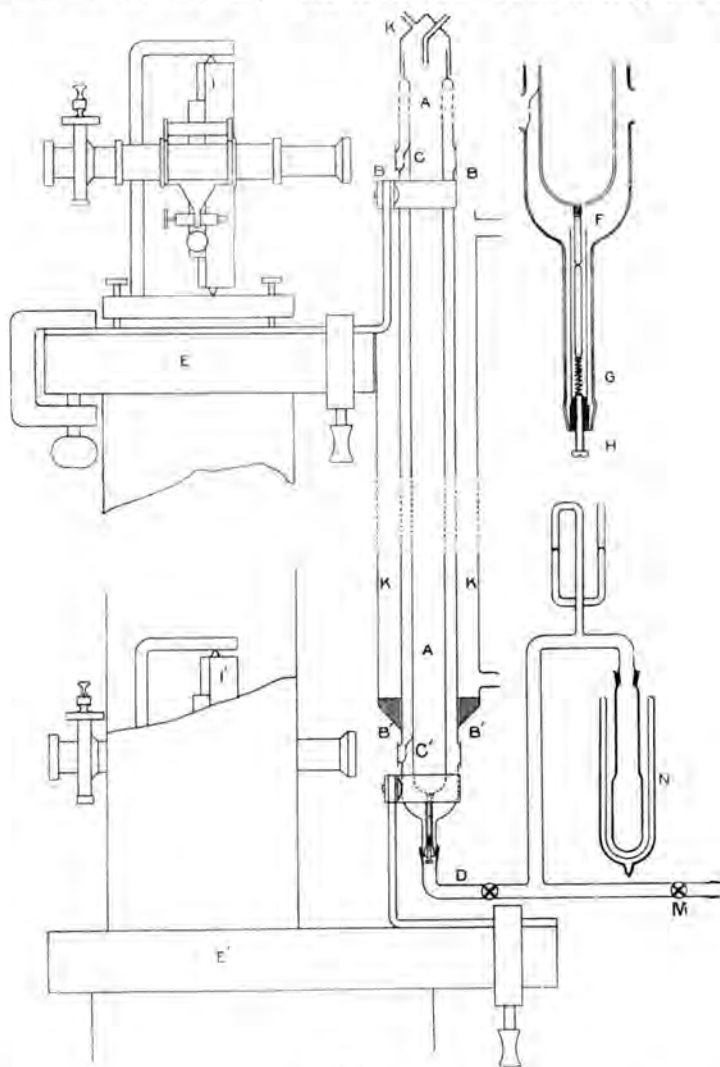


Fig. 1.

rigidly on a stone pillar, a bad conducting, elastic support (F, G) being inserted to prevent oscillations of the long freely hanging inner tube, which would have made measurements impossible. The micrometer eyepieces of the microscopes were calibrated by repeated measurements of some mM . divisions of a standardmeter.

During the measurements the vacuum was maintained by a charcoal tube (N), cooled in liquid air, which as well as the vacuum glass had previously been completely exhausted through the tap M . That part of the outer jacket, which was used for the measurement, was kept at constant temperature by running water.

Before and after each experiment at low temperature one or more measurements were made, with the inner tube kept at room temperature, in order to ascertain whether the tube had returned to its original length.

Before filling the tube with liquid hydrogen, the tube was first cooled by blowing through it for long time hydrogen, cooled with the aid of liquid air. The apparatus could stand this great cooling to 20° K, but the bottom of the inner tube burst at a first measurement at 100° C. by filling the tube with boiling water.

The temperature measurements were made as follows: from the pressure in the gass-reservoir the boiling point at the surface of the bath could be determined. The temperature-difference between the highest and the lowest point could be calculated from the height of the liquid-columns.

Because of the uncertainty of the boiling point of the ethylene it was considered advisable to read the temperature on a gold-resistance-thermometer, which was calibrated with the platinum-thermometer Pt₂₃¹⁾. Also some measurements were made at $\pm 100^\circ$ C. This temperature was obtained by circulating boiling water, supplied by vacuum pipes, through the inner tube. The temperature was read on a mercury-thermometer, divided in hundredths of degrees.

3. Results.

The length of the inner tube, measured between the two platinum points, at 13.1° C., was 893,64 mM. ± 0.02 . By means of a simple calculation the length-difference between inner and outer tubes, both from point to point, could be determined from the measured distances of the points. After having applied some corrections for small temperature-differences we obtain the following results. (See the table on the following page).

From the foregoing the linear expansion of 1 M. of Jena-glass 16^{III} follows:

Temperatures:	Linear expansions:
from 13.1 to 97° 8 C.	0.671 10^{-3} M.
—102.8	—0.770
—182.5	—1.176
—252.8	—1.294

4. Remarks.

The accuracy of the micrometer-measurements may be supposed to be about 2 à 3 μ . The results however do not possess this accuracy, as the points did not come back exactly to their original place. Still the differences are but small, as the foregoing tables show.

¹⁾ The calculations and the temperature-observations for these and following measurements are done by Miss H. v. D. HORST, whom we thank very much for her accurate assistance.

Date	Temp. inside	Temp. outside	$L_{inner} - L_{outer}$	Number of determinations
Measurement in liquid hydrogen.				
6.2.23	13.1	9.1	0.068 mms.	12
6.2.23	— 252.8	9.1	1.226	5
2 nd filling	— 252.8	9.1	1.224	5
7.2.23	13.1	9.1	0.073	5
so that the contraction is 1.157 mms. at a temperaturefall from 13°.1 to — 252°.8 C.				
Measurement in liquid oxygen.				
10.2.23	13.1	9.1	0.071	5
10.2.23	— 182.5	9.1	1.132	9
2 nd filling	— 182.5	9.1	1.129	9
12.2.23	13.1	9.1	0.089	5
20.2.23	13.1	9.1	0.076	6
20.2.23	— 182.5	9.1	1.126	6
21.2.23	13.1	9.1	0.073	6
so that the contraction is				
10.2.23: 1.051 mms.				
20.2.23: 1.051 „				
at a temperaturefall from 13°.1 to — 182°.5 C.				
Measurement in liquid ethylene.				
27.3.23	14.1	14.1	— 0.081	6
28.3.23	— 102.8	14.1	0.613	15
14.4.23	14.1	14.1	— 0.084	6
from which follows contraction of 0.695 mms. from 14°.1 to — 102°.8 C.				
Measurement at the boiling-point of water.				
30.11.23	13.1	13.1	0.070	10
6.12.23	13.1	13.1	0.053	5
6.12.23	97.8	13.1	— 0.532	10
10.12.23	13.1	13.1	0.076	4
so that a temperature-increase from 13°.1 to 97°.8 C. causes an expansion of 0.599 mms.				

The values obtained for the contraction at ethylene- and oxygen-temperatures are ± 3 and $\pm 6\%$ smaller than those, that follow from Comm. No. 95b from measurements of the expansion of a rod of Jena-glass 16^{III}. As the measured vacuum tube was already more than ten years old, it was our intention to repeat the measurements with new Jena-glass in order to observe, how far the age of the glass influences the thermal expansion. Because of lack of time this intention, as well as a measurement with a bath of liquid helium still waits completion.

5. Representation of the observations by a formula.

As it appeared to be impossible to represent the results by a third degree equation of the form:

$$l = l_0 \left[1 + \left\{ a \frac{t}{100} + b \left(\frac{t}{100} \right)^2 + c \left(\frac{t}{100} \right)^3 \right\} 10^{-6} \right]$$

as was the case in Comm. No. 95b, and as it was also impossible to obtain another formula with 3 coefficients which would better represent the results, we calculated the coefficients of an equation of the form:

$$l = l_0 \left[1 + \left\{ a \frac{t}{100} + b \left(\frac{t}{100} \right)^2 + c \left(\frac{t}{100} \right)^3 + d \left(\frac{t}{100} \right)^4 \right\} 10^{-6} \right]$$

and obtained for them and for the corresponding coefficients of the formula for the cubical expansion the following values:

$a = 716.8$	$k_1 = 2150$
$b = 48.33$	$k_2 = 136$
$c = 9.02$	$k_3 = 27$
$d = 10.9$	$k_4 = 33.$

6. Graphical representation of the thermal expansion.

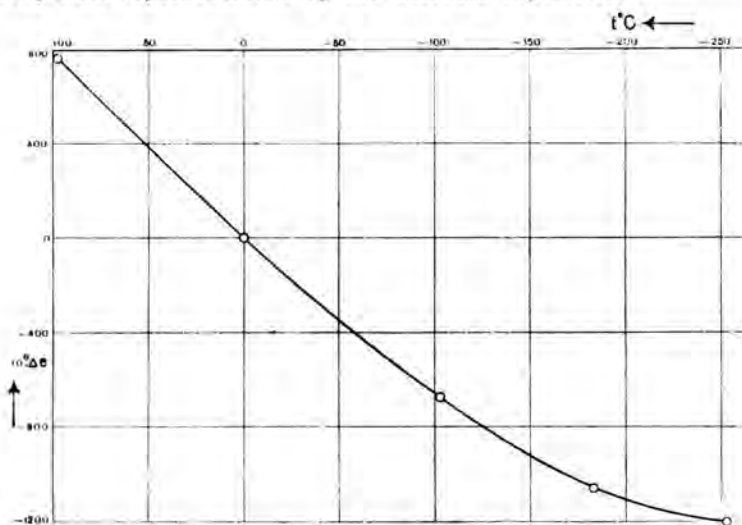


Fig. 2.

With the aid of the foregoing formula the expansion of 1 M. between 13° and 0° C was calculated and after that the length-change from 0° C. downward. Fig. 2 represents the length-change above and below 0° C. and shows, how small this change still is in the hydrogen domain.

7. The expansion coefficient.

Though the number of the observations is too small to deduct from them the expansion-coefficient accurately, the general values can still be represented graphically.

We have:

$$\Delta l = l_0 \int_{t_1}^{t_2} a_t dt.$$

a_t being the expansion coefficient, Δl the length-extension from t_1° to t_2° , l_0 the length at 0° C.

Also is

$$\Delta l = l_0 \bar{a}_{t_1 t_2} (t_2 - t_1)$$

the mean expansion coefficient between t_1 and t_2 being $\bar{a}_{t_1 t_2}$; and so

$$\int_{t_1}^{t_2} a_t dt = \bar{a}_{t_1 t_2} (t_2 - t_1).$$

So the curve, which represents a_t in an a_t, t -diagram, must be drawn so that the left and the right terms of the foregoing equation represent the same areas. So we derive the curve of fig. 3 from the following mean expansion coefficients:

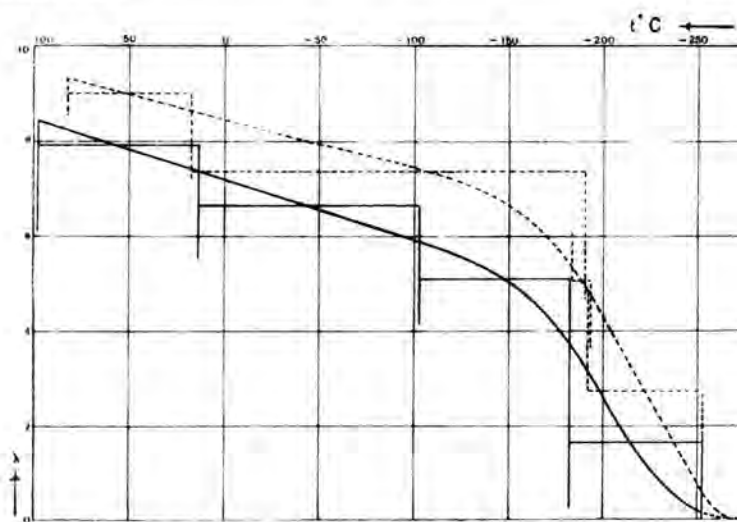


Fig. 3.

$t_2 - t_1$	$10^6 \bar{a}_{t_1 t_2}$
97.8 - 13.1	7.93
13.1 - (-102.8)	6.64
102.8 - (-182.5)	5.10
182.5 - (-252.8)	1.65

It is clear that, at low temperature, a_t does not vary linearly with the absolute temperature, but shows the character of the specific heat.

In the last mentioned figure there is also represented the relative expansion coefficient of the unknown kind of glass of LINDEMANN with regard to quartz, derived from his observations. From a comparison with our results it appears, that this curve actually almost represents the character of the glass-expansion. If we suppose that the same is the case for the other substances, of which LINDEMANN has measured the expansion with regard to quartz, we may conclude from fig. 4 in which the

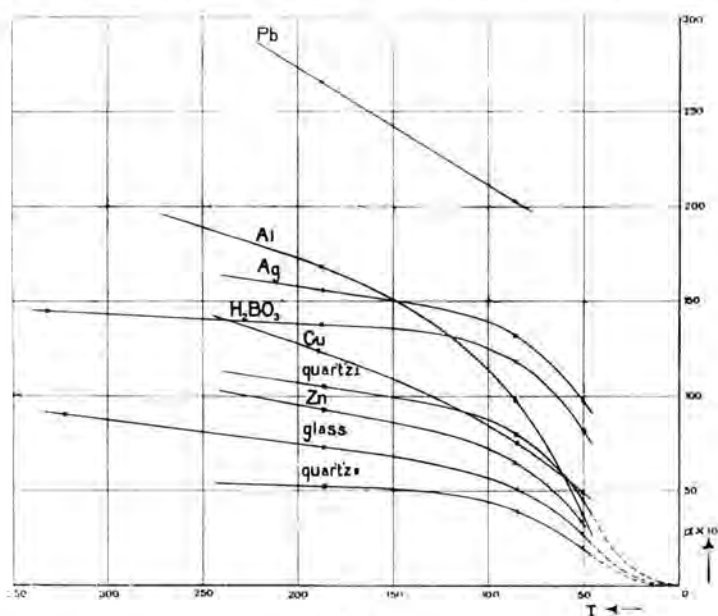


Fig. 4.

expansion coefficient for several solid substances after their results are represented graphically as accurately as possible, that for most substances the form of the curve of the expansion-coefficient is the same as for glass.

Though a further investigation is desirable, our observations, just as those of LINDEMANN, agree better with the law of DEBIJE, after which at sufficiently low temperatures, the expansion-coefficient is proportional to T^3 , than with the law of BORN after which at the temperatures in question the expansion-coefficient would be proportional to T .

Physics. — *"Isotherms of mon-atomic substances and their binary mixtures. XXV. The same of di-atomic substances. XXXI. The compressibility of hydrogen- and helium-gas between 90° and 14° K."* By F. P. G. A. J. VAN AGT and H. KAMERLINGH ONNES. (Comm. N^o. 176b from the Physical Laboratory at Leiden).

(Communicated at the meeting of June 27, 1925).

§ 1. *Introduction.* The investigation of the compressibility of hydrogen- and helium-gas at the boiling-point of hydrogen made by PALACIOS MARTINEZ and KAMERLINGH ONNES (Comm. Leiden N^o. 164) has been continued by us particularly at lower temperatures. Also some measurements have been made at the same and at higher temperatures. All the measurements were differential, a method which unexpectedly did not succeed in the first mentioned investigation, as the pressure difference between the hydrogen- and the helium-sides for the high densities appeared to be too great for simultaneous pressure-measurements of both gases. Finally the contents were interchanged in order to investigate if possible asymmetries in the apparatus could influence the results.

The new experiments were especially made for the purpose of determining accurate values for the second virial-coefficient in the empirical equation of state

$$pv = A + Bd + Cd^2 + Dd^3 \text{ etc. } ^1)$$

in order to verify and extend the determinations of the same quantity of KAMERLINGH ONNES and DE HAAS. (Comm. Leiden N^o. 127).

In the case of the smaller densities, which were used in our measurements ($d_A \leq 12$) the influence of the coefficients from C on could be neglected, so that our method was particularly adapted for accurate determination of the B 's.

With the B -values obtained it was possible to calculate the corrections for reducing the scales of the international hydrogen- and helium-thermometers to the Avogadro-scales of these gases.

§ 2. *The apparatus.*

This was practically the same as that used by PALACIOS MARTINEZ and KAMERLINGH ONNES, discussed in their above-mentioned communication. Only the couplings in the capillaries connecting the pipettes to the thermometer were removed, and the ends of the capillaries soldered

¹⁾ Comm. Leiden N^o. 71.

together. Though this made it somewhat less easy to dismount the apparatus, we decided to do it, after the lead-packing in these couplings, after having kept well closed for some time, began to leak at the most unsuitable moments. The new thermometer T_8 took the place of T_3 , which was accidentally broken. Later thermometer T_7 was replaced by T_9 for the measurements below the boiling-point of hydrogen, for, as already mentioned in § 1 PALACIOS MARTINEZ and KAMERLINGH ONNES did not succeed in measuring differentially the third and fourth densities because of the great pressure difference in the thermometers. By replacing one thermometer by a somewhat smaller one of a volume previously accurately calibrated, we succeeded in measuring, differentially, the four densities for hydrogen and helium at the same time.

The volumes of the new thermometers were:

$$T_9 = 103.195 \text{ cM}^3 \quad T_8 = 110.431 \text{ cM}^3.$$

After the whole apparatus had been dismounted, new measurements of the dead space volumes were necessary. For these we obtained:

$$\begin{aligned} v'_1 &= 0.762 & v_1 &= 0.772 \\ v'_m &= 0.066 & v_m &= 0.067. \end{aligned}$$

A thermo-regulator, filled with methyl-chloride, was first used, to maintain a constant temperature in the waterbath containing the pipettes for the pressure determinations at room-temperature. Later the same result was obtained by surrounding the water-bath with a thick mantle of very porous rubber which did not allow the room-temperature, differing only slightly from the bath-temperature, to change too much. In this way the use of the regulator, generally a difficulty, could be avoided. The following figure represents the result of the method.

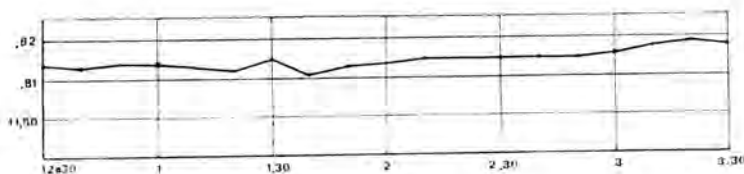


Fig. 1.

§ 3. Measurements and calculations.

These were made in the same way as communicated in detail in Comm. N^o. 164.

In the case of the determinations at the boiling-point of hydrogen the thermometers and pipettes were filled with ± 1000 mM. hydrogen and helium (zero-pressure) whilst for the measurements below the boiling-point it was necessary to reduce this pressure to about one half in order to avoid condensation of the hydrogen. This made it possible (see fig. 2)

to measure at $\pm 18^\circ \text{ K.}$ with 4, at $\pm 16,5^\circ \text{ K.}$ with 3, at $\pm 15,5^\circ \text{ K.}$ with 2 densities, and even at $14,5^\circ \text{ K.}$ a measurement with the smallest

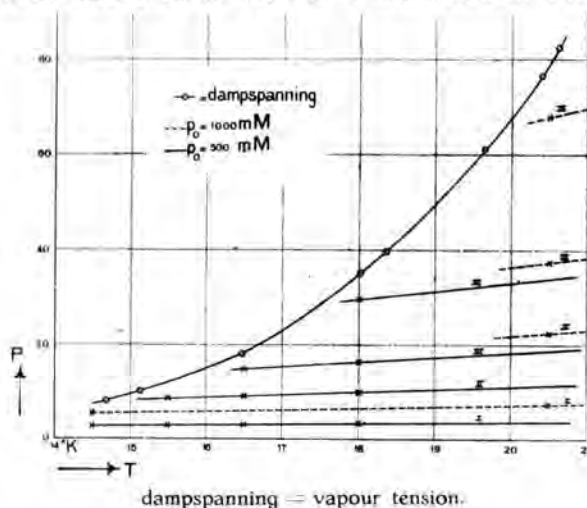


Fig. 2.

density ($d_A = \pm 0.7$) could be made, which could be combined with a determination at about the same temperature with the international hydrogen thermometer, of about twice the density.

Because of the size of the apparatus a smaller zero-pressure was not possible.

Afterwards measurements with the contents interchanged were made with the same zero-pressure and at $\pm 18^\circ \text{ K.}$ so that here also 4 densities could be worked with. The thermometers and pipettes were very carefully exhausted and washed before filling with the new and interchanged gases. The measurements could again be made simultaneously for both sides to the greatest density included.

For the calculation of pressures, virial-coefficients and densities we refer to Comm. N^o. 164 (pag. 22).

The following data underlie the calculation of the virial-coefficients at the temperatures of the waterbath.

Hydrogen ¹⁾		Helium ²⁾	
$A_{A0^\circ \text{ C.}}$	0.99942	$A_{A0^\circ \text{ C.}}$	0.99970
$B_{A0^\circ \text{ C.}}$	0.000580	$B_{A0^\circ \text{ C.}}$	0.000512
$A_{A100^\circ,20 \text{ C.}}$	1.36626	$A_{A100^\circ,35 \text{ C.}}$	1.36667
$B_{A100^\circ,20 \text{ C.}}$	0.000863	$B_{A100^\circ,35 \text{ C.}}$	0.000673

¹⁾ Comm. Leiden N^o. 100b.

²⁾ Comm. Leiden N^o. 102b.

From these data and with $\alpha_A = 0.0036618$ the corrections to be applied to the Celsius scales of the international hydrogen- and helium-thermometer in order to reduce these scale onto the Celsius-Avogadro scales of hydrogen and helium, based upon $\alpha_A = 0.0036618$, could be calculated, by means of the relation

$$\Delta_A = t_{Ax} - t_{ix} = \frac{t_{Ax} \cdot p_0}{A_{A0^\circ \text{C.}} \cdot \alpha_A} \times \left(\frac{B'_{100}(1 + 100\alpha_A) - B'_0}{100} - \frac{B'_T(1 + \alpha_A t_{Ax}) - B'_0}{t_{Ax}} \right)^{1)}$$

The temperature-determination will be discussed in detail in the following Communication.

§ 4. Results of the measurements.

1. *The temperature of the waterbath.* The readings of the mercury-thermometer P. T. R. N^o. 46371, corrected after several determinations of its zero-point, were repeatedly controled with the helium- and hydrogen-thermometer. The results were very satisfactory. Some of them are given in the following table.

Mercury-therm.	Helium-therm.	Hydrogen-therm.
15.531	15.540	—
15.527	15.532	—
12.753	12.755	12.752
12.758	12.764	—

2. *The gasquantities.*

Date	Measurements	H_2
23.1.23	in waterjacket	667.91
29.1.23	at 18 ^o .14 K.	—
"	at 15 ^o .67 K.	—
31.1.23	in waterjacket	667.85
7.2.23	at 90 ^o .23 K.	—
12.2.23	in waterjacket	667.89

¹⁾ Comm. Leiden Suppl. N^o. 23 pag. 904. This equation agrees with Suppl. N^o. 51a equation (25).

Of another filling:

Date	Measurements	H_2	He
17.6.24	in waterjacket	690.29	741.44
19.6.24	at 69°,85 K.	—	—
21.6.24	in waterjacket	690.33	741.43
24.6.24	at 16°,67 K.	—	—
25.6.24	in waterjacket	690.29	741.44
26.6.24	at 14°,54 K.	—	—
8.7.24	in waterjacket	690.28	741.42

Of the interchanged fillings:

Date	Measurements	H_2	He
17.7.24	in waterjacket	686.30	686.19
18.7.24	at 18°,22 K.	—	—
19.7.24	in waterjacket	686.44	686.32

In this case both gasquantities appear to have increased, from which one might conclude to a small leak at each side. This leak, however, should be just as large for the helium-side as for the hydrogen-side. Hence it seems more probable that for one of the two measurements the temperature has been read incorrectly.

3. Values of $p\nu_A$.

a. the left side (movable point-tube) is filled with hydrogen, the right side (stationary point-tube) with helium.

For the sake of completeness the results of PALACIOS MARTINEZ and KAMERLINGH ONNES ¹⁾ at the same temperature, recalculated with the same virial-coefficients at 0° C. and 100° C. and using the same expansion of Jena-glass 16^{III} that underlies all the present results, must be included here.

¹⁾ PALACIOS MARTINEZ and KAMERLINGH ONNES, Comm. Leiden N^o, 164.

The results communicated there were calculated for helium with $A_{A0} = 0.99950$ and $B_{A0} = 0.000499$, with the temperature correction for the expansion of glass obtained by extrapolating LINDEMANN's measurements, and so these differ somewhat from those given here.

N ^o .	Hydrogen			Helium		
	d_A	$p v_A$	O.—C.	d_A	$p v_A$	O.—C.
Measurements at 90°,23 K. ¹⁾						
1	0.71898	0.33011	+ 0.00001			
2	2.11256	0.32991	— 3			
3	3.55674	0.32977	+ 1			
Measurements at 69°,86 K.						
1	0.74379	0.25551	+ 0.00003	0.74310	0.25582	+ 0.00003
2	2.19020	0.25518	— 2	2.2150	0.25591	— 3
3	3.68698	0.25487	— 4	3.7153	0.25607	— 2
4	6.64996	0.25436	+ 3	6.6706	0.25641	+ 2
Measurements at 20°,55 K.						
1	1.32349	0.074561	+ 0.000001	1.32680	0.075229	+ 0.000037
2	6.42783	0.072163	+ 2	6.68009	0.075170	0
3	8.98884	0.070957	0	9.36906	0.075158	— 1
4	11.4336	0.069804	— 4	11.98147	0.075148	0
Measurements at 20°,53 K.						
1	1.33822	0.074449	— 0.000075	1.33583	0.075149	— 0.000001
2	3.84188	0.073332	— 5	3.99821	0.075127	— 1
2*				4.00075	0.075137	+ 9
3	6.4228	0.072124	+ 10	6.70706	0.075094	— 8
4	11.5316	0.069687	— 5	12.0625	0.075056	+ 2
4*	11.5322	0.069678	— 14			
Measurements at 20°,51 K. ²⁾						
1				1.33622	0.075153	+ 0.000083
2				3.95905	0.075046	+ 0
3				6.62529	0.075024	+ 2
4				11.8983	0.074973	— 1

¹⁾ The helium measurements were discarded as later an impurity was found in the filling.

²⁾ The hydrogen-thermometer was broken at the beginning of the measurements.

Measurements by PALACIOS MARTINEZ and KAMERLINGH ONNES:

Nº.	Hydrogen			Helium		
	d_A	$p\nu_A$	O.—C.	d_A	$p\nu_A$	O.—C.
Measurements at 20 ^o ,51 K.						
1	1.32857	0.074442	+ 0.000046	1.28965	0.074987	+ 0.000002
2	3.81226	0.073214	+ 5	3.82072	0.074984	+ 18
2*	3.81205	0.073202	— 7	3.82048	0.074945	— 21
3	6.37529	0.071990	+ 6	6.39307	0.074949	+ 2
4	11.4486	0.069555	— 4	11.48163	0.074906	— 3
Measurements at 20 ^o ,49 K. ¹⁾						
1	1.36628	0.074323	— 0.000005			
2	6.43773	0.071937	+ 3			
3	9.00150	0.070728	+ 4			
4	11.4495	0.069566	— 3			
Measurements at 20 ^o ,49 K. ¹⁾						
1	1.31556	0.074350	+ 0.00004			
2	6.37416	0.071930	— 8			
3	8.93236	0.070725	+ 5			
4	11.4188	0.069538	+ 1			

Here follow again the results of our own measurements.

Nº.	Hydrogen			Helium		
	d_A	$p\nu_A$	O.—C.	d_A	$p\nu_A$	O.—C.
Measurements at 18 ^o ,16 K. ²⁾						
1	0.72114	0.066140	+ 0.000032			
2	2.13567	0.065380	— 5			
3	3.59389	0.064624	— 32			
4	6.48021	0.063202	+ 4			

¹⁾ On the helium side only the first density was measured.²⁾ See note for the measurements at 90^o.23 K. (note 1 p. (679).

N ^o .	Hydrogen.			Helium		
	d_A	$p\nu_A$	O.—C.	d_A	$p\nu_A$	O.—C.
Measurements at 16 ^o ,65 K. ¹⁾						
1	0.74516	0.060743	0.000197	0.74442	0.060897	—0.000045
2	2.20766	0.059776	0	2.23038	0.060905	0
3	3.71491	0.058982	0	3.73868	0.060868	0
Measurements at 15 ^o ,64 K. ²⁾						
1	0.72123	0.056851				
2	1.33022	0.056514				
Measurements at 14 ^o ,50 K. ³⁾						
1	0.74508	0.052630				
2	1.32974	0.052284				
2*	1.32014	0.052297				

b. Interchanged fillings. The left side (movable point-tube) is filled with helium, the right side (stationary-point-tube) with hydrogen. (See table following page).

Before stating the coefficients calculated from these data, for which the corresponding differences between observed and calculated $p\nu_A$'s are

¹⁾ If one tries to represent these 3 points by an equation, one finds impossible B -values, and improbable values for O.—C. It seemed better therefore to give little weight to the first density which at these low temperatures is measured with pressures of but a few cm of mercury, and to draw a straight line through the points 2 and 3. The control which would have been given by more points, is lacking in this case.

²⁾ At first we found at 15^o,67 K.:

1. 0.721228 0.056829.
2. 2.136585 0.055871.

The very large value for B_A which results from these, renders it probable that there is an error in one of the two measurements. Therefore values for d_A and $p\nu_A$ were calculated from a measurement of CATH and KAMERLINGH ONNES (Comm. Leiden N^o. 156, table 1*b*) at a somewhat lower temperature, with the differential thermometer filled with helium and hydrogen. Combination of this $p\nu_A$ with measurement N^o. 1, both reduced to the same temperature, gives a B_A , which is in complete agreement with all the others, whilst N^o. 2 does not give that agreement.

³⁾ A second point is obtained from the measurements of CATH and KAMERLINGH ONNES mentioned in ²⁾. Here two determinations could be used, one at a somewhat lower, the other at a somewhat higher temperature.

Nº.	Helium			Hydrogen		
	d_A	$p\nu_A$	O.—C.	d_A	$p\nu_A$	O.—C.
Measurements at 18,22 K.						
1	0.74063	0.066770	+ 0.000099 ¹⁾	0.74035	0.066294	+ 0.000005
2	2.1940	0.066635	+ 1	2.21855	0.065536	— 7
3	3.6909	0.066599	+ 1	3.71861	0.064787	+ 2
4	6.6472	0.066523	0	6.68772	0.063282	— 4
4*	6.6581	0.066526	— 3			

already given in the foregoing tables, we can make the following remarks:

1. The measurements at 20°,50 K. may certainly (see PALACIOS MARTINEZ and KAMERLINGH ONNES) be supposed to have an accuracy for the $p\nu_A$'s of $1/10000$. The same is true for the measurements at 70° and 90° K. For the other measurements, at which the zero-pressure was always 500 mM., this accuracy is reached for the normal-volumes, but not for the $p\nu_A$'s, as here pressures of 2 à 3 cM. of mercury had to be measured. Moreover once or twice abnormal errors appeared, which are seen in the columns O—C, and which are possibly due to the still too narrow tap-openings, which perhaps were filled up with tap-grease, so that with very small pressure differences there was not a free passage.

2. The accuracy of the B -values is seen best from the complete agreement of the results at 20°,53 K. and 20°,55 K. as well as from the agreement with the B 's of PALACIOS MARTINEZ and KAMERLINGH ONNES at these temperatures.

Also at 18°,2 K. the measurements with normal and with the interchanged fillings gave the same values.

With the B -values, derived from only two points, one has to be very careful in drawing conclusions, as appears clearly from the measurement at 15°,6 K., but particularly when the two points are not measured isothermally. The B_A 's lying on a smooth curve, (see below) inspire confidence.

The smaller B -values at 70° and 90° K. are proportionally less accurate for the greater values $p\nu_A$. The same is true for these of helium at 70° K. and more so for the very small B -values in liquid hydrogen. Still we obtain as the average of three determinations at about the same temperature

$$-0.0000072$$

¹⁾ This point has been discarded for the calculation of B_A .

whilst PALACIOS MARTINEZ and KAMERLINGH ONNES obtained:

$$-0.0000075.$$

3. After the fillings were interchanged, no deviations, but exactly the same results were obtained, so that there is no reason to suppose any asymmetry.

4. The measurements, including those with interchanged fillings confirm the conclusion, which PALACIOS MARTINEZ and KAMERLINGH ONNES drew, concerning the possible presence of quanta-influences in the form of a term $Qd^{2/3}$ in the equation of state. We also find that the measurements do not necessitate the interpolation of such a term in the equation of state.

5. The B -values of KAMERLINGH ONNES and DE HAAS at $20^{\circ}.6$ and $17^{\circ}.8$ K. differ about 2 and 4 % with those, determined here, whilst the value at 16° K. differs completely.

4. *Virial-coefficients of hydrogen.*

At the measured temperatures following coefficients were obtained:

T	A_A	B_A
$90^{\circ}.23$ K	0.33019	— 0.0001202
69.86	0.25562	1939
20.55	0.075182	4700
20.53	0.075158	4740
18.16	0.066472	5053
16.65	0.060938	527
15.64	0.057250	5533
14.50	0.053063	581
interchanged fillings:		
18.22	0.066663	5055
From PALACIOS MARTINEZ and KAMERLINGH ONNES:		
20.51	0.075031	— 0.000478
20.49	0.074973	472
20.49	0.074972	476

Fig. 3 represents the B -values obtained, and also the results of KAMERLINGH ONNES and BRAAK ¹⁾ and of KAMERLINGH ONNES and DE HAAS (resp. indicated by \square and \triangle).

¹⁾ Comm. Leiden N^o. 100a.

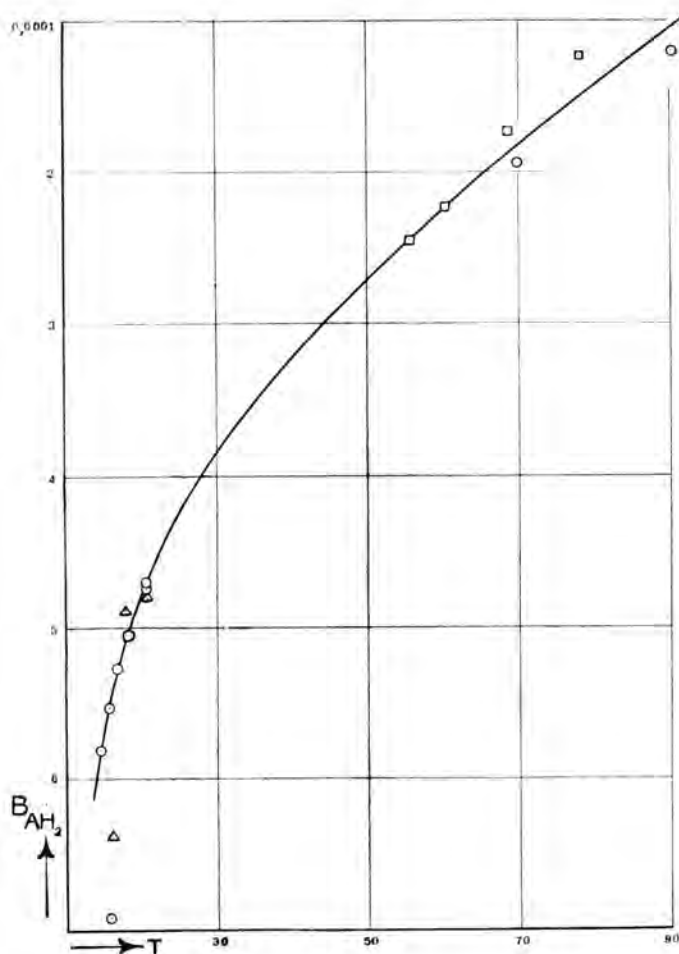


Fig. 3.

From the B -values result the following corrections, to be applied to

Corrections of the international hydrogen-thermometer
onto the Celsius-Avogadro scale.

$$(a_A - a_{iH_2} = -0,000\,0009)^1)$$

T	t	$\Delta_A = t_{A\alpha} - t_{H_2\alpha}$
90.23 K.	- 182.86C	+ 0.067
69.86	203.23	72
20.55	252.54	12 1
20.53	252.56	122
18.16	254.93	131
16.65	256.74	137
15.64	257.45	146
14.50	258.59	155

¹⁾ The numbers given here are somewhat different from those given in Comm. Leiden Suppl. N^o. 51a Table XI, owing to the somewhat changed value of $\alpha_A - \alpha_{iH_2}$.

the temperatures on the Celcius-scale of the international hydrogen-thermometer, in order to reduce these temperatures onto the Celsius-Avogadroscale of this gas, (Fig. 4).

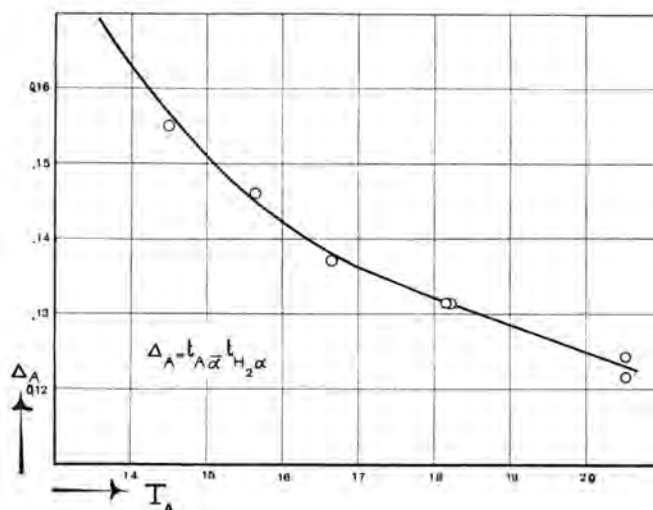


Fig. 4.

5. Virial-coefficients of helium.

T	A_A	B_A
69.86	0.25572	± 0.0001003
20.55	0.075198	$- 0.0000042$
20.53	0.075162	90
20.51	0.075082	91
18.22	0.066689	244
16.65	0.060960	245
From PALACIOS MARTINEZ and KAMERLINGH ONNES:		
20.51	0.074963	$- 0.0000074$

We obtain from this graphically the BOYLE-point of helium at $22^{\circ},1$ K. From the foregoing results can be calculated the following corrections for the intern. helium-thermometer. (See table following page).

In fig. 5 the results of KAMERLINGH ONNES¹⁾ are also given, indicated by \square .

¹⁾ Comm. Leiden N^o. 102b.

Corrections for the international helium-thermometer onto
the Celsius-Avogadro scale.

$$(\alpha_H - \alpha_{iHe} = 0,000\,000\,3^{\circ})$$

T	t	$\Delta_A = t_{A\alpha} - t_{He\alpha}$
69.86 K.	- 203.33C.	+ 0.031
20.55	252.54	41
20.53	252.56	42
20.51	252.58	43
18.22	254.87	46
16.65	256.44	46

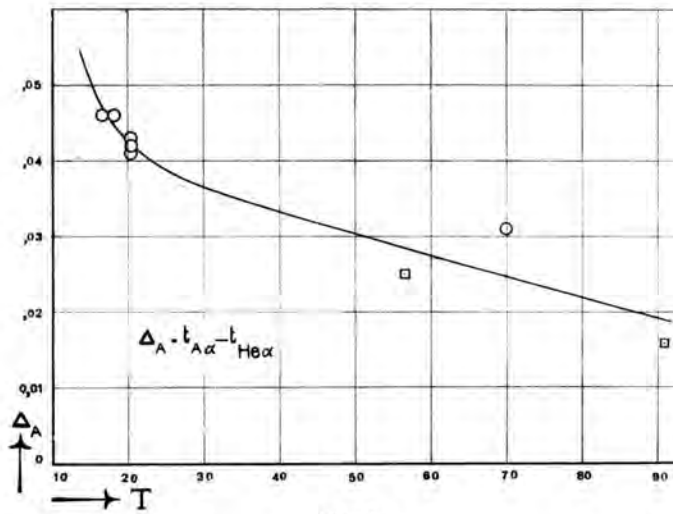


Fig. 5.

Physics. — *"Isotherms of di-atomic substances and their binary mixtures.*

XXXII. *On the behaviour of hydrogen according to the law of corresponding states."* (Comm. N^o. 176c from the Physical Laboratory at Leiden). By F. P. G. A. J. VAN AGT. (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of June 27, 1925).

In order to see how far hydrogen deviates from the law of corresponding states the values of B_A and T given in the previous communications are converted into the reduced magnitudes ¹⁾).

The following table is obtained where

$$B' = \frac{B_A}{A_A}$$

$$\mathfrak{B} = \frac{p_k}{RT_k} \cdot B'$$

$$t = \frac{T}{T_k}$$

Hydrogen		
T	t	\mathfrak{B}
90.23	2.7194	0.03835
69.86	2.1055	0.07991
20.55	0.6194	0.6586
20.53	0.6187	0.6644
18.22	0.5491	0.7981
18.16	0.5473	0.8008
16.65	0.5018	0.9111
15.64	0.4714	1.018
14.50	0.4371	1.1535
From PALACIOS MARTINEZ and KAMERLINGH ONNES :		
20.51	0.6181	0.6712
20.49	0.6175	0.6633
20.49	0.6175	0.6689

¹⁾ Comm. Leiden Suppl. N^o. 23. Die Zustandsgleichung. Math. Enz. V. 10, p. 116.

In the first place these values can be compared with the values of \mathfrak{B} from the "mean reduced equation of state" of KAMERLINGH ONNES in the form VII 1:

$$10^3 \mathfrak{B} = 117,796 - \frac{228,038}{t} - \frac{172,891}{t^2} - \frac{72,765}{t^4} - \frac{3,1788}{t^6} \quad 1)$$

obtained from the observations:

of AMAGAT for hydrogen, oxygen, nitrogen and ether;

of RAMSAY and YOUNG for ether;

of YOUNG for isopentane.

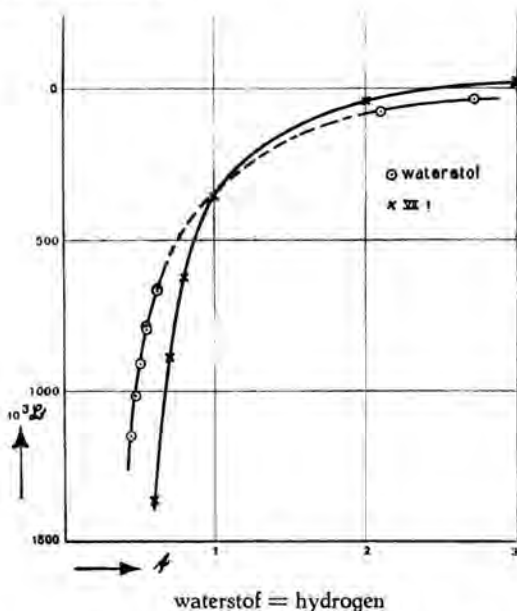


Fig. 1.

It seems valid to consider the \mathfrak{B} -values below 20,°50 K. and above 69,°86 K. in fig. 1, as lying on the same curve.

The diagram becomes more remarkable when besides the \mathfrak{B} -values of hydrogen, those \mathfrak{B} 's are represented, which can be calculated from the B' -values, which CATH and KAMERLINGH ONNES derived from their provisional corrections on the experimental Avogadroscals of hydrogen, oxygen, argon and neon (See table following page).

It then appears from fig. 2, that at temperatures above $t = 1$ the \mathfrak{B} -values form a regular series almost corresponding with the increase of the critical temperature. Here again the general rule, given by KAMERLINGH ONNES and KEESOM ²⁾ is proved, that for substances, for which association is excluded, the critical temperature has an important influence on the whole network of isotherms with regard to the law of corres-

1) Comm. Leiden Suppl. N^o. 23. p. 117.

2) Comm. Leiden Suppl. N^o. 23. § 34c.

Argon			Nitrogen		
T	t	$10^3 \mu$	T	t	$10^3 \mu$
249.04	1.653	— 81.61	241.40	1.916	— 55.90
230.03	1.527	111.4	208.88	1.658	97.29
207.57	1.378	147.9	189.31	1.502	129.2
191.06	1.268	180.1	170.17	1.350	172.8
170.81	1.134	235.8	157.59	1.251	201.1
161.64	1.073	261.9	145.58	1.155	238.9
150.30	0.998	303.7	132.99	1.055	294.8
139.95	0.929	350.6	120.75	0.958	373.9
125.01	0.830	464.6	109.65	0.870	456.7
109.69	0.728	591.6	90.65	0.719	628.0
90.63	0.602	862.2	84.19	0.668	718.8
87.56	0.581	943.1	76.37	0.606	871.2
94.55	0.561	989.2	71.53	0.567	1009.2
81.32	0.540	1056.3	69.57	0.552	1060
Neon			Oxygen		
T	t	$10^3 \mu$	T	t	$10^3 \mu$
230.15	5.144	+ 59.0	243.51	1.578	— 126.0
208.86	4.668	54.1	214.46	1.390	159.8
185.16	4.145	42.6	180.76	1.171	239.8
170.96	3.821	36.1	170.36	1.104	284.9
157.77	3.526	31.2	157.87	1.023	316.2
145.58	3.254	23.0	145.83	0.945	371.0
133.19	2.977	14.8	133.10	0.863	437.0
120.73	2.698	1.64	120.20	0.779	531.7
90.69	2.027	— 55.8	90.58	0.587	912.2
82.28	1.839	75.5	87.09	0.564	999.1
72.71	1.625	116.6	84.15	0.545	1085.9
64.15	1.434	162.4			
55.91	1.249	224.8			

ponding states. At least for hydrogen, neon, nitrogen and argon this relation exists. Oxygen on the contrary, which for clearness has not

been included in the figure, was almost coinciding with nitrogen. Hence for this substance the rule does not hold. We also see the same difference noted by KEESOM ¹⁾ in a diagram of CATH and KAMERLINGH ONNES ²⁾ of their vapour pressure determinations.

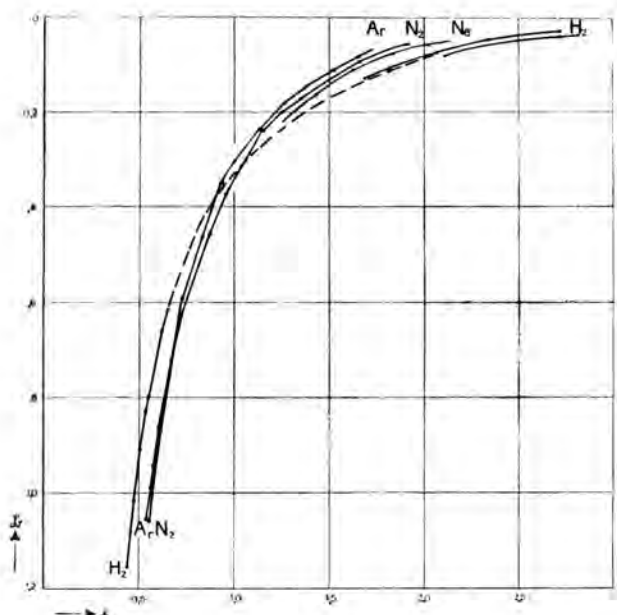


Fig. 3.

It cannot be said how far the method of determination influences the accuracy of the B -values. CATH ³⁾ has already remarked, that the B' -values of argon determined by him, are generally somewhat greater than those, which result from the measurements of KAMERLINGH ONNES and CROMMELIN.

Also some \mathfrak{B} -values of hydrogen, derived from the determinations of KAMERLINGH ONNES and BRAAK are included in the figure; they lie somewhat higher than our values.

On inspecting this diagram the question arises whether, for all this substances, the \mathfrak{B} -lines would or would not intersect at about $r=1$. Also in regard to this we regret that the time was too short to determine the B -values of neon below the critical temperature.

Finally we can complete with our B -values the diagram of CATH and KAMERLINGH ONNES ⁴⁾, which indicates the changing of $\frac{d(v_1)}{dp}$ with the temperature for the same substances.

¹⁾ Memorialvolume presented to H. KAMERLINGH ONNES 1922. p. 123.

²⁾ Comm. Leiden N^o. 152b.

³⁾ Thesis for the Doctorate, Leiden 1917 p. 77.

⁴⁾ Comm. Leiden N^o. 156a p. 31.

Here use is made of the relation:

$$\frac{d(\gamma)}{d\lambda} = \frac{1}{v_k} \frac{d(pv)}{dp} = \frac{B'}{v_k} = K_4 \cdot \mathfrak{B}^{1)}.$$

In this way is obtained:

Hydrogen		
T	$1/t$	$\frac{d(\gamma)}{d\lambda}$
90.23 K.	0.3677	— 0.12645
69.86	0.4749	0.26349
20.55	1.6146	2.1715
20.53	1.6162	2.1907
18.22	1.8211	2.6314
18.16	1.827	2.640
16.65	1.993	3.004
15.64	2.121	3.358
14.50	2.288	3.803

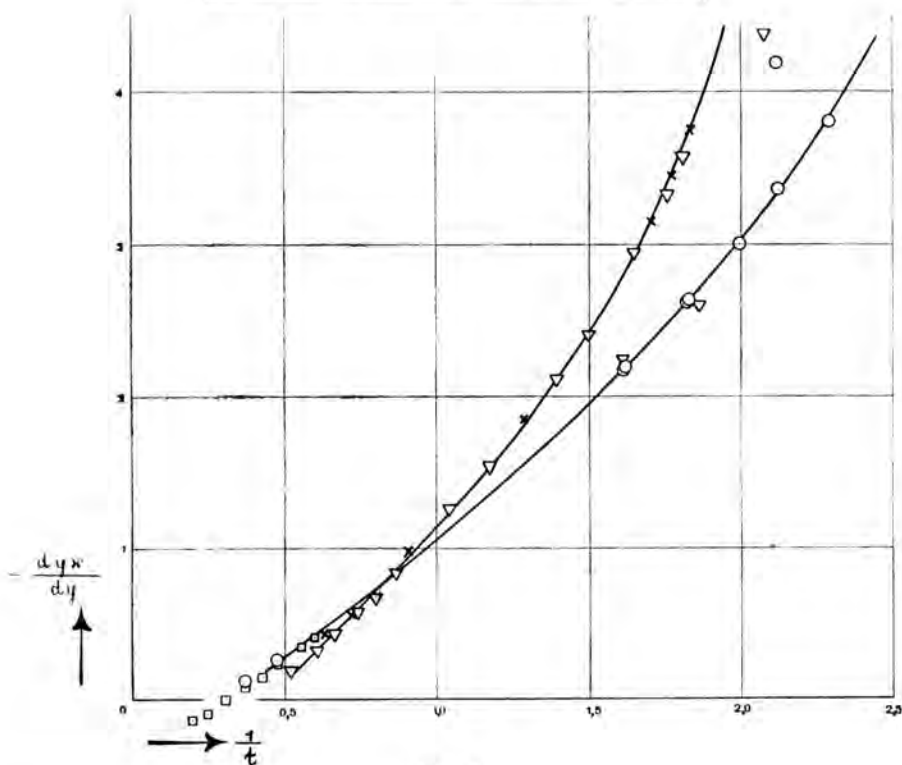


Fig. 3

¹⁾ Ibid. p. 29.

For reducing the results to reduced magnitudes, use is made of the following data:

	p_k	T_k	ν_k
Hydrogen ¹⁾	12.751	33.18	0.002909
Neon ²⁾	26.86	44.74	
Nitrogen ³⁾	33.490	125.96	0.004027
Argon ⁴⁾	47.996	150.65	0.003357
Oxygen ⁵⁾	49.713	154.27	0.003324

¹⁾ Comm. Leiden N^o. 151c.

²⁾ " " " 151b. ν_k is not known sufficiently.

³⁾ " " " 145c.

⁴⁾ " " " 131a.

⁵⁾ " " " 117.

Physics. — "*On the measurement of very low temperatures. XXXIII. The comparison of the constant volume hydrogen- and helium-thermometers with various zeropoint-pressures.*" (Communication N^o. 176d from the Leiden Physical Laboratory). By F. P. G. A. J. VAN AGT and H. KAMERLINGH ONNES.

(Communicated at the meeting of June 27, 1925).

1. *Introduction.*

The experiments made with the constant volume differential thermometer, described in the Communication N^o. 176b, enable us to compare the hydrogen- and helium-scales with each other directly and with very different zeropoint-pressures, for it was possible, using pipettes, to increase considerably the density in the thermometers. The hydrogen- and helium-thermometers were placed side by side at the same height in the low temperature bath, whilst the pressures of both gases were read on the same manometer¹⁾.

The *B*-values previously mentioned enable the corrections, necessary to reduce the temperatures of the hydrogen- and helium-scales for various zeropoint-pressures onto the Avogadro-scales of these gases, to be calculated, so that afterwards the latter could be compared.

During the same time Prof. BEATTIE has carried out in the Leiden Laboratory his research²⁾ on the comparison of the hydrogen- and helium-thermometers with various pressures in quartz reservoirs. The fact that the results thereby obtained are not in agreement with those that have been obtained for hydrogen- and helium-thermometers in glass reservoirs certainly raises the importance of both determinations.

2. *The temperatures of the hydrogen- and helium-thermometers on the Celsiusscale.*

If no direct measurements of the zeropoint-pressure had been made, we calculated from the known density (d_A) of the gas in the thermometer at the time of the measurement at the low temperature the pressure which this quantity of gas would exert if it occupied the same volume at 0° C., use being made of the empirical equation of state at 0° C.

¹⁾ See further in Comm. Leiden N^o. 156.

²⁾ Rapport N^o. 1 première Commission 4^{ième} Congrès International du Froid, London, p. 3.

with the same coefficients that were the basis of the calculation of the quantity of the gas.

The thus found values of p_0 could then be used, together with the directly measured values of the gas pressure in the thermometers at the low temperature (p_t) and with the help of the well known relation

$$t_s = \frac{p_t - p_0}{p_0 \alpha}$$

to calculate the temperatures on the Celsius scales of the hydrogen- and helium-thermometers¹⁾. The coefficients of expansion on which these scales are based were calculated in the following way:

CATH and KAMERLINGH ONNES adopted for the coefficients of expansion of the international helium- and hydrogen-thermometers the respective values

$$\alpha_{He} = 0.0036614, \text{ resp. } \alpha_{H_2} = 0.0036627.$$

The provisional international temperaturescale is derived from the scale of the international helium-thermometer, based on 0.0036614 with the help of the provisional correction-table given in Comm. N^o. 156a table V, col. 2²⁾. An Avogadro scale is thus formed for helium based on 0.0036617³⁾.

As KEESOM and KAMERLINGH ONNES³⁾ remark, the scale of the international hydrogen-thermometer, on the other hand, with the help of the corrections calculated with the B -values of KAMERLINGH ONNES and BRAAK, reduces to an Avogadro scale based on 0.0036616⁸⁾. This has the consequence that, extrapolating to -273°C . the Celsius-Avogadro scale for hydrogen should lie 0.003 degrees lower than that for helium (the provisional international scale).

We have preferred to evaluate the Celsius-Avogadro scales for helium and hydrogen on such a basis that, if extrapolating to -273°C ., they both give the same value.

For this purpose the expansioncoefficient was calculated in each case for a determined zeropoint-pressure from the expression:

$$\alpha = \frac{A_{A0^\circ \text{C}} \times 0.36618 + (B_{A100^\circ \text{C}} - B_{A0^\circ \text{C}}) d_A}{100 (A_{A0^\circ \text{C}} + B_{A0^\circ \text{C}} \times d_A)} \quad ^4)$$

which is in agreement with

$$\alpha = 0.0036618 + \left(\frac{B_{100}}{A_0} - 1.36618 \frac{B_0}{A_0} \right) \frac{d}{100} - \left(\frac{B_{100}}{A_0} - 1.36618 \frac{B_0}{A_0} \right) \frac{B_0}{A_0} \frac{d^2}{100} \quad ^5)$$

where for short

¹⁾ Compare the definitions of the temperaturescales in Comm. Leiden Suppl. N^o. 51a.

²⁾ Since reprinted in Suppl. N^o. 51a, table Xa.

³⁾ Suppl. N^o. 51a, p. 31.

⁴⁾ Comm. Leiden N^o. 101b.

⁵⁾ The last term is neglectable except at high densities such as appear here.

$$B_{100} = B_{A100^{\circ}\text{C}}$$

$$B_0 = B_{A0^{\circ}\text{C}}$$

$$A_0 = A_{A0^{\circ}\text{C}}$$

$$d = d_A.$$

The value of $\alpha_A = 0.0036618$ is thus used as a basis, whilst, with the already mentioned values of the virial-coefficients, the following values of the expansion-coefficients for the international helium- and hydrogen-thermometers were obtained

$$\alpha_{i\text{ He}} = 0.0036614^6$$

$$\alpha_{i\text{ H}_2} = 0.0036627^3.$$

The results were still corrected for the small temperature-differences between the different points of a measurement, besides for the first point of some measurements, also for the probable error in the read pressure at the low temperature (p_r), which caused the abnormal deviation (0—C) in the p_{vA} 's, as this error could be calculated from this deviation.

§ 3. *The temperatures on the Celsius-Avogadro-scales of hydrogen and helium based on $\alpha_A = 0.0036618 \cdot (t_{Ax})$.*

The values found could be used to calculate the corrections onto these scales. For this purpose the following expression was used

$$\Delta A = t_{Ax} - t_x = \frac{t_{Ax} p_0}{A_{A0^{\circ}\text{C}} \alpha_A} \cdot \left[\frac{B'_{100}(1 + \alpha_A \cdot 100) - B'_0}{100} - \frac{B'_T(1 + \alpha_A t_{Ax}) - B'_0}{t_{Ax}} \right]^1)$$

$$\text{where } B' = \frac{B_A}{A_A}$$

and where for α_A and the virial-coefficients at 0 and 100° C. the already mentioned values were used.

In the following tables (p. 698—700) the so found temperatures and also the corrections for the hydrogen- and helium-thermometers are given. In order to make the results clearer, the temperatures, which all lie below —140° C., have been reduced from the Celsius-Avogadro-scales onto the (Kelvin) Avogadro-scales of both gases using

$$t_{Ax} = T_{Ax} - \frac{1}{\alpha_A}^2)$$

and these are shown under (T_{Ax}).

Finally each isotherm furnishes a direct temperature determination on the Avogadro-scale "36618", if they are extrapolated to the density $d_A = 0$, for which condition the equation

1) Comm. Leiden Suppl. N^o. 23 p. 904. This equation is in agreement with Suppl. N^o. 51a eqn. (25).

2) Comm. Leiden Suppl. N^o. 51a p. 9.

$$\frac{T_{A\infty}}{T_{A0^{\circ}\text{C}}} = \frac{A_A}{A_{A0^{\circ}\text{C}}} \quad ^1)$$

still furnishes a value for $T_{A\infty}$.

§ 4. *Difference in the indication between the Celsius scales of the helium- and hydrogen-thermometers with different zeropoint-pressures.* (See the tables on the following page).

When the here obtained differences between the helium- and hydrogen-scales were graphed against the zeropoint-pressures (Fig. 1), it was seen that for the same density they increase with decreasing temperature, which is in agreement with earlier measurements.

At the same time it appears that at each temperature they decrease to zero proportionately with the zeropoint-pressure.

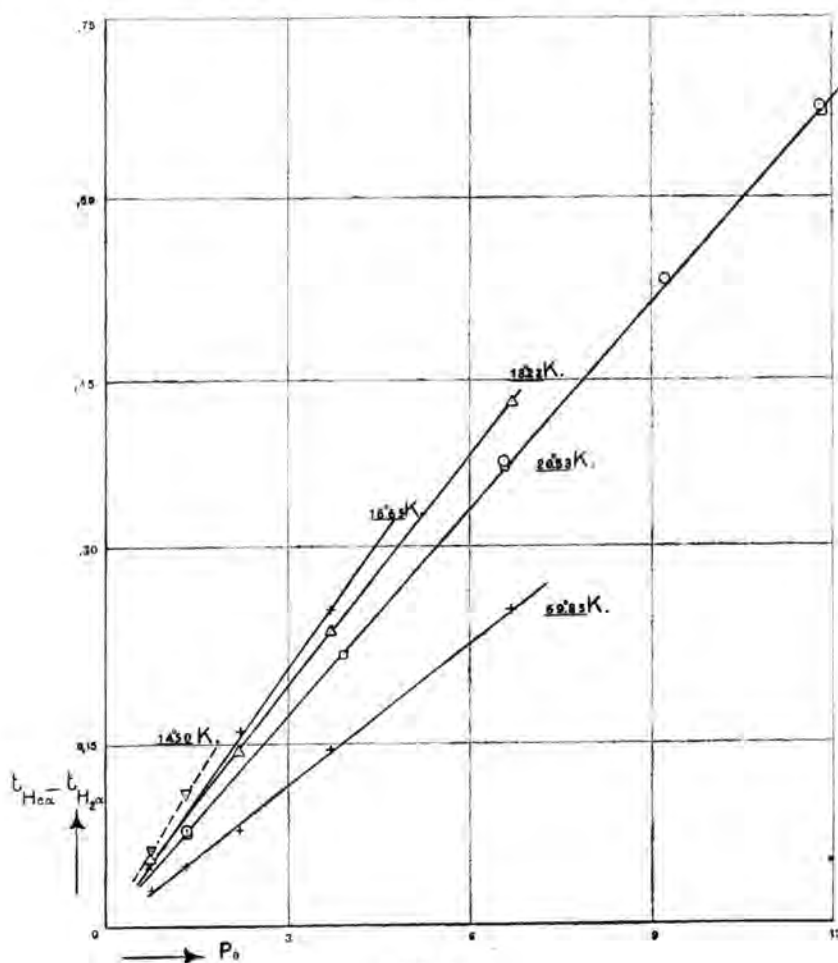


Fig. 1.

¹⁾ Comm. Leiden Suppl. N^o. 51a p. 6.

№.	Hydrogen		Helium		
	p_0	t_x	p_0	t_x	$t_{He x} - t_{H_2 x}$
Measurement at 69°,86 K.					
1	0.74369	— 203.272	0.74316	— 203.243	+ 0.029
2	2.19171	203.357	2.21682	203.287	0.073
3	3.69274	203.426	3.72128	203.301	0.129
4	6.67180	203.559	6.69134	203.305	0.254
Measurement at 20°,55 K.					
1	1.32374	— 252.668	1.32730	— 252.589	+ 0.079
2	6.44806	253.134	6.70094	252.751	0.383
3	9.03050	253.367	9.41120	252.835	0.532
4	11.50279	253.589	12.05136	252.913	0.676
Measurement at 20°,53 K.					
1	1.33849	— 252.675	1.33634	— 252.598	+ 0.077
2	3.84811	252.908	4.00520	252.685	0.223
3	6.44297	253.144	6.72808	252.771	0.373
4	11.6020	253.615	12.1334	252.943	0.672
Measurement at 20°,51 K. 1)					
1	1.32882	— 252.709	1.29011	— 252.643	+ 0.066
2	3.81848	252.942	3.82704	252.720	0.222
2*	3.81826	252.945	3.82681	252.729	0.210
3	6.39516	253.182	6.41208	252.802	0.380
4	11.51797	253.647	11.5457	252.964	0.683
Measurement at 18°,22 K. 2)					
1	0.74069	— 254.888	0.740232	— 254.945	+ 0.057
2	2.19580	254.953	2.22011	255.097	0.144
3	3.69676	255.000	3.72452	255.243	0.243
4	6.67883	255.105	6.70978	255.536	0.431
4*	6.67879	255.104			
Measurement at 16°,65 K.					
1	0.74505	— 256.517	0.74448	— 256.474	+ 0.043
2	2.2092	256.663	2.2322	256.500	0.163
3	3.7209	256.816	3.7448	256.562	0.254
Measurement at 14°,50 K.					
1	0.74497	— 258.676	0.74452	— 258.612	+ 0.064
2 3)	1.3156	258.546	1.3181	258.442	0.104
2* 3)	1.3177	259.085	1.3189	258.974	0.111

1) From PALACIOS MARTINEZ and KAMERLINGH ONNES. 2) Different filling.

3) Calculated from CATH and KAMERLINGH ONNES, Comm. Leiden №. 156.

§ 5. *Temperature-measurements on the Avogadroscale of hydrogen and helium based on $\alpha_A = 0.0036618$.*

Nº.	Hydrogen			Helium		
	p_0	Δ_A ¹⁾	T_{Ax}	p_0	Δ_A	T_{Ax}
Measurement at 90°, 23 K.						
1	0.71886	+ 0.036	90.232			
2	2.11393	0.106	90.226			
3	3.56201	0.179	90.217			
extrapolating to $d_A = 0$:			90.221			
Measurement at 69°, 86 K.						
1	0.74369	+ 0.040	69.859	0.74316	+ 0.018	69.864
2	2.19171	0.117	69.842	2.21682	0.054	69.849
3	3.69274	0.201	69.841	3.72128	0.090	69.855
4	6.67180	0.363	69.858	6.69134	0.159	69.890
extrapolating to $d_A = 0$:			69.848			68.855
Measurement at 20°, 55 K.						
1	1.32374	+ 0.122	20.544	1.32730	+ 0.041	20.542
2	6.44806	0.592	20.548	6.70094	0.207	20.546
3	9.03050	0.829	20.552	9.41120	0.290	20.545
4	11.50279	1.056	20.557	12.05136	0.372	20.549
extrapolating to $d_A = 0$:			20.538			20.542
Measurement at 20°, 53 K.						
1	1.33849	+ 0.128	20.540	1.33634	+ 0.043	20.535
2	3.84811	0.359	20.541	4.00520	0.125	20.530
3	6.44297	0.600	20.546	6.72808	0.208	20.527
4	11.6020	1.081	20.550	12.1334	0.374	20.521
extrapolating to $d_A = 0$:			20.536			20.532
Measurement at 20°, 51 K.						
				1.33673	+ 0.043	20.515
				3.96589	0.127	20.511
				6.64578	0.213	20.511
				11.96723	0.382	20.528
			extrapolating to $d_A = 0$:			20.510

¹⁾ In all these tables Δ_A signifies: $t_{Ax} - t_{He,x}$ for helium.
and $t_{Ax} - t_{H_2,x}$ for hydrogen.

№.	Hydrogen			Helium		
	p_0	Δ_A	T_{Ax}	p_0	Δ_A	T_{Ax}
Measurement at 20°,51 K. ¹⁾						
1	1.32882	+ 0.125	20.506	1.29011	+ 0.041	20.488
2	3.81848	0.358	20.506	3.82704	0.122	20.492
2*	3.81826	0.358	20.503	3.82681	0.122	20.483
3	6.39516	0.600	20.508	6.41208	0.204	20.492
4	11.51797	1.081	20.524	11.5457	0.367	20.493
extrapolating to $d_A = 0$:			20.502			20.488
Measurement at 20°,49 K. ¹⁾						
1	1.36657	+ 0.125	20.483			
2	6.45804	0.593	20.492			
3	9.04328	0.830	20.495			
4	11.51885	1.057	20.498			
extrapolating to $d_A = 0$:			20.487			
Measurement at 20°,49 K. ¹⁾						
1	1.31581	+ 0.123	20.493			
2	6.39403	0.595	20.487			
3	8.97346	0.836	20.491			
4	11.4878	1.070	20.491			
extrapolating to $d_A = 0$:			20.486			
Measurement at 18°,16 K.						
1	0.721025	+ 0.070	18.164			
2	2.13708	0.213	18.164			
3	3.59932	0.359	18.154			
4	6.50035	0.646	18.166			
extrapolating to $d_A = 0$:			18.163			
Measurement at 16°,65 K.						
1	0.74505	+ 0.078	16.651	0.74448	+ 0.024	16.650
2	2.2092	0.231	16.658	2.2322	0.071	16.661
3	3.7209	0.380	16.654	3.7448	0.119	16.648
extrapolating to $d_A = 0$:			16.651			16.643

¹⁾ From PALACIOS MARTINEZ and KAMERLINGH ONNES.

Nº.	Hydrogen			Helium		
	p_0	Δ_A	T_{Ax}	p_0	Δ_A	T_{Ax}
Measurement at 14°,50 K.						
1	0.74496	+ 0.088	14.502	0.74452	+ 0.026	14.504
Measurement at 18°,22 K. (different filling)						
1	0.74023	+ 0.074	18.219	0.74069	+ 0.027	18.229
2	2.22011	0.222	18.215	2.19580	0.078	18.215
3	3.72452	0.372	18.219	3.69676	0.130	18.220
4	6.70978	0.671	18.225	6.66783	0.236	18.221
4*				6.67879	0.236	18.222
extrapolating to $d_A = 0$:			18.215			18.218

The method of temperature-measurement followed here thus gives practically the same temperature results, even with very divergent zero-point-pressures and even with densities many times the density of the international gas-thermometers, where the corrections of the Avogadro-scale exceed one degree (for hydrogen). This is true for each gas individually, as well as for the comparison of the two gases.

If only those measurements are considered which have a zeropoint-pressure of 1000 mM., or where these are lacking those with densities lying immediately above and below it, then only the following differences remain between these experimental Avogadro-scales of hydrogen and helium:

T	p_0	$T_{AxHe} - T_{AxH_2}$
69.86	± 0.74	+ 0.005
	2.19	+
20.55	1.32	— 2
20.53	1.34	— 5
18.22	0.74	— 10
	2.21	0
16.65	0.74	— 1
	2.23	+ 3
14.50	0.74	+ 2

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Chemistry. — ERNST COHEN and W. D. J. VAN DOBBENBURGH: "*The influence of minute traces of Water on Equilibria of Solution*". I.

(Communicated at the meeting of June 27, 1925)

Introductory.

In the course of our investigations on the metastability of matter made in co-operation with Messrs MOESVELD, HELDERMAN, BRUINS and KOOP¹⁾, our attention has been drawn to salicylic acid, as, from more than one point of view, it is of importance to get better acquainted with the relations of stability between the modifications in which this substance can appear.

During this investigation, to which we hope to return later on, we have become acquainted with phenomena so very remarkable, and, as we found out, unknown up to the present, that we have suspended our intended investigation for the moment, in order to study these new phenomena quantitatively. This paper contains a description of the results obtained up to this time.

For the sake of lucidity we do not dwell on the relation between the investigation treated in this paper, and of the metastability of matter which has led to the measurements which are to be described. For us the thing was to determine the solubility in benzene of salicylic acid which had been recrystallized from different solvents. All the solubility determinations have been carried out at 30°.50 C.

A. The Materials used.

§ 1. *a. Salicylic acid.* The material with which we started our work was obtained from different factories. When it was found that the different preparations gave identical results, we have, in most cases, used a preparation of KAHLBAUM at Berlin („für kalorimetrische Bestimmungen"), and after recrystallizing it from the solvents which will be mentioned later on, taken it for our investigation.

b. Benzene. A preparation which had been supplied as not containing thiophene, really answered this requirement. For some days it was left in contact with an ample quantity of phosphorous pentoxide, and then slowly

¹⁾ Zeitschr. f. physik. Chemie **94**, 450, 465, 471 (1920); **108**, 81, 97, 100, 109 (1924); **113**, 145 (1924); **115**, 151 (1925).

distilled ¹⁾ by means of an electric lamp which was used as heater. The flask in which the distillate was collected, was protected from moisture by a tube, filled with CaCl_2 . It was closed afterwards with a glass stopper. The stock of benzene obtained in this way was in contact with the air only when the liquid was poured out of the flask.

c. *Ether*. This substance was treated like the benzene. The flask in which it was kept was closed with a cork.

d. *Water*. This liquid was slowly distilled out of a heavily tinned apparatus.

B. The Preparations of Salicylic Acid.

§ 2. The two preparations, mentioned under A. a. in § 1, were crystallized either from water, or from dried ether, in the way as is described hereafter, and then dried as indicated in every different case.

1. Preparations recrystallized from water.

a. To a certain quantity of solid salicylic acid so much water is added, that at about 100° all is dissolved, then it is filtered through a hot water funnel. By heating the filtered solution the acid is again completely dissolved. Then the flask which contains the solution, is quickly cooled in water of room temperature. The crystallized acid is sucked off on a hard filter, first dried in air between filter paper, and then dried in vacuo over P_2O_5 (for 48—72 hours).

b. The same method, as is described under a. is followed, but the crystallization is allowed to be very gradual.

c. Again the same method as under a. is applied, but the crystallization is very rapid, by pouring the solution on ice ("chilled").

When the preparations had been kept in vacuo over P_2O_5 for 48—72 hours they were sufficiently dry. This was controlled by investigating the change of weight of a few grammes of the preparation, dried in this way, after keeping it in the dessicator in vacuo for a longer period. In this way it was seen that drying for 24 hours longer did not lead to any perceptible change of weight.

2. Preparations recrystallized from ether.

A solution of salicylic acid in dry ether, saturated at room temperature, was put into a conical filtering flask, the tube of which is connected with a water-jet vacuum pump. The neck of the flask is closed with a rubber stopper, through which passed a rather wide glass tube. The latter is connected with three washing bottles, filled with strong sulphuric acid, care being taken that specks of the acid cannot enter the filtering flask by interposing an empty absorption bulb. When the water-jet vacuum pump is set going a (rapid) current of dry air passes through the solution. In

¹⁾ SIDGWICK, Journ. chem. Soc. London **117**, (2) 1340 (1920).

TH. W. RICHARDS, E. K. CARVER and W. C. SCHUMB, Journ. Am. Chem. Soc. **41**, 2019 (1919).

this way some 50 grammes of dry acid can be obtained in a few hours. This preparation was likewise kept in vacuo in a dessicator over P_2O_5 .

C. The Solubility determinations.

Experimental.

1. General Remarks.

§ 3. The salicylic acid was shaken with the benzene in flasks A, as is shown in fig. 1 (capacity about 50 c.c.) When the solid and the solvent had been put in by means of a funnel with a wide stem, the flasks were sealed, and then placed into the acatene shaking apparatus, previously described by ERNST COHEN and H. R. BRUINS¹⁾. In our thermostat, in which this apparatus was placed, was always a BECKMANN thermometer, graduated in 0.01° . The thermometers used were compared with an instrument graduated in 0.1° , which had been calibrated by the Physikalisch Technische Reichsanstalt at Charlottenburg, and of which we had controlled the zero point. The temperature regulation was done by means of an OSTWALD regulator (capacity of the reservoir about 500 c.c.) which we filled with tetrachlorethane²⁾.

The temperature fluctuations of the thermostat were, during short periods, never greater than one or two hundredths of a degree.

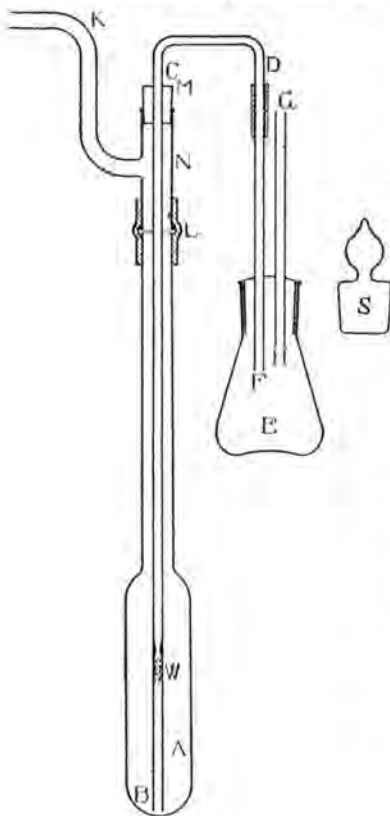


Fig. 1.

§ 4. The tapping of the saturated solutions was done by means of the apparatus shown in Fig. 1. When the shaking apparatus had been stopped, the solid was allowed to settle, the top part of the long neck of flask A was cut off, and the tube BCD, previously heated and containing a piece of cotton wool W at its lower end, was placed into it as quickly as possible. By means of a rubber bulb the filtered, clear, saturated solution is pressed into the flask E, which is immediately closed with a carefully ground glass stopper S. The flask is placed for a moment in cold water, in order to lessen the vapour tension over the solution, then it is completely dried and the flask with its contents is weighed.

¹⁾ Zeitschr. f. physik. Chemie **93**, 43 (1918).

²⁾ Zeitschr. f. physik. Chemie **117**, 143 (1925), § 6.

Of every saturated solution two samples were tapped out of the same flask; for every sample we used a separate tapping tube (*BCD* in Fig 1) which had been previously heated to the temperature of the experiment.

All the weighings (up to $\frac{1}{10}$ milligram) were carried out on a BUNGE balance. The weights were calibrated according to the well known method of F. KOHLRAUSCH.

2. *Analysis of the saturated solutions.*

§ 5. The technical part of the determinations was as follows: After weighing the saturated solutions in the flask *E*, which is closed with the stopper *S*, (which had been weighed beforehand) the benzene is removed by passing a dry current of air over it.

For this purpose we place the glass stopper with the tubes *G* and *F* on the flask, connect the tube *G* with the water- jet vacuum pump, the tube *F* with a battery of absorption bulbs, filled with strong sulphuric acid, interposing an empty flask, in which, eventually, specks of the acid can collect, and set the pump to work. In this way it is possible to remove 15 grams of benzene in about 6 hours.

§ 6. Different experiments have proved that this method gives accurate results, viz. that salicylic acid is not volatile in benzene vapour at temperatures below 25°. If, in the way we described, the benzene is evaporated from solutions of a concentration as we have in our actual series of experiments, we find back the quantity of salicylic acid which had been weighed into the flask, as is seen from the following determinations:

a. Weighed into the flask 0.4140 gms. of acid with about 15 gms. of benzene.

Found 0.4140 gms. of acid.

b. Weighed into the flask 0.3380 gms. of acid with about 15 gms. of benzene.

Found 0.3383 gms. of acid.

It may be pointed out here that in these determinations as well as in the later definite ones, the flasks *E*, after the removal of the benzene, were, for further control, kept for one night in the desiccator in vacuo, over phosphorous pentoxide, beside a dish filled with dry salicylic acid, so as to keep the desiccator filled with saturated vapour of this acid¹). Change of weight could not be ascertained.

§ 7. In order to form an opinion about the possibility of reproducing the solution equilibria, and about the accuracy of the analyses, we set to work as follows: We put two parts of the same preparation of salicylic acid into two separate quantities of the same preparation of benzene, shook both flasks for the same period at the same temperature, and analysed the saturated solutions thus obtained, every solution in two separate parts *a*, *b*, respectively *c* and *d*.

¹ See also A. L. TH. MOESVELD, Dissertation, Utrecht 1918 page 27.

In this way we found :

Solution 1: a.	1.04	} gms. of salicylic acid in 100 gms. of the saturat- ed solution.
b.	1.04	
Solution 2: c.	1.04	
d.	1.04	

D. Final Determinations.

§ 8. All our solubility determinations have been inserted in Table 1. Some measurements which were made simultaneously for another purpose, have not been included. This is the reason why a few numbers in the first column are wanting. (See table next page.)

For further explanation of the Table we wish to observe :

The previous treatment of the solution saturated at 30°.50 C. is called *normal*, when solution equilibrium is reached from a lower temperature.

The asterisks, placed behind the solubility figures in the last column, indicate that of the solutions in question two separate flasks have been shaken. In all other cases the figures refer to two separately tapped samples of the same saturated solution.

§ 9. On closer consideration of the table we observe :

A. When the acid is crystallized from ether it never reaches a solubility in benzene greater than 1.11, neither with the normal previous treatment of the saturated solution, nor after reaching equilibrium from a high temperature. Under these circumstances we find values lying between 1.03 and 1.11. The highest figures (1.10 and 1.11) are found when equilibrium is reached from a higher temperature.

B. Preparations, crystallized from water, give, for the solubility in benzene, values lying between 1.04 and 1.38, the highest figures appearing when the solutions in contact with solute have been heated to a higher temperature. Preparations, rapidly crystallized from water, give, in general, higher values than those which have slowly crystallized from water.

C. If the acid is first crystallized from ether, and then from water, the solubility rises very markedly, (f.i. from 1.05 in experiment 3, to 1.35 in experiment 4). If, on the other hand, we crystallize first from water, and then from ether, there is a marked decrease in the solubility, (f.i. from 1.38 in experiment 31, to 1.06 in experiment 32).

§ 10. In experiment 32 we wish to call attention to the following : When experiment 31 had been made, we removed as much as possible of the saturated solution, by withdrawing it in a pipette from the shaking flask. This is laid in a horizontal position, the tube *BCD* is inserted, *K* is connected with the water-jet vacuum pump, *D* with a battery of absorption bulbs containing sulphuric acid, and dry air is sucked over the solute, until the benzene is totally removed. Then the solute is completely dissolved in dry ether which is then removed in the same way as the benzene. Then the solubility in benzene of this preparation is determined.

TABLE 1. Temperature 30°.50 C.

No. of the Experiment	Preparation crystallized from ;	Previous treatment of the saturated solution at 30°.50 C.	Period of shaking in hours	Solubility gms. of solute in 100 gms. of saturated solution
3	ether	normal	20	1.03* 1.06*
4	ether, then from water	normal	23	1.36* 1.34*
9	water	first shaken for 3 hours at 48°, then at 30°.50	3	1.18 1.18
10	water	first shaken for 3 hours at 48°, then at 30°.50	24	1.22 1.23
11	ether	normal	3	1.08 1.08
12	ether	normal	21	1.09 1.09
13	water	first shaken for 3 hours at 65°, then at 30°.50	3	1.33 1.33
14	water	first shaken for 3 hours at 65°, then at 30°.50	21	1.31 1.31
15	ether	first shaken for 3 hours at 65°, then at 30°.50	3	1.10 1.10
16	ether	first shaken for 3 hours at 65°, then at 30°.50	73	1.11
17	ether	normal	286	1.09 1.06
18	ether	normal	290	1.08 1.07
19	water	normal	264	1.11 1.12

TABLE 1. Temperature 30° 50 C. (Continued).

No. of the Experiment	Preparation crystallized from:	Previous treatment of the saturated solution at 30° 50 C.	Period of shaking in hours	Solubility gms. of solute in 100 gms. of saturated solution
22	water slowly	normal	3	1.04
				1.04
				1.04
				1.04
23	water slowly	normal	48	1.05
				1.06
				1.06
				1.06
24	water chilled on ice	normal	3½	1.12
				1.13
25	water slowly	normal	4	1.06
				1.06
27	water slowly	normal	12	1.07
				1.08
28	water chilled on ice	normal	3	1.14
				1.14
29	water chilled on ice	normal	6	1.10
				1.09
30	water chilled on ice	first shaken for 3 hours at 70°, <i>without</i> solute, then at 30° 50 C.	3	1.13
				1.13
31	water chilled on ice	first shaken for 3 hours at 70°, <i>with</i> solute, then at 30° 50 C.	3	1.38
				1.38
32	Solute from experiment 31, after recrystallizing from ether in the shaking-flask	first shaken for 3 hours at 70°, <i>with</i> solute, then at 30° 50 C.	3	1.06
				1.06
34	first from ether, then slowly from water	normal	3	1.07
				1.07

TABLE 1. Temperature 30°.50 C. (Continued).

No. of the Experiment	Preparation crystallized from:	Previous treatment of the saturated solution at 30°.50 C.	Period of shaking in hours	Solubility gms. of solute in 100 gms. of saturated solution
38	water chilled on ice	first shaken for 3 hours at 70°, with solute, then at 30°.50 C.	3	1.24
				1.24
39	first from ether, then slowly from water	first shaken for 3 hours at 70°, with solute, then at 30°.50 C.	3	1.23
				1.23

In this way we found the figure 1.06, whereas this had first been 1.38.

§ 11. An accidental circumstance gave us at last the key to these very remarkable results.

One day we had dissolved a greater quantity of acid in boiling water, and then had poured it on ice, in order to chill the preparation suddenly. After filtration, to remove the mother liquor, we placed the acid in vacuo over phosphorous pentoxide. Though it was not quite dry the next day, we made a solubility determination with part of this preparation.

In this determination equilibrium was reached in the normal way; we found the figures 1.37 and 1.38.

When the preparation had been in vacuo over P_2O_5 for 24 hours more, we found for the solubility in benzene the values 1.12 and 1.12.

§ 12. As these experiments point to the possibility, that minute traces of water had great influence on the solubility of salicylic acid in benzene, our investigation was carried on in this direction, and, as will be seen from what follows, with good results.

Our method was as follows: A preparation, crystallized from dry ether, was powdered very fine in an agate mortar, and kept in vacuo over P_2O_5 .

Two shaking-flasks, carefully dried were closed with glass stoppers, their weight was determined, and a certain quantity of the acid (about 1 gm.) was very carefully weighed in them. In one of the flasks water is put by means of a capillary pipette, it is again weighed, and then dry benzene (about 45 gms.) is poured into the two flasks, after which they are weighed with their contents; then they are sealed. Every time two similar flasks (one without, the other with water) were shaken simultaneously, and for the same length of time (5 to 6 hours) at 30°.50 C. Then the contents of both were analyzed in the way described above.

In the solubility figures thus found, we notice the influence of the quantities of water added, while a (very small) amount of moisture (if present) of the identical materials used was not taken into consideration.

§ 13. In this way we obtained the results, summarized in Table 2, in which the solubility is again expressed in parts of salicylic acid per 100 gms. of the saturated solution.

TABLE 2. Temperature 30°.50 C.

Solubility in wet Benzene				Solubility in dry Benzene		
No. of the Experiment	Thousandths of perc. by weight of water in the benz.	Analysis 1	Analysis 2	No. of the Experiment	Analysis 1	Analysis 2
40	4	1.01 ⁵	1.01 ⁵	40	1.00 ³	1.00 ⁹
41	14.7	1.04 ⁹	1.05 ⁰	41	1.00 ³	1.00 ¹
42	37.4	1.09 ⁴	1.09 ⁷	42	1.00 ⁷	—
43	68.2	1.18 ⁸	1.19 ³	43	1.01 ³	1.01 ⁴
44	104.2	1.30 ⁸	1.31 ⁰	44	1.01 ⁵	1.01 ¹
45	147.8	1.34 ⁷	1.34 ⁹	45	1.01 ¹	1.01 ⁴
46	217.1	1.35 ³	1.34 ⁹	46	1.01 ¹	1.02 ⁰
47	313	1.35 ¹	1.35 ²	47	1.02 ¹	1.02 ⁰
48	excess	1.35 ⁴	1.35 ⁸			

§ 14. Before going deeper into the results, given in Table 1, by the light of the results summarized in Table 2, we wish to call attention to the fact that the literature contains a few data concerning the solubility of water in benzene ¹⁾. The data given by TH. W. RICHARDS, CARVER, and SCHUMB, seem the most reliable; they found at 5°.5 C., for the solubility 0.036 per cent by weight (gms. of water in 100 gms. of the saturated solution); SIDGWICK gives the same figure, and GROSCHUFF found 0.03 % at 3°, and 1.14 % at 40° C. The solubility of water in benzene in the presence of salicylic acid is unknown ²⁾.

§ 15. If we consider the results summarized in Table 1 by the light of the data in Table 2 we shall see that the phenomena, described in Table 1, can easily be explained, if we first direct our attention to what follows.

Whereas the method of treatment of the benzene used (previous treatment and distillation with P₂O₅) gives us a practically dry product ³⁾, from solutions of salicylic acid we obtain a preparation which always occludes minute quantities of the solvent used, as is generally the case when

¹⁾ HERZ, Ber. d. d. chem. Ges. 31, 2669 (1898); HANTZSCH and SEBALDT, Zeitschr. f. physik. Chemie 30, 278 (1899); TH. W. RICHARDS, CARVER en SCHUMB, Americ. Chem. Soc. 41, 2019 (1919); SIDGWICK, Journ. chem. Soc. London 117, 1340 (1920); GROSCHUFF, Zeitschr. f. Elektrochemie 17, 341 (1911).

²⁾ Comp. NERNST, Zeitschr. f. physik. Chemie 8, 110 (1891), especially pag. 116.

³⁾ See note 1 pag. 703.

crystals are formed from solutions¹⁾. The occluded water, present in the crystals which have been formed by crystallization from water, cannot be removed from the crystals in vacuo over P_2O_5 ; sometimes after a very long period when the crystals are powdered. Melting or subliming is necessary if we wish to reach this result quickly.

Further it is to be borne in mind, that in crystallizing from ether, the crystals formed easily get moist, in connection with the consequent cooling, and that therefore it is possible, that traces of occluded water are formed during crystallization.

§ 16. In general, the solubility figure, found by us, will be governed by the quantity of water which, originally present in the occlusions, passes from these into the benzene, when a certain amount of solid acid dissolves into the benzene. In the preparations crystallized from ether, we might think the presence of this liquid possible, on account of the method of drying, and that traces of ether, passing into the benzene, increase the solubility of the acid in the medium thus formed. As, however, traces of ether can be easily recognized by the smell, and as we have never noticed this smell, we have as yet no reason to believe in the influence of ether. However we intend to study this point at some future time.

§ 17. Ad. § 9A. The values between 1.03 and 1.11 for preparations, crystallized from ether, are explained by the presence of water in the vacuoles, which dissolves when the solid acid dissolves in the benzene. If the solid acid with the benzene is raised beforehand to a higher temperature, a greater quantity of occluded water is dissolved in the benzene, and consequently a higher figure will be found for the solubility of the acid.

§ 18. Ad. § 9B. It is obvious that a greater amount of occluded water can be present in the preparations which are crystallized from water, than in those which have been formed from etherial solutions, and correspondingly a higher solubility figure is obtained. If solute crystallized from water is dissolved at a higher temperature, the benzene gets more watery than in the preparations formed from ether, and the solubility will consequently be higher. If so much occluded water has got into the benzene that the latter (at the temperature of the experiment, 30°.50 C.) is saturated with water, the solubility will not rise with a greater quantity of occluded water; a constant final figure is found (1.36) as the experiments actually prove.

§ 19. Ad. § 9C. The results mentioned here will be easily understood after our exposition given above.

¹⁾ TH. W. RICHARDS, *Zeitschr. f. physik. Chemie* **46**, 189 (1903); Also *Proc. Americ. Philos. Soc.* **42**, 28 (1903); Also: *Experimentelle Untersuchungen über Atomgewichte*, Hamburg und Leipzig, 1909, Pag. 659.

§ 20. That the solubility rises with the increase of the water percentage of the benzene is in agreement with the figures which refer to dry benzene in Table 2. During the period in which the experiments 40 to 47 were made, the flask, containing the dry benzene, was opened frequently for a moment, in order to take out some of the liquid, so that water from the atmosphere could be absorbed. Indeed, the figures of the solubility indicate a slight increase.

§ 21. In the literature we have found only one accurate investigation on the solubility of salicylic acid in benzene (at a series of temperatures) viz. of WALKER and WOOD¹⁾. As i.a. they have also carried out some experiments at 30°.5 C., we have chosen this temperature for our determinations, so as to have a point of comparison. As WALKER and WOOD do not give further particulars about purification and drying of their preparations, we mention only that they find for the solubility 0.981 gms. of salicylic acid in 100 gms. of the saturated solution, whereas our lowest value is 1.00. Since, for want of data, we cannot form a notion of the accuracy which they attained, we shall not enter into a further discussion of their results.

§ 22. We shall postpone a discussion of several points to a later time, and mention only that the matter treated above suggests a method to determine accurately the quantity of liquid (sometimes very small) in the vacuoles of crystals²⁾. We shall return to this subject at some future period.

SUMMARY.

It was demonstrated that very minute traces of water markedly increase the solubility of salicylic acid in benzene. Herein lies a method for the accurate determination of the quantity of liquid contained in the vacuoles of crystallized substances.

Utrecht, June 1925.

VAN 'T HOFF-Laboratory.

¹⁾ Journ. chem. Soc. London **73**, 618 (1898).

²⁾ See also ERNST COHEN and H. R. BRUINS, *Zeitschr. f. physik. Chem.* **94**, 443 (1920)

Mathematics. — "On the generalisation of the series of VACCA". By
Prof. J. C. KLUYVER.

(Communicated at the meeting of September 26, 1925.)

1. Some time ago Prof. G. VACCA simplified the proof of his remarkable expansion of EULER's constant C in a series of rational terms¹⁾. His method however does not allow to arrive at my somewhat generalised expansion²⁾, a simple proof of which may be conducted as follows. Putting

$$C(n) = \sum_1^n \frac{1}{k} - \log n,$$

it is easily proved that $C(n)$ decreases and that on the contrary $C(n) - \frac{1}{n}$ increases, as n tends to infinity. Therefore, a and m being integers, we infer that

$$0 < \left\{ C(am) - \frac{1}{am} \right\} - \left\{ C(m) - \frac{1}{m} \right\} < \frac{a-1}{am}.$$

Now we have by definition

$$\left\{ C(am) - \frac{1}{am} \right\} - \left\{ C(m) - \frac{1}{m} \right\} = \sum_1^{am-1} \frac{1}{k} - a \sum_1^{m-1} \frac{1}{ak} - \log a,$$

hence, denoting by β_k either $a-1$ or -1 according as k is, or is not a multiple of a , we get

$$\left\{ C(am) - \frac{1}{am} \right\} - \left\{ C(m) - \frac{1}{m} \right\} = - \sum_1^{am-1} \frac{\beta_k}{k} - \log a,$$

and, as we have for $m \rightarrow \infty$

$$0 = - \sum_1^{\infty} \frac{\beta_k}{k} - \log a,$$

¹⁾ G. VACCA. Sulla costante di Eulero. Rendiconti d. R. Accad. Nat. d. Lincei. Vol. I, serie 6a, p. 206, 1925.

²⁾ These Proceedings 27, p. 314.

Quarterly Journal. Vol. L, p. 185, 1924.

it follows that

$$0 < \left\{ C(am) - \frac{1}{am} \right\} - \left\{ C(m) - \frac{1}{m} \right\} = \sum_{am}^{\infty} \frac{\beta_k}{k} < \frac{a-1}{am}.$$

In this equation m is changed successively into $am, a^2m, a^3m, \dots, a^{q-1}m$, and we obtain by adding the q equations

$$\left\{ C(a^q m) - \frac{1}{a^q m} \right\} - \left\{ C(m) - \frac{1}{m} \right\} = \sum_{h=1}^{h=q} \sum_{a^h m}^{\infty} \frac{\beta_k}{k}.$$

Evidently at the righthandside a definite term $\frac{\beta_k}{k}$ occurs as many times as the sequence $am, a^2m, a^3m, \dots, a^q m$ contains a term less than k . Therefore, if x is an integer satisfying the inequalities

$$a^q m < na < x < (n+1)a < a^{q+1}m,$$

we may write

$$\left\{ C(a^q m) - \frac{1}{a^q m} \right\} - \left\{ C(m) - \frac{1}{m} \right\} = \sum_{am}^{x-1} \frac{\beta_k}{k} \left[{}^a\log \frac{k}{m} \right] + q \sum_x^{\infty} \frac{\beta_k}{k},$$

where $[{}^a\log k]$ stands for the integer part of ${}^a\log k$.

Because we have

$$\sum_n^{\infty} \frac{\beta_k}{k} = -\frac{1}{x} - \frac{1}{x+1} - \dots - \frac{1}{a(n+1)-1} + \sum_{a(n+1)}^{\infty} \frac{\beta_k}{k},$$

we have also

$$\left| \sum_x^{\infty} \frac{\beta_k}{k} \right| < \frac{a-1}{x} + \frac{a-1}{a(n+1)} < \frac{2a(a-1)}{a^q m}.$$

consequently, if q , and at the same time x , tends to ∞ , the product

$q \sum_x^{\infty} \frac{\beta_k}{k}$ tends to zero, and we have established the result

$$C - \left\{ C(m) - \frac{1}{m} \right\} = \sum_{am}^{\infty} \frac{\beta_k}{k} \left[{}^a\log \frac{k}{m} \right].$$

If we put here $m=1$, we obtain

$$C = \sum_n^{\infty} \frac{\beta_k}{k} [{}^a\log k].$$

and this expansion of the constant C , in which the integer a is arbitrary, is a generalisation of the series of VACCA, who only considers the case $a = 2$, $\beta_k = (-1)^k$, and writes

$$C = \left(\frac{1}{2} - \frac{1}{3}\right) + 2\left(\frac{1}{4} - \frac{1}{5} + \frac{1}{6} - \frac{1}{7}\right) + 3\left(\frac{1}{8} - \dots - \frac{1}{15}\right) + \\ + 4\left(\frac{1}{16} - \dots - \frac{1}{31}\right) + \dots$$

2. It is also possible to deduce in a more direct way the corresponding expansions of the coefficients C_h of the power series

$$\zeta(1+s) = \frac{1}{s} + C + \sum_1^{\infty} C_h s^h,$$

that for any value of s represents the RIEMANN function $\zeta(1+s)$. Supposing $s > 0$ we have also

$$\zeta(1+s) = \sum_1^{\infty} \frac{1}{k^{1+s}}$$

and as evidently

$$(1 - a^{-s}) \zeta(1+s) = - \sum_1^{\infty} \frac{\beta_k}{k^{1+s}},$$

we get the identical relation

$$1 + C s + \sum_1^{\infty} C_h s^{h+1} = \sum_1^{\infty} \frac{\beta_k}{k} \left(\frac{sk^{-s}}{a^{-s} - 1} \right).$$

Here we refer to the expansion

$$\frac{y e^{ty}}{e^y - 1} = 1 + \sum_1^{\infty} y^h \bar{g}_h(t),$$

holding for $|y| < 2\pi$ and for any value of t , in which $\bar{g}_h(t)$ stands for the polynomial

$$\bar{g}_h(t) = \frac{t^h}{h!} - \frac{1}{2} \cdot \frac{t^{h-1}}{(h-1)!} + \frac{B_1}{2!} \cdot \frac{t^{h-2}}{(h-2)!} - \frac{B_2}{4!} \cdot \frac{t^{h-4}}{(h-4)!} + \frac{B_3}{6!} \cdot \frac{t^{h-6}}{(h-6)!} - \dots,$$

involving the BERNOULLIAN numbers B_n .

For sufficiently small values of s we have therefore, putting $y = -s \log a$, $t = {}^a \log k$

$$\frac{sk^{-s}}{a^{-s} - 1} = - \frac{1}{\log a} + \sum_1^{\infty} s^h (-1)^{h-1} (\log a)^{h-1} \bar{g}_h({}^a \log k),$$

and finally we arrive at the equation

$$1 + Cs + \sum_1^{\infty} C_h s^{h+1} = -\frac{1}{\log a} \sum_1^{\infty} \frac{\beta_k}{k} + \\ + \sum_{k=1}^{\infty} \frac{\beta_k}{k} \sum_{h=1}^{\infty} s^h (-1)^{h-1} (\log a)^{h-1} \bar{g}_h (^a\log k).$$

But, as the righthandside is identically equal to a power series in s , we necessarily must conclude to

$$C_h = (-1)^h (\log a)^h \sum_1^{\infty} \frac{\beta_k}{k} \bar{g}_{h+1} (^a\log k),$$

and especially to

$$C = \sum_1^{\infty} \frac{\beta_k}{k} \bar{g}_1 (^a\log k) = \sum_1^{\infty} \frac{\beta_k}{k} \left(^a\log k - \frac{1}{2} \right).$$

For not specified values of a and k the probable value of $^a\log k - \frac{1}{2}$ is $[^a\log k]$; hence remembering that we already found

$$C = \sum_a^{\infty} \frac{\beta_k}{k} [^a\log k] = \sum_1^{\infty} \frac{\beta_k}{k} [^a\log k],$$

we may remark that the sum of the series

$$\sum_1^{\infty} \frac{\beta_k}{k} \left(^a\log k - \frac{1}{2} \right)$$

is not altered, when $^a\log k - \frac{1}{2}$ is replaced by its probable value.

Botany. — "*The results of the temperature-treatment in summer for the Darwin-Tulip.*" First part. (Communicated N^o. 17, Laboratory for Plant-physiolog. Research, Wageningen, Holland.) By A. H. BLAAUW and Miss M. C. VERSLUYS.

(Communicated at the meeting of September 25, 1925).

§ 1. *Introductory, material and treatment.*

In the summer of 1922 and of 1924 bulbs of the Darwin-Tulip, Pride of Haarlem were exposed to 65 different combinations of temperatures in all between lifting and replanting. The results will be communicated in three parts: in the first and the second part the experiments of the summer 1922, in the 3rd those of 1924, which were based upon the results of the 1922-experiments. Finally in connection with the treatments in 1924 some test-experiments were made in the summer of 1925, the results of which cannot be published until 1926 in a 4th part. With a view to the cultures however we have thought best not to delay publishing the data hitherto found. Besides an occasional reference will be made to the detailed description: "*The periodical development of the Tulip*" by R. MULDER, which research will appear in some time as communication N^o. 16.

The material supplied by C. G. VAN TUBERGEN of Haarlem, was sent to us directly after lifting and sorted, so that the experiments of 1922 could be started on July 20.

What the condition of the bulb is at that time, may be read in the above-mentioned research of R. MULDER. Here it will suffice to mention, that in July 20, 1922 at the beginning of the different temperature-treatments the greater number of the bulbs (save the scales with the reserve-food) had formed 2, 2 to 3, or 3 *foliage-leaflets* (found in 12 of the 17 bulbs opened). As finally 4 to 5 foliage-leaves are formed, the experiments *after the lifting begin still in the leaf-forming period* (stage I). This is quite different from the Hyacinth, where as a rule the foliage-leafformation ends after the lifting, the growing-point is raised (stage II) and next is going to form the flower-cluster. (See 1920.)

These tulips were treated simultaneously with the first series of experiments on the Hyacinth (see 1924) and were initially considered as a provisional experiment to find out, whether in a plant so closely related important differences might occur.

Just as the Hyacinth they were exposed to $1\frac{1}{2}^{\circ}$ — 5° — 9° — 13° — 17° — 20° — 23° — $25\frac{1}{2}^{\circ}$ — 28° — 31° and 35° , 10 at a time for 2, 4, 6 and 10 weeks; after 2, 4 and 6 weeks they were placed in about 17° and next

10 weeks after the beginning of the experiments, these $11 \times 4 = 44$ groups each consisting of 10 experimental tulips, were planted ca 1 October.

Besides after 2, 4, 6 and 10 weeks 10 tulips were fixed in alcohol 96 % in order to trace the progress of leaf- and flower-formation and of the young bud in the 11 different temperatures during that time. These data will be discussed in the *second part*.

This being only an experiment for control and orientation, only 10 tulips were planted and the effect was traced till the flowering. Not until the third part data are given on the yield of new tulips.

§ 2. *The root-wall at the beginning of October.*

In the second part we shall discuss the events occurred during the summer, observed on bulbs fixed in alcohol, after 2, 4, 6 and 10 weeks and for convenience' sake we shall discuss in this first part, what is externally directly perceptible *after* those 44 temperature-treatments.

On planting, beginning of October '22 many points of difference were to be noticed in the condition of the *root-whorl*. The more or less advanced state of this root-wall was photographed and recorded by us independently, and from this a conclusion was drawn :

Furthest developed is the root-whorl after a treatment of 10 weeks in 13° , when the roots already protrude from the root-wall. Next in progress are those groups, which have been exposed to 10 weeks 17° , 6 weeks $13^{\circ} + 4$ weeks 17° and 10 weeks 9° .

It is a striking fact that the root-whorl develops most rapidly in such low temperatures (low "*celerrimum*", see 1924).

The greatest contrasts appear, as may be understood, in the series remaining for 10 weeks in the 11 different temperatures. An impression of this is given in fig. 1, showing bulbs from those 11 temperatures photographed from below on one side at the beginning of October. Furthest developed is the root-whorl at 13° , next 9° and 17° , then 20° , 23° , $25\frac{1}{2}^{\circ}$, then 5° ; whilst at 28° , 31° , 35° , the root-wall is developed as little as at $1\frac{1}{2}^{\circ}$. The dry brown scale has been removed for the greater part in these bulbs in order to show the root-wall. From these bulbs one average type has been inserted in the photo-series. While 20° , 23° and $25\frac{1}{2}^{\circ}$ are about equal, $25\frac{1}{2}^{\circ}$ seems a little farther.

We intentionally say that in the low temperatures 9° — 13° — 17° a *celerrimal* (most rapid) development of the root-whorl takes place; — we do not speak of an *optimal* development, for it may very well be, that in higher temperatures the development of the roots, though slower, is equally good or better with respect to the whole plant. That indication of most rapid (*celerrimal*) development, as in this case of the root-wall, is material with a view to the treatment for early flowering.

To this subject we shall revert, when treating the development of other organs.

A. H. BLAAUW and Miss M. C. VERSLUYS: "THE RESULT OF THE
TEMPERATURE-TREATMENT IN SUMMER FOR THE DARWIN-TULP".

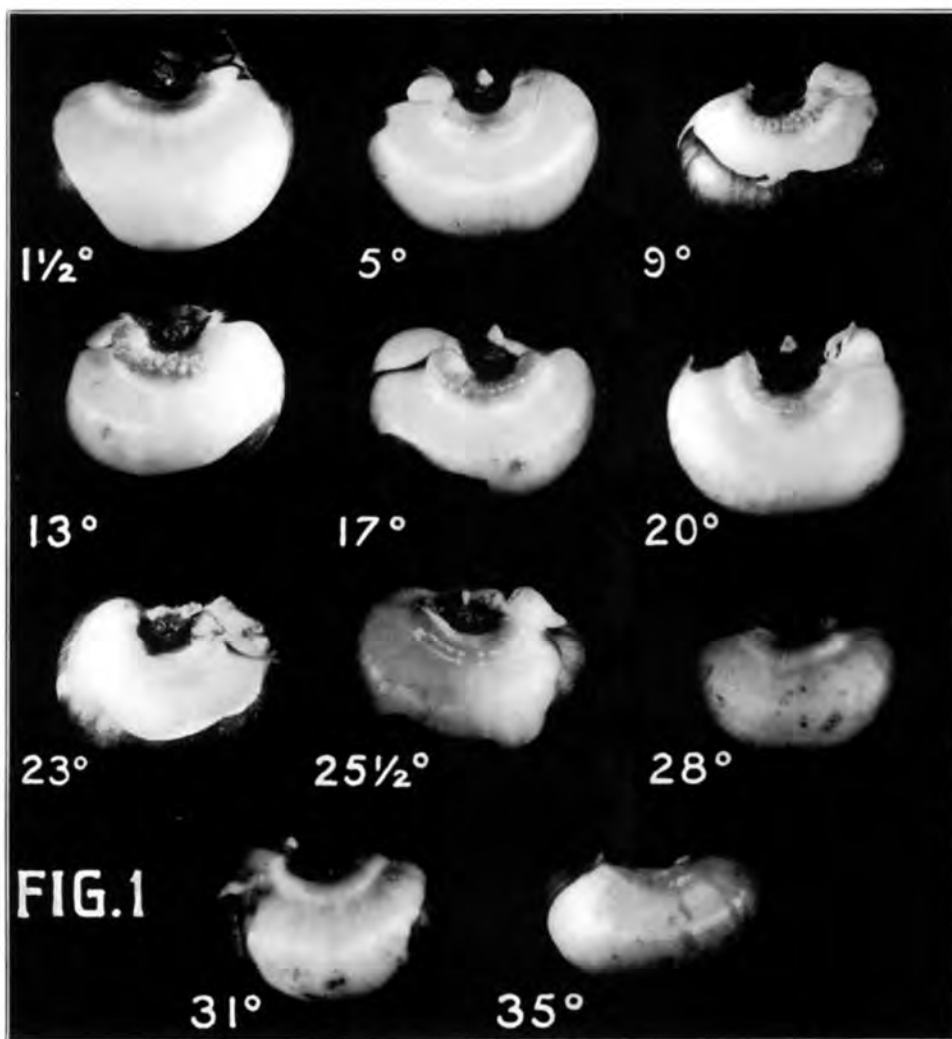


Fig. 1. Condition of the root-wall after a treatment for more than 10 weeks in 11 different temperatures.

§ 3. *Coming up.*

At the beginning of October 10 bulbs of each of the 44 treatments were planted in the open, 5 cms. deep and covered moreover with a layer of 4 to 5 cms. peat-dust. Next it was observed at different points of time which group appeared first i.e. stretched quickest. The winter (1922—1923) had been very mild.

Whilst the tulips, exposed to 10 weeks 5° (!) showed on January 4 already ca 3 cms. above the peat-dust and appeared quickest of all on Jan. 11, 4 of the 10 of the group 10 w. $1\frac{1}{2}^{\circ}$ (!) showed just above ground, 9 of the 10 of 10 weeks 5° showed 4 to 5 cms. above the peat-dust, 4 of the 10 of the group 10 weeks 9° just appeared; a *celerrimal* stretching therefore in those groups which had experienced an uncommonly low temperature in the previous summer.

Table 1 clearly shows the condition on Febr. 11, 1925 after the peat-dust had been removed. According to the description made, the 44 groups have been given a successive number, denoting the advance in growth in length, which is in accordance with the order of succession of coming up in those weeks.

TABLE 1. Order of succession of coming up, on February 11, 1925.

Exposure	2 weeks	4 weeks	6 weeks	10 weeks
$1\frac{1}{2}^{\circ}$	6	7	5	2
5°	7	6	3	1
9°	7	6	5	2
13°	8	7	6	4
17°	7	7	7	7
20°	8	8	8	8
23°	8	8	8	8
$25\frac{1}{2}^{\circ}$	6	8	9	10
28°	8	8	9	10
31°	6	8	9	10
35°	8	9	10	10

Nº. 1: 9—17 cms., Nº. 2: 9—12 cms., Nº. 3: 7—9 cms., Nº. 4: 4—7 cms.,
 Nº. 5: 3—5 cms., Nº. 6: 2—4 cms., Nº. 7: 1—4 cms., Nº. 8: $\frac{1}{2}$ — $3\frac{1}{2}$ cms.,
 Nº. 9: 0—3 cms., Nº. 10: 0 cm., above ground.

We conclude that in spring on coming up (stretching) the *celerrimum* follows after an exposure to still lower temperatures than could be ascertained in Oct. with respect to the root-whorl.

This may be due either to the fact that stalk with leaves has a still lower celerrimal temperature than the root-system — or to the fact that celerrimum is found lower in the after-effect months later (February as contrasted with October).

Again the necessity is felt of distinguishing a *celerrimum* from an *optimum* in judging these intricate processes of the whole plant, for as we shall soon observe in description and photographs these plants (celerrimal as to stretching) had by no means had an optimal treatment.

§ 4. *Coming into bloom.*

After coming up the appearance of the flower and the coming into bloom was traced. Those different data on succession of coming up and flowering were recorded in detail for weeks together. A brief survey concerning the flowering will suffice here. For the progress of that growth and flowering after various treatments of the bulbs in the preceding summer a mild winter as the one of 1922—1923 is material. When bulbs variously treated are further cultivated not in a hothouse, but — as in our case — in the fields, and a long, continuous, severe winter follows, passing rather suddenly and late into warm spring-weather, many differences in more or less quick stretching and flowering due to an earlier temperature treatment are effaced, because after a long restraint owing to the winter, growth and flowering succeed rapidly in the various experimental groups. When however the winter is very mild, as was the case in '22-'23, or when the results of the experiments could be observed in a greenhouse where the bulbs were protected from frost, the difference of rate of growth and flowering are evident. And this is important, because they indicate to us the most suitable treatment for early flowering, which may require a treatment quite different from the optimum for the ordinary field-culture or especially for new bulb-formation. To this shall revert later on. It stands to reason, that the successive numbers, judged from 10 specimens, are only valuable as to their strong contrasts and that to differences for instance of 6 and 7 cannot be attached much value; hence little irregularities occur, which would not have been expected otherwise; it is doubtful whether they are valuable or not. But the chief points are without doubt directly to be read from this table 2. It should be remembered that all bulbs, kept in the 11 temperatures shorter than 10 weeks, were stored in 17° for the rest of the time. Hence the shorter they were kept in one of the other 10 temperatures, the slighter the influence was and the smaller the differences are.

1⁰. After a 2 weeks' stay it may be noticed, that the lower temperatures only slightly influenced the *rate* of flowering, that the higher temperatures (above 20°) are distinctly inhibitory. This is the after-effect of a 2 weeks' treatment after 8 months!

2⁰. Whereas the effect of 2, 4 and 6 weeks mutually shows but a very

A. H. BLAAUW and Miss M. C. VERSLUYS: "THE RESULTS OF THE
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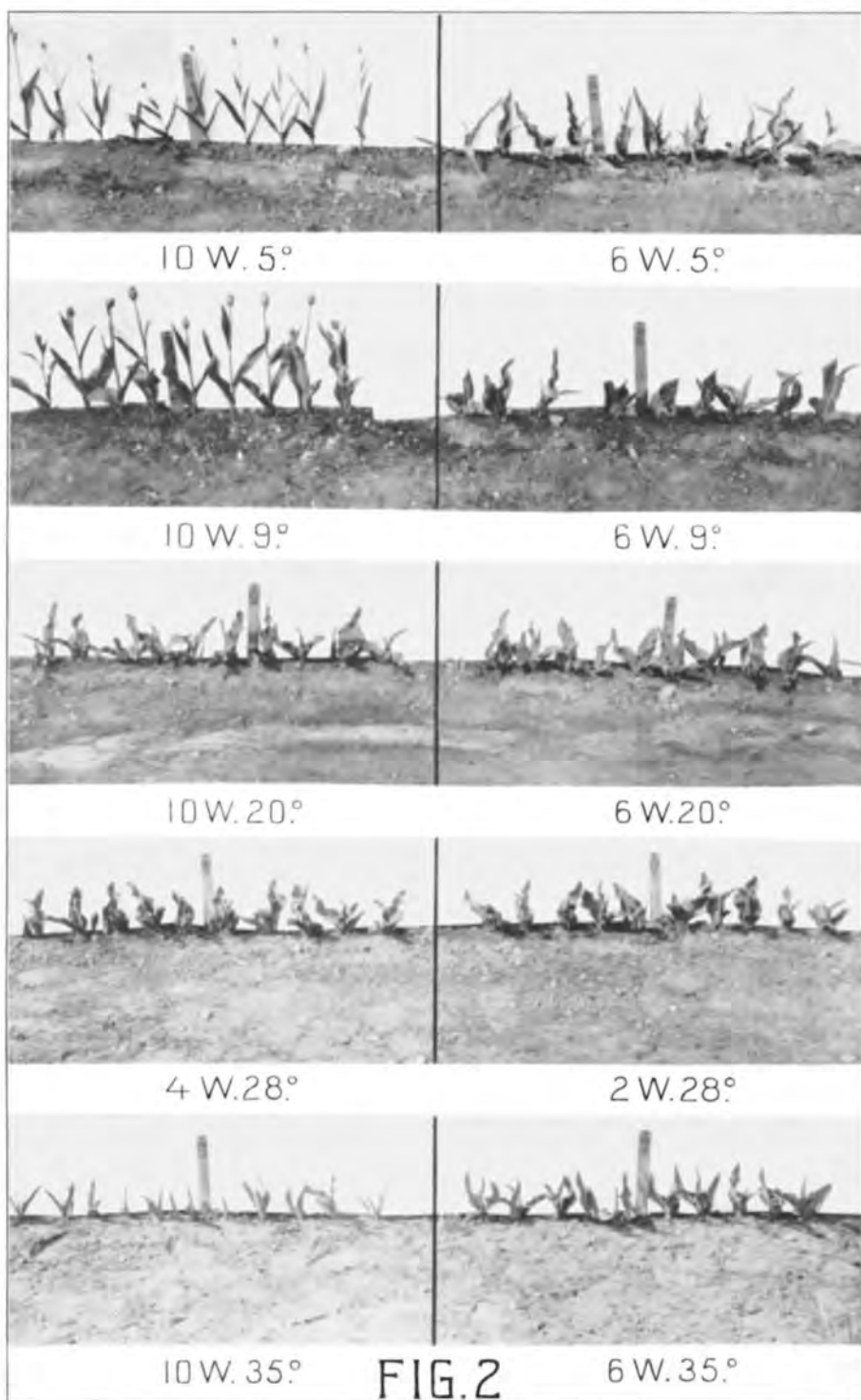


Fig. 2. Photographs of a number of experimental groups on March 30, 1923 chiefly illustrating the earliest flowering groups and the different foliage.

TABLE 2. Order of succession of coming into bloom.

Exposive	2 weeks	4 weeks	6 weeks	10 weeks
$1\frac{1}{2}^{\circ}$	6	6	6	3
5°	5	6	6	2
9°	6	6	5	1
13°	5	5	4	3
17°	5	5	5	5
20°	6	7	7	8
23°	7	7	8	9
$25\frac{1}{2}^{\circ}$	7	7	8	10
28°	9	10	10	10
31°	9	10	10	11
35°	10	10	11	12

Nº. 1: April 17, all the 10 tulips flowering.

Nº. 2: April 17, 6 of the 10 tulips flowering.

Nº. 3: April 17, 1 of the 10 flowering.

Nº. 10—12: May 2, still closed.

slight difference, the treatment in the 6th to 10th week (month of September) is essential to the more or less rapid stretching and flowering, as is evident from the 4th column.

The first to flower were the Tulips, kept in 9° for 10 weeks and then planted in the fields. If this treatment is applied to the Hyacinth, not a single flower-cluster appears. From this the great difference between these closely related bulbs already appears. Even the greater number of those kept in 5° flowered on April 17 and must have finished their flower (see 2nd part § 10. fig. 3) in the ground after Oct. 1. Besides on April 17 a few of the continuous exposure to $1\frac{1}{2}^{\circ}$ and 13° were already flowering. This as to the *celerrimum* of flowering; but it does by no means hold good for the *optimum* of flowering and of the plant as a whole.

This we shall see in considering the results of these treatments on plant and flower in a short report of the notes concerning them and in connection with some photos. (See fig. 2.)

As stated above, the differences show strongest in 10 weeks' continuous treatment. Starting from a specimen from 10 weeks' 9° which was the first to open, we find fairly broad leaves with big flower-buds on March 30, whereas the experimental groups in 9° for a *shorter* time and especially in a temperature *lower* than 9° are less developed in a diminishing degree, partly as poor plants with narrower leaves and more deformed half green flowers, partly not even coming up at all (e.g. after $1\frac{1}{2}^{\circ}$).

We stated above and shall discuss later on (§ 10) that the flowers of 10 w. $1\frac{1}{2}^{\circ}$ and 5° must have been formed partly (from 5°) or quite (from $1\frac{1}{2}^{\circ}$) in the ground after October. Though 10 w. 5° was the first to show above ground, 10 w. 9° was the first to open and excelled the poor plant of 5° far as to flower and leaf. The condition on March 30, '23 we find in fig. 2, from which it may be seen that shorter (than 10 w.) in 9° was sure to give later flowering, and lower than 9° a poorer plant.

Further the flowering falls the later according as the temperature in the previous summer was higher. This gradually decreases from 10 w. 9° to 20° and higher (conf. fig. 2: 10 w. 9° and 10 w. 20° on March 30). But the foliage-leaves develop quite vigorously in the higher temperature, so that from $1\frac{1}{2}^{\circ}$ to $25\frac{1}{2}^{\circ}$ or 28° the foliage increases in breadth and grows more undulating; this is most conspicuous in the 10 weeks' treatment (5° — 9° — 20° — 28° ; conf. fig. 2). At 6 w. 5° — 9° — 20° — 28° etc. (and next 17°) the contrasts have been effaced for a great part, so that it is evident how important the treatment in the month of September (i.e. in the last month before planting) is with respect to the rate of flowering and the development of the foliage. Above $25\frac{1}{2}^{\circ}$ — 28° the foliage diminishes, so that after a treatment with 10 w. 35° it is again poorer and not undulating. Then the plant is not only later, but also less favourable; in this case therefore we have not only passed a *celerrimum*, but also the optimum.

The lower temperatures, as 9° and 13° , may cause a loss in foliage-surface, but they promote a *celerrimal* development. That is material with respect to early flowering. But we shall revert to this point, because a more favourable combination of temperatures is possible (See 3rd part and the 4th part to be published next year).

Fig. 2 taken as early as March 30, gives a picture of the *celerrimal* treatment as to flowering (promoting early flowering). Some weeks after the groups from higher temperatures (20° and higher) are flowering likewise.

Several abnormal flowers, especially from highest and lowest temperatures, were fixed, but they require a detailed special morphological description, which we cannot enter into in this series of papers. To the kinds of abnormalities we shall briefly revert in the 2nd part (conclusion § 11).

As to flowering it is a very striking and surprising thing, that in those very earliest flowering specimens, exposed to 9° — 17° , the number of floral organs is abnormally great compared to the normal monocotyledonous base $6 + 6 + 3$, for perianth and stamens and the whorl of carpels. A more detailed discussion will be found in the following §.

§ 5. *The number of foliage-leaves and floral organs.*

We have accurately traced the number of foliage-leaves and floral

organs, formed in a certain temperature. First of all we accurately counted and recorded the figures of the specimens (planted in the field) in April and May 1923. Afterwards the material fixed in alcohol during the treatment in the summer of 1922 was examined (See part 2). In so far as leaves or whorls of floral organs were ready as primordia, their number could be added to the figures of the specimens planted. From those numbers, found in April-May, only those were used, which referred to the bulbs that had surely formed the parts concerned in that temperature, — not therefore (in very low or high temperatures), when they had formed those parts afterwards in about 17° (after-treatment) or in the ground.

As mentioned before, the experiments were started on July 20, 1922 when 2 or 3 foliage-leaves had been formed. We add various tables on the number of leaves and floral organs, arisen during treatment in the temperatures mentioned (1st column), exclusively in so far as the leaf-series or a definite whorl of floral organs has been finished. Behind the temperature between brackets the number of weeks is found, after which this stage is reached. To give a direct picture of the variation in the number of the leaves or of the floral organs in their different whorls, the whole material is given first, i.e. how many times the number (e.g. 3, 4, 5, 6, etc.) of the organ concerned occurred. Next the number of observations (n), the average (M) and the mean error (m) have been given.

TABLE 3. Number of foliage-leaves.

Number :	2	3	4	5	6	7	8	n	M	m
1½° (10 w.)	—	3	3	10	0	1	1	18	4.78	±0.30
5° (6 w.)	—	7	9	17	5	1	—	39	4.59	±0.16
9° (2 w.)	—	13	15	36	8	1	—	73	4.58	±0.11
13° (2 w.)	2	7	10	39	17	3	—	78	4.91	±0.12
17° (2 w.)	—	15	13	28	18	2	—	76	4.72	±0.13
20° (2 w.)	—	14	21	38	6	—	—	79	4.46	±0.10
23° (2 w.)	—	14	16	48	2	—	—	80	4.48	±0.09
25½° (2 w.)	—	14	20	43	2	—	—	79	4.42	±0.09
28° (4 w.)	—	9	29	25	—	—	—	63	4.25	±0.09
31° (10 w.)	—	—	8	9	1	0	—	19	4.79	±0.22

Conclusions :

10. after 2 or 3 foliage-leaves had been formed before July 20, the number was increased to 4 or 5 in all temperatures from 1½° to 31°, before the flower-formation begins. The rate, at which this happens, is

very rapid with the temperatures 9° — $25\frac{1}{2}^{\circ}$ (within a fortnight), but grows much slower in the very low and very high temperatures. (See period in weeks between brackets.)

20. The temperature has a very *slight* influence on the *number* of foliage-leaves still to be formed on the central growing-point. In the main the average number remains 4 or 5. Considering the great number of observations (*n*) in temperatures 9° — 28° and the trifling mean error (*m*), the average values (*M*) may be relied upon, and it must be concluded, that after 20° and higher the formation of the average number of foliage-leaves is somewhat slighter than after exposure to 13° and 17° . The *slightly* higher figure after 10 weeks in 31° we shall not take into consideration on account of the small number.

Summarizing we recapitulate that the *number* of foliage-leaves, only partly formed, is influenced, but extremely little, by so diverging temperatures, that if we may accept some difference, the treatment in 13° may be considered to be among the most favourable as to the *number*. This in connection with what now follows on the number of floral organs.

In counting the *number of tepals* inner and outer whorl were taken together, as especially in the case of an increased number of floral organs they cannot be distinguished with certainty. In contingent transitional forms between foliage-leaves, tepals or stamens, which, considering the large number ($n \times$ the number of floral organs concerned) were not very numerous, the organ was added to that whorl to which it chiefly belonged according to its structure.

TABLE 4. Number of tepals.

Number	6	7	8	9	10	11	12	n	M	m
9° (6 w.)	—	4	5	15	9	4	—	37	9.11	± 0.19
13° (4 w.)	—	3	10	19	16	7	2	57	9.35	± 0.16
17° (2 w.)	2	15	32	13	10	3	—	57	8.40	± 0.17
20° (2 w.)	28	18	25	2	2	—	—	75	7.09	± 0.12
23° (4 w.)	26	19	14	0	0	1	—	60	6.87	± 0.13
$25\frac{1}{2}^{\circ}$ (4 w.)	38	15	4	2	—	—	—	59	6.49	± 0.10
28° (6 w.)	29	3	2	2	—	—	—	36	6.36	± 0.14

Conclusions :

10. Whilst the *number* of foliage-leaves still to be finished is but very slightly or scarcely influenced by the temperature, and the average number 4 or 5 is only finished in every temperature, before the growing-point is going to form the floral organs, the number of tepals is strongly

influenced by the temperature in which the bulbs are stored, so that in 13° or 9° the average number of tepals originated is one and a half times the monocotyledonous base (2×3).

20. From 13° to 28° the number of tepals decreases and approximates more and more the normal number 6, a figure rarely found after 9° and 13° (never in these experiments) and not prevailing until $25\frac{1}{2}^{\circ}$ and especially 28° . (Higher and lower temperatures are not given, because e.g. in 5° and 31° after 10 weeks the flower-formation is not advanced far enough yet, and is not finished before the bulbs are planted in the open.)

30. From the above and from the data on the number of foliage-leaves it likewise appears, that the increase in the number of tepals by no means occurs at the expense of the number of foliage-leaves.

We shall now mention in a similar way the *number of stamens*, combining likewise the inner and outer whorls and in the case of transitional forms adding these to the whorl which the structure of the organ resembles most. (See sub "number of tepals".) Though an increased number of tepals and stamens makes it hard to discover, which belong to the outer and which to the inner whorl or may be to a third whorl, it may be possible to decide this after more accurate, purely morphological studies. In these experimental morphological researches however, we have had to restrict ourselves to these conclusions.

TABLE 5. Number of stamens.

Number :	5	6	7	8	9	10	11	n	M	m
9° (6 w.)	—	2	6	9	12	6	—	35	8.40	± 0.19
13° (4 w.)	—	—	9	14	24	8	2	57	8.65	± 0.14
17° (4 w.)	—	4	16	26	8	2	—	56	7.79	± 0.12
20° (4 w.)	—	22	25	10	1	—	—	58	6.83	± 0.10
23° (4 w.)	1	25	24	9	—	—	—	59	6.69	± 0.10
$25\frac{1}{2}^{\circ}$ (4 w.)	1	29	19	3	—	—	—	52	6.46	± 0.09
28° (10 w.)	—	17	3	1	—	—	—	21	6.24	± 0.12

Conclusions :

10. We find here exactly the same phenomenon as with the number of tepals. The largest number of stamens is formed in 13° and also in 9° , though the average attained is slightly lower than in the case of the tepals.

20. From 13° to 28° the average number gradually decreases, so that the *highest* temperatures approximate the monocotyledonous base 2×3

most in the average (M) and the actual number 6 is most frequent in this case (see especially 28°). In 13° it is never formed; in 9° in 2 of the 35 cases.

The figure 5, so "below normal", rarely occurs, probably without connection with the temperature employed, more as a "chance" deviation. Here we see it occurring twice (in 2 most favourable temperatures) with the stamens. Also after exposure to 31° and after Oct. 1 in the ground the figure 5 was found a few times in stamen- and tepal-whorl.

30. The whorls of tepals and of stamens therefore are not increased in number of parts at the expense of each other, but the lower temperatures have this perfectly parallel effect on the whorls of these two organs.

In table 6 the *number of carpels* is given in a similar way.

TABLE 6. Number of carpels.

Number :	2	3	4	5	6	n	M	m
9° (10 w.)	—	7	10	1	1	19	3.79	±0.18
13° (4 w.)	2	18	31	2	—	53	3.62	±0.09
17° (4 w.)	1	28	28	—	—	57	3.47	±0.07
20° (4 w.)	1	34	21	—	—	56	3.36	±0.07
23° (4 w.)	—	33	24	—	—	57	3.42	±0.07
25½° (6 w.)	—	27	15	—	—	42	3.36	±0.08
28° (10 w.)	—	16	5	—	—	41	3.24	±0.10

Conclusions :

10. In this case we have only to deal with one whorl, so normally 3 parts; hence the differences are not so striking as in tables 5 and 4. Besides it is possible, that as the effect on the stamen-whorls is a little less than on the tepals, the influence of this 5th whorl is still slighter than on the whorls lying more to the outside. Nevertheless the effect is perfectly parallel. It appears that the average number (sub M) at 9° and 13° is highest, and that considering the very slight mean error (m) of 0.07 to 0.10, doubtlessly the higher temperatures approximate the normal number 3 more than the low temperatures 9° and 13°.

20. This is still more evident in the detailed figures in the preceding columns. At 9° and 13° the climax of variation is found with 4 carpels, at 17° there are just as many with 3 as with 4 carpels, at 20° and higher the climax falls at (the greater number has) 3 carpels.

30. A few cases occur with 2 carpels, i.e. *below* the normal base, a most rare feature, likewise in the other floral whorls. In our opinion it has nothing to do with the continuous phenomenon we ascertained, viz. 'a

great number of floral organs in lower temperatures', for it occurs here — in exceptional cases — as well, where the average is high (13° in 2 from the 53 cases, where there also occur 2 cases with 5 carpels).

It has become evident, that the greater number of floral organs in the lower temperatures is neither formed at the expense of the foliage-leaves, nor at their mutual cost, as e.g. in the case the flowers are double or full, when the inner whorls grow like tepals. (See the many cases described by K. ORTLEPP 1908 and 1915, and D. J. HILL 1766.) Every whorl increases its own number, especially at 9° and 13° most of all the outer whorls (tepals).

It was however not immaterial, to verify this parallel behaviour by every individual flower. For this purpose we give in table 7 a survey of the *sum of the floral organs*, which must normally amount or approximate the figure 15 (5 whorls of 3 organs).

TABLE 7. The whole number of floral organs.

Number:	15	16	17	18	19	20	21	22	23	24	25	n	M	m
9° (10 w.)	—	—	1	1	1	2	5	0	2	3	2	17	21.59	±0.58
13° (4 w.)	—	—	—	4	3	8	10	13	6	6	3	53	21.55	±0.26
17° (4 w.)	—	—	8	9	6	16	8	6	2	1	—	56	19.68	±0.24
20° (4 ₂ w.)	17	5	10	7	5	7	3	—	—	—	—	54	17.20	±0.27
23° (4 ₁ w.)	18	8	8	9	7	6	0	1	—	—	—	57	17.04	±0.25
25½° (6 w.)	18	7	12	9	1	0	2	—	—	—	—	49	16.53	±0.22
28° (10 w.)	14	3	1	0	1	2	—	—	—	—	—	21	15.90	±0.37

It appears, as was probable from the preceding, that likewise in the aggregate number of floral organs the same feature strikes the eye.

So the number of floral organs may be controlled with the temperature and experimentally by storing in 9° or 13° the number of floral organs may be increased far above the morphological base, and conversely by storing especially in 26° or 28° the base may be closely approximated.

§ 6. *On the combinations of the number of floral organs in the successive whorls.*

As the results discussed in § 5, which never occurred in the treatment of the Hyacinth (cluster) may be of interest for experimental morphology, we want to subject the figures in this paragraph to a closer examination. While 6 + 6 + 3 is the normal figure for the structure of the tulip, for the

whole family of Liliaceae, and the base for the whole group of Monocotyledons, the question of the frequency of this combination presents itself, and likewise whether with a greater number of floral organs formed by low temperatures, there occur combinations more frequent than whatever other combinations.

For this purpose we have destined the combinations of these floral organs from the base $6 + 6 + 3$ up to and including $8 + 8 + 4$, i.e. the pure tetramerous tulip-flower. This includes 18 possible combinations (see the table subjoined). If we include combinations higher than 8 and 4 (carpels) the number of possibilities becomes much greater. Moreover the number of times that a certain combination occurs, becomes rarer and is restricted to the lower temperatures, in which a great number of varied combinations may occur. As to the tepals in 75 cases we find 2 flowers with 9, 2 with 10 after 20° , at 23° not any flower with 9, not any with 10 and one with 11 in 60 cases (tab. 4). As to the stamens in 20° only one of the 58 flowers has 9 stamens (tab. 5). More than 4 carpels have been found only a few times in 13° and 9° (tab. 6). Quite different from all others was one specimen exposed to 13° with 18 tepals, 21 stamens, 10 carpels! We did not insert this specimen in the preceding tables.

Let us therefore abide by the 18 combinations 6—6—3 to 8—8—4.

334 of the 539 flowers, (from fixations and field-experiments) which after 44 different temperature-treatments could be examined, belong to these 18 combinations. In a perfectly equal division (without preference) each of these combinations should have 18, 55, i.e. 18 or 19 flowers. We find however as summed up in table 8.

Conclusions :

Certain combinations of figures are surely more frequent in the whorls of floral organs than others; conversely there are certain combinations rarely or never occurring. In the second column of table 8, which is the principal, all flowers belonging to these combinations have been recorded, so not only those formed in one temperature, but also those formed partly in e.g. 5° and then 17° , or 5° and later outside in the field, etc. In the 7 following columns the same has been given in detail for those flowers which have certainly been formed in 9° , 13° , etc. Their number amounts to 217 out of 334; no special columns have been given of the remaining 117 formed in different temperatures (e.g. 4 w. 5° + 6 w. 17° , 6 w. 5° + 4 w. 17° , 10 w. 5° + outside in the field, etc.), because in that case the number per column would grow very low and a conclusion could scarcely be drawn.

1^o. On our observing the second column, it is at once apparent, that the base 663 is not arbitrary, but quite frequent, that 884 is no more a combination as accidental as e.g. 683 or 864, etc., but that after 663 it has a much greater chance of originating than other combinations; next 773 is rather frequent; then 774 and fairly often 873 and 874.

2^o. Some combinations as 683, 684, 864 are — at least in these 44

TABLE 8. Number of flowers occurring in 18 different combinations of numbers of floral organs.

Numbers of tepals stamens, carpels	Number per combination of 334 flowers from all exposures together	Formed in 9°. The 17 remaining flowers occurred in combinations with higher fig.	Formed in 13°. The remaining (28) with higher figures	Formed in 17°. 32 with higher figures	Formed in 20°. only 5 are exceptions to these combinations	Formed in 23°. only 2 exceptions	Formed in 25½°: 4 exceptions	Formed in 28°: 1 exception
663	84				18	18	17	14
664	9				1	2	1	2
673	15				3	3	5	
674	9				2	1	4	
683	1			1				
684	0							
763	19			1	1	2		
764	5					1	1	1
773	33	1	0	5	6	6	7	1
774	27		2	0	4	7	6	
783	7		1	2	1	1	1	
784	4			1	0	1		
863	12			3	2			
864	1							
873	23		1	4	1	2	2	
874	24		2	2	5	4	1	
883	12		1	1	1	1	0	1
884	49	1	3	14	6	6	0	1
Number	334	2	10	34	51	55	45	20
Chance per comb. (round numbers)	19	(1)	(1)	2	3	4	3	2

temperature treatments — extremely rare or even never occurring. So we may communicate here (see part 3) that in 883 flowers exposed in 65 different modes, the combination 684 has never occurred.

30. On our considering the frequency of these combinations further in connection with the temperature applied, taking into account only those

flowers, which have positively been formed in that temperature (9° to 28°), we see how much the origin of a certain combination is due to that exposure. The combination 663 is the most frequent — that is only in exposure to 20° and higher: at 17° and lower this combination never or very seldom occurs (see part 3). After exposure to 17° the combination 884 is most frequent, but never or rarely occurs after $25\frac{1}{2}^{\circ}$ and upwards, whilst an exposure to 13° and 9° yields figures for most of the flowers, exceeding those of these 18 combinations. The intermediate combinations 773 and 774 are most frequent in (17°), 20° , 23° , $25\frac{1}{2}^{\circ}$, and are rarely formed by a higher temperature (28°) or lower temperatures.

So experimental morphology teaches us, that in the case of the Tulip the pure monocotyledonous base (663) greatly depends upon definite temperatures, and that we are capable of fairly eliminating this base through temperatures below 20° and of forming e.g. by exposure to 17° a rather high percentage of tetramorous tulip-flowers (ca 21 % of the flowers formed in 17° were purely tetramorous).

40. In 6 of the 18 combinations, i.e. 33 %, tepals and stamens occur in equal numbers, which may give rise to a very regular arrangement in the primordia. Now the question is, whether the number of flowers containing an equal number of tepals and stamens exceeds 33 %. It appears, that 214 of the 334 flowers, therefore not 33 % but 64 %, are among these 6 combinations, so that there exists a preference for an equal number of stamens and tepals, at least with the figures 6, 7 and 8.

§ 7. Is for instance the tetramorous flower a passing result of the temperature?

The question immediately rises whether certain combinations, e.g. pure tetramorous flowers, preserve this feature more or less in the young bulbs, formed by these bulbs, i. e. whether the feature is transmitted as a property to the lateral buds, likewise when the vegetative descendants are exposed next year to a temperature-combination, closely approximating the base 6—6—3.

To solve this question a crop of tulips, yielding purely tetramorous flowers (8-8-4) in May 1924, was lifted in July and from this crop 48 bulbs of main buds and 124 largest bulbs of the more advanced lateral buds were stored for 7 weeks in 26° + 4 weeks in 17° . The 48 main-bud-bulbs yielded 70 flowers.

Several of them yielded more than one flower-stalk, which is rather striking, considering it had occurred only 5 times in the 440 bulbs treated in 44 modes.

101 of the 124 largest more advanced lateral buds gave one flower-stalk. In May 1925 the following combinations occurred:

In the 70 flowers from main-bud bulbs	In the 101 flowers from the further lateral buds
6—6—3 48 times	5—6—3 1 times
6—6—4 4 ..	5—7—3 1 ..
6—7—3 7 ..	6—5—3 1 ..
6—7—4 3 ..	6—6—3 91 ..
7—6—4 1 ..	6—6—4 4 ..
7—7—3 2 ..	8—8—3 1 ..
7—7—4 3 ..	8—8—4 1 ..
8—8—4 2 ..	12—10—? 1 ..

So 139 of the 171 flowers (on bulbs, vegetatively descendant from bulbs with purely tetramerous flowers) showed the combination 6-6-3 and only 3 the combination 8-8-4 after an exposure to 7 w. 26° + 4 w. 17°.

It is evident, that *the number of floral organs again depends upon the the temperature every year* and there is no question at all of making the property permanent in the bud (the future new bulb). This however has nothing to do with the question whether by mutual pollination, i. e. generatively, the tetramerous condition is more or less maintained; this however is not probable.

Finally we mention one purely pentamerous tulip (10—10—5) in our grounds in 1924. The bulbs yielded by this were also exposed to 26° (7 w.) and 17° (4 w.) In 1925 only the main-bud-bulb gave a flower purely trimerous.

The literature cited will be mentioned at the end of the third part.

September 1925.

Physics. — "On a misconception in the probability theory of irreversible processes". By Mrs T. EHRENFEST-AFANASSJEWÄ.

(Communicated at the meeting of June 27, 1925).

Often it is thought that the two following statements contradict each other:

STATEMENT I. *A given course of a mechanical system with very many degrees of freedom is as probable as the contrary course, and*

STATEMENT II. *From every state which is not the most probable, the system tends with great probability toward the most probable state.*

This impression really is false and arises from the confusion of two statements, both equally true, as will be shown in what follows by means of a simplified scheme. — Consider a continuous series of discrete points lying in a plane with all integers (positive and negative) as abscissae, and with ordinates H which comply with the following conditions:

1. The ordinates are positive integers between $H_{min}=0$ and $H_{max}=H_m$.
2. The successive ordinates always differ by 1.
3. The various values of the ordinates have different probabilities (i. e., appear although infinitely often yet in differing proportions), and this probability increases from above to below. (Thus the ordinate $H=0$ has the greatest and the ordinate H_m the least probability).

A point whose ordinate is greater than those of the two adjacent ones we will call a "peak"; a point whose ordinate is less than those of the two adjacent ones, a "valley". — The succession of two points shall be called a "descending slope" whenever the point with the smaller abscissa (the beginning") has a greater ordinate than that with the greater abscissa ("the end"). In the contrary case we shall call it a "rising slope". — We shall say that our curve "rises" at a point P whenever it is the beginning of a rising slope; if the point P is the beginning of a descending slope we shall say that the curve "descends" at this point.

Now let us ask two questions:

QUESTION A. Given a certain height H . How great is the probability $W(H \rightarrow (H-1))$ that the curve descends at this point? — This probability, as may easily be derived from property 3¹⁾ is greater than $1/2$ for all values of H that differ from zero. For $H=H_m$ it is equal to 1, for all points at a height $H=H_m$ are peaks. But for $H=0$ it is equal to 0, for at this height all points are valleys. — Consequently it follows,

¹⁾ Cf. PAUL und TATIANA EHRENFEST, Ueber zwei bekannte Einwände gegen das Boltzmannsche H -Theorem. Phys. Zschr. 8, 1907, 311.

that for points at every height $H \neq 0$ the probability $W(H \rightarrow (H+1))$ that the curve rises there is less than $\frac{1}{2}$. Thus we obtain:

THEOREM A. For all heights except $H=0$ the probability that the curve descends is greater than that it rises.

QUESTION B. To compare the probability of a descending and a rising slope between the same two heights H and $H-1$. — The answer is:

THEOREM B. The probability for a descending and a rising slope between two particular heights H and $H-1$ are equally great.

We see this by asking how a certain height H which just has been reached at a point P can again be reached at a point P' . This can occur if the point P is the beginning of a raising slope $H \rightarrow (H+1)$, and then necessarily the point P' is the end of a descending slope $(H+1) \rightarrow H$, for we consider the point P' , at which, after point P , the height H is reached for the first time, in which case the height $H-1$ is not reached at all between the points P and P' ; or if point P is the beginning of a descending slope $H \rightarrow (H-1)$ and P' the beginning of a rising slope $(H-1) \rightarrow H$, in which case neither of these two particular slopes can occur more than once between P and P' . We also notice that point P' can not be missing from our curve, for each height between H_m and O is reached infinitely often.

Thus in any finite part of our curve the count Z_I of the slopes $H \rightarrow H-1$ and Z_{II} of the slopes $H-1 \rightarrow H$ must be the same or differing by no more than one, and in the limit for $Z_I = \infty$ is $\frac{Z_{II}}{Z_I} = 1$.

That is to say, the probabilities for the two slopes are the same.

What relation then exists between the two theorems A and B and the two statements I and II? What frequently is not perceived properly is that statement II is a consequence of theorem A while statement I is not directly connected with theorem A, but is a consequence of theorem B. — The two statements I and II clearly are conflicting with each other as little as the two theorems A and B. — However, since the occurrence side by side of I and II is often considered a paradox, we shall consider further how theorem B depends on A.

The probability of a descending slope $H \rightarrow (H-1)$ is the product of two probabilities: the probability $W(H)$ that the beginning lies at the height H , and the probability $W(H \rightarrow (H-1))$, that the curve descends at that point.

The probability of a rising slope $(H-1) \rightarrow H$ is the product of two others probabilities, $W(H-1)$ that the beginning lies at the height $H-1$, and $W((H-1) \rightarrow H)$ that the curve rises at that point.

Thus from (3) it follows:

$$W(H) < W(H-1)$$

and from theorem A:

$$\begin{aligned} W(H \rightarrow (H-1)) &> \frac{1}{2} \\ W((H-1) \rightarrow H) &< \frac{1}{2}. \end{aligned}$$

thus

$$W(H \rightarrow (H-1)) > W((H-1) \rightarrow H).$$

It is thus quite easily possible that the two products

$$W(H) \cdot W(H \rightarrow (H-1))$$

and

$$W(H-1) \cdot W((H-1) \rightarrow H)$$

are equally large. However, the topological considerations above must be taken as the rigorous proof of this equality.

Attention may also be called to the following: the quasi-periodic return of the ordinates of our curve to each value assumed once occurs only by definition (1, 2, 3) and is independent of the sort of phenomenon of which it is taken as an image.

Leiden, May 1925.

Anatomy. — C. J. VAN DER HORST: "*The Cerebellum of fishes. I. General morphology of the cerebellum.*" (Central Institute for Brain research. Amsterdam). (Communicated by Dr. C. U. ARIËNS KAPPERS.)

(Communicated at the meeting of September 26, 1925).

Concerning the general structure of the cerebellum of fishes three quite different lines of development can be distinguished which in their final stages, as found in Selachians, Chondrosteans and Teleosts, deviate to such a degree that it makes a direct comparison of these cerebella very difficult and has been the cause of erroneous interpretations.

To comprehend the development and morphological significance of the different parts of the cerebellum of fishes it is necessary to begin with a simple shaped and yet well developed cerebellum like that of *Ceratodus*. This cerebellum has been fully described by HOLMGREN and VAN DER HORST. It has practically the shape of a thick plate, but for a ridge in its middle part which protrudes downward into the fourth ventricle, and extends almost the total length of the cerebellum. It is rather flat in longitudinal direction but in crosssection it is crescentshaped, which is especially apparent in the middle part, at the level of the entrance of the trigeminus. Here two longitudinal furrows, one at the side of the ventricular and one on the outer surface, clearly indicate the boundary between the cerebellum and the oblongata. The granular mass is found at the side of the ventricle over the whole breadth of the cerebellum at this level, whereas the outer surface wholly consists of molecular matter.

The caudal border of the cerebellum of *Ceratodus* is convex. In cross-section the cerebellum has here the shape of a flat plate consisting of a granular and a molecular layer, which covers the fourth ventricle. On both sides this plate is connected with the dorsal border of the oblongata by means of the choroid membrane. Further frontad this plate is more and more curved until its edges fuse with the dorso-lateral margins of the oblongata. Where the fusion takes place, the granular mass curves outward and in this way the small but well defined auricles are formed.

The granular mass of the auricle continues in a caudal direction, though it can be clearly distinguished from it, into the lobus liniae lateralis anterior. This lobe forms the most dorso-lateral part of the oblongata and extends in a caudal direction to about the level where the first vagus roots leave the brain. I consider it better to call this nucleus which belongs to the dorsal root of the anterior lateral line nerve lobus liniae lateralis dorsalis and I will do so in this article. At the ventral side of this dorsal lobe the crista

cerebellaris is found, which stretches far more in caudal direction than the lobe. At the frontal end it continues with the molecular layer of the

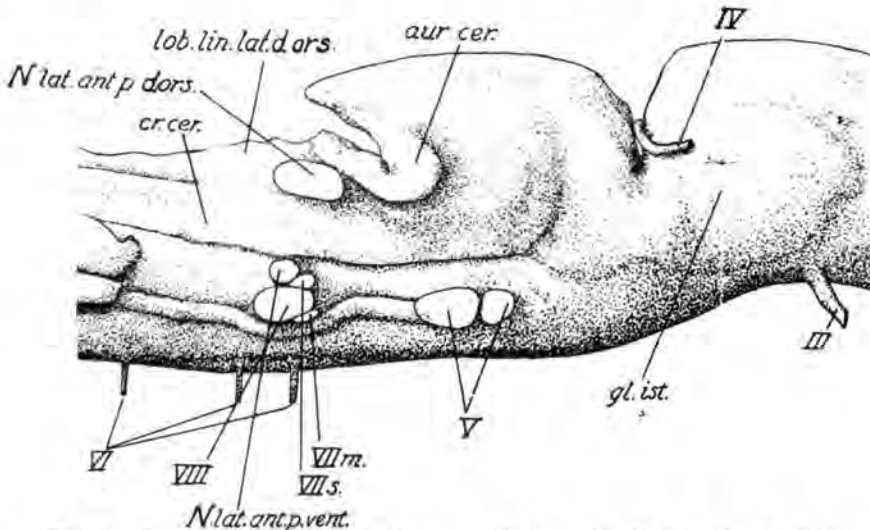


Fig. 1. Cerebellum and medulla oblongata of *Ceratodus* from the lateral side.
After HOLMGREN and VAN DER HORST.

cerebellum. The lobus lineae lateralis posterior is situated ventral to the crista, being the nucleus of the N. lateralis posterior and also of the ventral root of the anterior lateralis. Herefore I think it is better to call this nucleus lobus ventralis.

In the frontal part of the cerebellum on both sides of the ventricle the granular layer becomes considerably thicker and the molecular layer at the outside becomes gradually thinner. Finally the granular mass reaches the surface of the lateral sides of the cerebellum, so that the molecular layer forms then only the dorsal surface. The lobus lineae lateralis ventralis is connected with this lateral granular mass, and this mass continues in a frontal direction along the lateral side of the midbrain to the level where the oculomotorius leaves the brain.

In the chapter about the cerebellum, principally compiled by me, HOLMGREN and VAN DER HORST identified this lateral granular mass with the ganglion isthmi. It is possible that the frontal part, covering the lateral side of the midbrain, is homologous with the ganglion isthmi, but the caudal part of this granular mass, situated in the frontal part of the cerebellum, certainly can not be identified with this ganglion. It is the eminentia granularis of teleosts, as will be explained later on. In the meantime I will call this granular mass in this article the eminentia granularis.

Because of the fact that the dorsal lateralis nucleus is connected with the auricle and the ventral lateralis nucleus with the eminentia granularis, it follows, that these two parts of the cerebellum have a similar function. Especially does HERRICK call attention to this fact, but because of this

functional similarity HERRICK did not see the morphological difference between these parts. According to him the eminentia granularis is homologous with the auricle.

In connection with this I should call attention to the fact, that in *Ceratodus* the two frontal lateralis roots exchange a great number of fibers, before they enter the brain. In this way the functional similarity between auricle and eminentia granularis is still increased. The only difference is, that the ventral lateralis nucleus is in close connection with the nucleus of the N. octavus, even to such an extent that it is impossible to distinguish these two nuclei.

The auricle belongs almost wholly to the area of the N. lateralis, whereas the eminentia granularis is not only in connection with the lateralis but also with the octavus. On the other hand the middle part of the cerebellum is principally the endnucleus of secondary tracts arising from the mesencephalon or which ascend from the spinal cord and the oblongata and which carry somato-sensory stimuli.

Starting from such a simple and yet well developed cerebellum, as is found in *Ceratodus*, it is possible to understand the morphological significance of the different parts of the cerebellum, as it has developed in different directions in the other orders of fishes.

In Selachians we find the middle part, the corpus cerebelli, enormously developed and the same is the case with the auricles, as has also been explicitly described by VOORHOEVE for a great number of sharks and rays. The auricle extends frontad along the total length of the cerebellum, so that the place, where the eminentia granularis might be expected, is covered by the auricle. In embryo's, in which the auricles are still smaller, the eminentia granularis is plainly visible, but during further development it is included more or less within the auricle. So we see, that the lobus liniae lateralis ventralis of Selachians is connected with the auricle, namely with the frontal part of it. But I will not enter into details here about the morphology of the cerebellum of Selachians.

Whereas the cerebellum of Selachians, upon becoming too large to form a flat plate, curves upwards in the middle part, in Crossopterygians it curves downwards in the ventricle (VAN DER HORST). In the median sagittal plane the skull cavity deeply penetrates into the cerebellum, so that the two lateral halves, forming the cerebellum, are connected in these fishes only by the ependyma and a thin layer of crossing fibers.

In Chondrosteans (*Acipenser*, *Polyodon*) the cerebellum is formed principally in the same manner, but for a few differences, by which this curving inwards of the cerebellum is less striking in Chondrosteans than in Crossopterygians. The main difference in this respect is, that the median fissure which remains in Crossopterygians between the two lateral halves of the cerebellum, disappears in Chondrosteans for the greater part, so that the curved in part is almost a solid mass. The second difference is, that the auricles in Crossopterygians are very small or lacking altogether.

whereas in Chondrosteans they are very large and furthermore they are situated far dorsally, so that they cover the lateral surface of the corpus cerebelli. So when comparing Chondrosteans with Teleosts one gets the impression, that the corpus cerebelli is not curved inwards into the ventricle, but only that the auricles are situated far dorsally.

This dorsal position of the auricles is a result of the curving inwards of the cerebellum. This makes it necessary for the ventricle to enlarge, and this enlargement occurs by the stretching out of the lateral sides of the fourth ventricle in a dorso-ventral direction. This becomes clear upon comparing fig. 2 of *Calamoichthys*, showing a section slightly caudal of the cerebellum, with fig. 3 of the same animal showing the most caudal

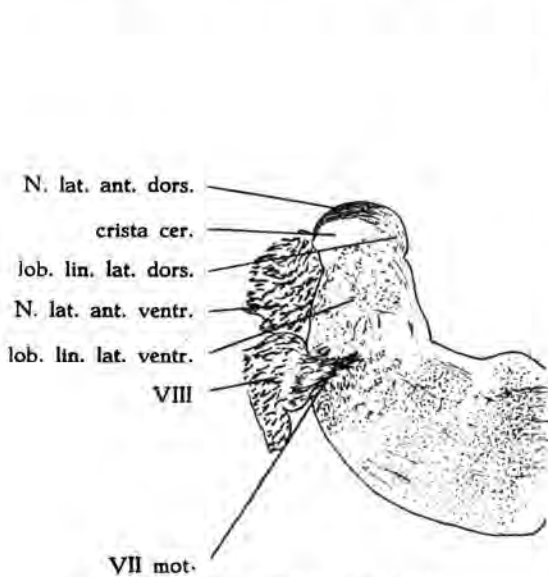


Fig. 2. *Calamoichthys calabaricus*.

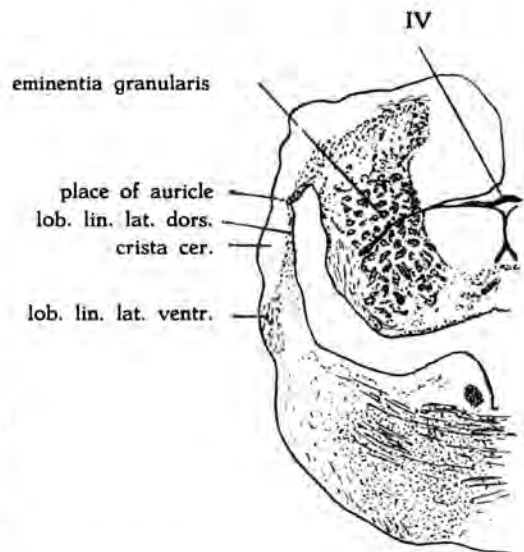


Fig. 3. *Calamoichthys calabaricus*.

section, in which the corpus cerebelli is connected with the dorso-lateral border of the oblongata.

Figure 4 shows a similar section of the brain of *Polypterus* and here we see a striking difference between the two Crossopterygians. In *Polypterus* the granular mass reaches the lateral surface at the place, where the caudal border of the cerebellum unites with the dorso-lateral margin of the oblongata. Here a distinct, though small, auricle is present. The choroid plexus had been removed from this brain, so that the lateral recess, that otherwise covers the auricle externally, is not visible in the sections. On the other hand in *Calamoichthys* the auricle is lacking absolutely, the crista cerebellaris being directly combined with the molecular layer of the cerebellum.

This slight development or total absence of the auricle in Crossopterygians is in close relation to another remarkable fact. In Chondrosteans and

Selachians, as in *Ceratodus*, the dorsal root of the lateralis anterior is much thicker than the ventral root. But in Crossopterygians the dorsal root is

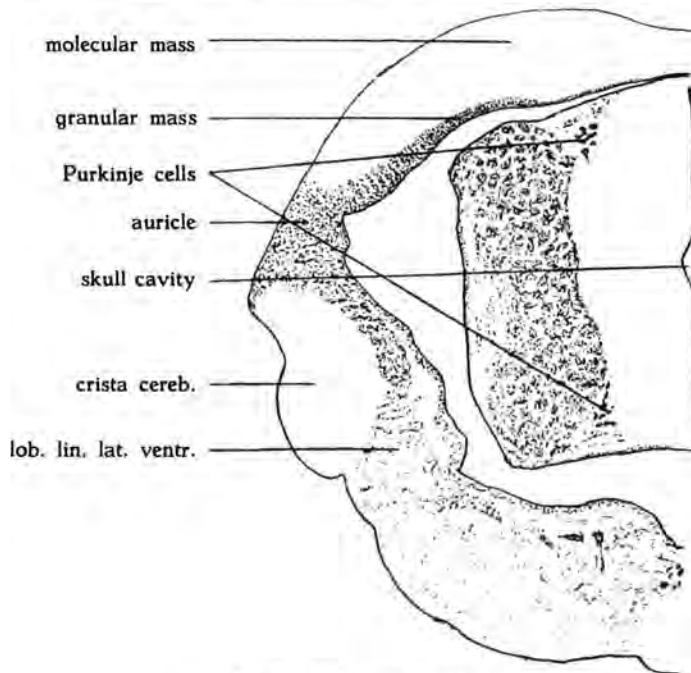


Fig. 4. *Polypterus bichir*.

small and the greater part of the lateralis fibers enters ventrally (fig. 2). So we see, that the dorsal lateral line lobe in Crossopterygians is relatively much smaller than in the other fishes mentioned above. And as the auricle is in close relation with the lobus liniae lateralis dorsalis, we need not be surprised, that also the auricle is here very small, or absolutely wanting. It is not necessary that this reduction of the dorsal lateralis root indicates, that the whole lateral line system is less developed in Crossopterygians, and as we will see still more in Teleosts, than in Chondrosteans and Selachians. As I mentioned above, in *Ceratodus* an important exchange of fibers is found between the two roots of the anterior lateralis before they enter the oblongata. In Crossopterygians the small dorsal root combines with the large ventral root directly outside the brain. It is quite certain, that fibers entering dorsally in Chondrosteans and Selachians will do so ventrally in Crossopterygians.

The eminentia granularis of the Crossopterygians and Chondrosteans has shifted in dorsal direction in the same way as the auricle. We find this eminentia quite at the dorsal surface of the cerebellum and in Crossopterygians it reaches the surface even in the median fissure. In Chondrosteans the eminentia is more distinct than in Crossopterygians.

A third line of development of the cerebellum is found in Holosteans

and Teleosts. We find the most simple condition which is easiest to be compared with that of *Ceratodus* in *Amia*. I was unable to obtain suitable material of *Lepidosteus*. The cerebellum of *Amia* shows principally the same structure as that of *Ceratodus*. It covers as a curved plate the frontal part of the oblongata. The caudal border is convex and forms here the roof of the fourth ventricle. Also the ependyma, forming a distinct lateral recess, is attached in the same place as in *Ceratodus*.

Whereas in *Ceratodus* the freely projecting caudal part of the cerebellum consists of an outer molecular and an inner, ventricular, granular layer, this caudal part in *Amia* is formed only by molecular substance (fig. 5). Only at the ventricular side and especially near the attachment of the ependyma scattered granular cells are found between the fibers. When studying the brain from this level in frontal direction, we see that soon a real granular mass appears in the sections (fig. 6), not at the ventricular side but in the middle of the molecular mass. The molecular substance situated at the dorsal side of this granular mass is the same as found in *Ceratodus*, whereas the ventral molecular mass consists of crossing fibers

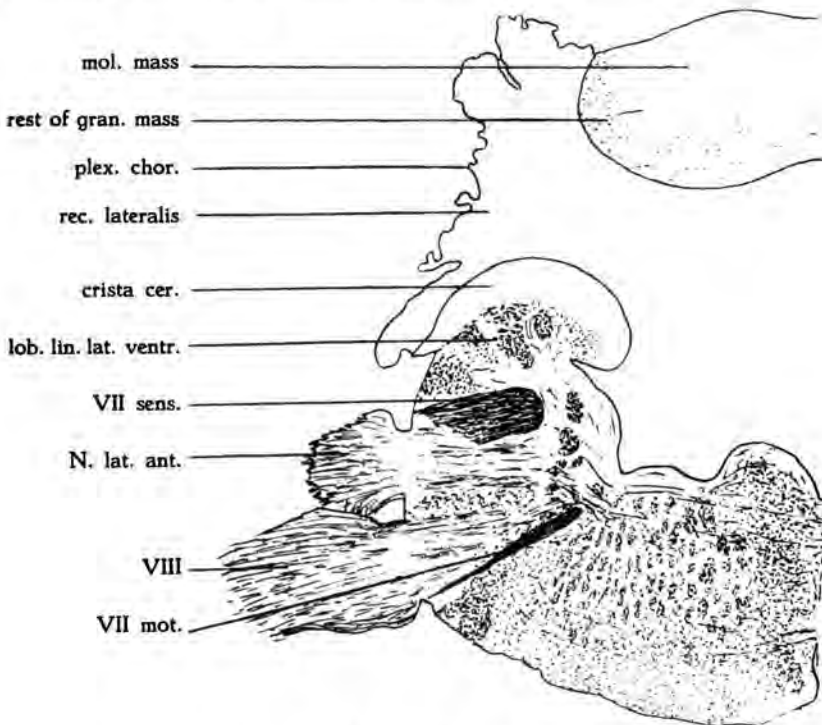


Fig. 5. *Amia* calva.

arising from the crista and forming the tractus vestibulo-cerebellaris. The fact, that groups of granular cells are scattered between the fibers shows, that the fibers have pushed away the granular substance, which was situated originally at the ventricular side.

Running from the crista to the cerebellum the fibers curve in caudal direction to cross over near the caudal border of the cerebellum. So we

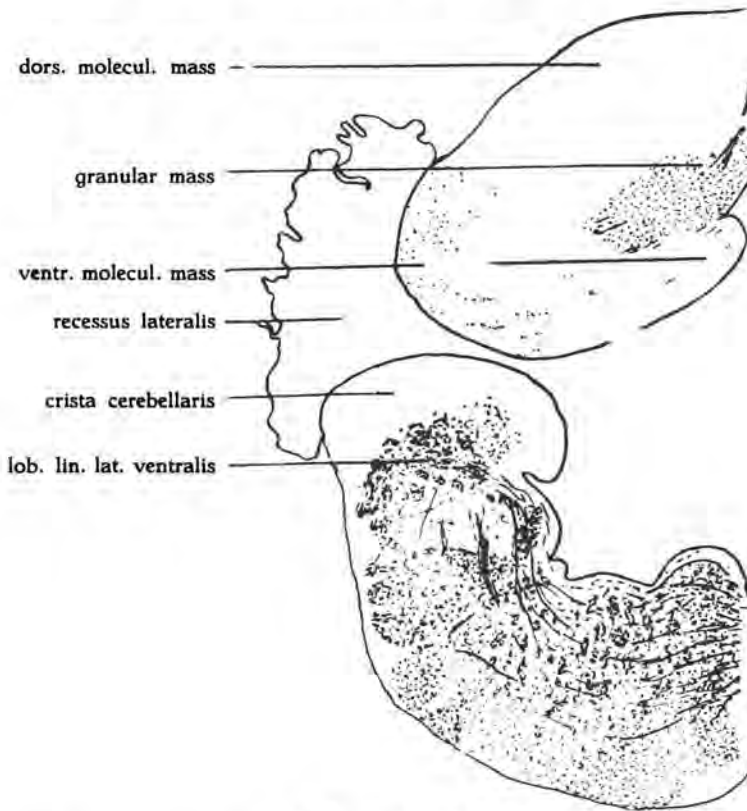


Fig. 6. *Amia calva*.

see, that the ventral molecular layer soon splits, in the median sagittal plane, into two parts (fig. 6), which, running in a frontal direction, are separated more and more. The two parts disappear wholly at the level, where the molecular mass combines with the crista cerebellaris (fig. 7).

Because the vestibulo-cerebellar fibers run from the crista along the ventricular side of the cerebellum and here push away the granular substance, it goes without saying, that an auricle cannot be present. Only the granules that are scattered through the whole ventral molecular mass, are a little more densely packed at the place, where cerebellum and oblongata unite and where the auricle might be expected. This accumulation of granules may be looked upon as a rest of the auricle. In *Amia* only a few granular cells are found here, in some Teleosts, e.g. *Esox*, by far more. The granules may also form a small compact group like in *Osmerus* (fig. 9).

As mentioned before, the dorsal root of the lateralis anterior is much smaller than the ventral root in Crossopterygians. This root is absolutely lacking in *Amia* and Teleosts. All lateralis fibers enter ventrally to the crista cerebellaris (fig. 5). BERKELBACH VAN DER SPENKEL mentions a

dorsal root of the lateralis anterior in *Silurus*, but this root is a bundle of fine lateralis fibers, forming the most frontal part of the entering nerve

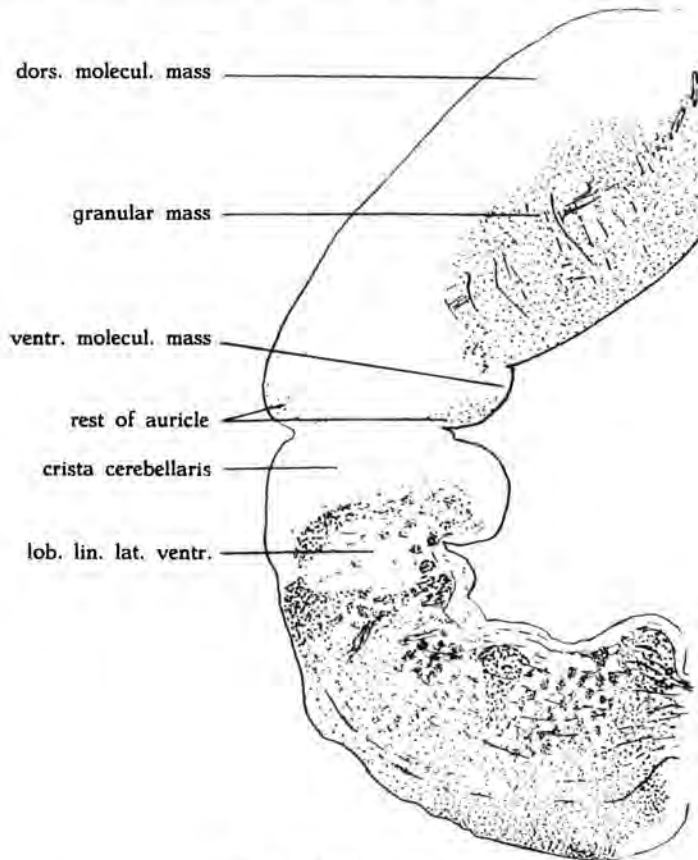


Fig. 7. *Amia calva*.

and ascending directly to the cerebellum. The fact that this ventral root consists of coarse and thin fibers, makes it apparent that the dorsal lateralis root is inserted in the ventral root in Teleosts.

According to SCHEPMAN in Cyclostomes the dorsal root consists only of coarse fibers and the ventral of thin ones, whereas in Teleosts both types of fibers occur in the ventral root.

If we continue our study of the cerebellum in *Amia* in a frontal direction, we see that the granular mass extends more and more in lateral direction, untill finally it reaches the lateral surface of the cerebellum. In figure 8 the granular mass is still covered by a thin layer of molecular substance, but this layer disappears a few sections more frontally. Here we find the molecular layer only at the external surface of the middle part of the cerebellum or the corpus cerebelli. The lateral mass of granular substance, found in the same way in Teleosts (fig. 11), has been described by FRANZ as *eminentia granularis*. In *Ceratodus* this lateral extension of granular substance occurs in quite the same way. So here it ought to be called

also eminentia granularis. The ventral lateralis nucleus passes over into this eminentia granularis.

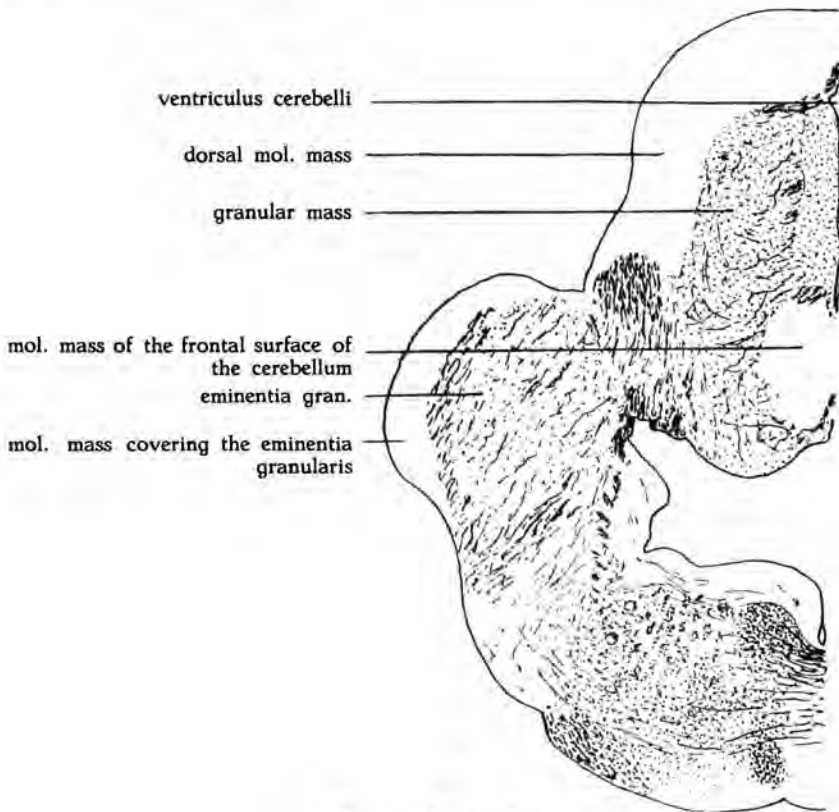


Fig. 8. *Amia calva*.

In the frontal part of the cerebellum the two eminentiae granulares are connected by a band of granular cells, which, situated along the roof of the fourth ventricle, form the most ventral part of the corpus cerebelli. In *Amia* the eminentiae can be clearly distinguished from this band of granules. In this fish the frontal extremity of the eminentia is seen some sections in front of that figured in fig. 8, whereas the band of cells above the ventricle reaches farther frontally and passes over in the granular mass of the valvula. But in different Teleosts the two eminentiae granulares cannot be separated from the granular mass between them nor from the granular substance of the valvula. Moreover it is known also by the fiber connections, that the valvula cerebelli belongs to the acustico-lateral area.

In *Ceratodus* the granular mass of the eminentia extends as a tongue far frontally along the lateral side of the midbrain (fig. 1) HOLMGREN and VAN DER HORST have called this part the ganglion isthmi. It is not impossible, that this granular mass really is the ganglion isthmi, because also this ganglion is related to the acustico-lateral area. But it may also

be possible, that this mass is the homologue of the *valvula cerebelli* which in this case should have extended along the lateral surface of the midbrain instead of curving into the ventricle of this brain part.

In Teleosts almost the same relations are found as in *Amia*; what was still in a rudimentary state in *Amia*, has developed farther in Teleosts. This concerns in particular the ventral molecular mass. Compared with *Amia* this mass extends by far more frontally and covers the whole ventricular side of the cerebellum. Also the place of attachment of the choroid plexus, covering the fourth ventricle, has shifted frontally, so that the caudal part of the cerebellum projects quite independently to the exterior.

In *Osmerus* the conditions are nearly the same as in *Amia*. Here also the cerebellum has the form of a thick curved plate (fig. 9). The ventral molecular mass extends here farther frontally (fig. 10), but still it disappears soon, when the cerebellum is attached to the dorso-lateral border of the oblongata. But in the more specialised Teleosts this ventral molecular layer extends below the whole corpus cerebelli. Moreover the cerebellum has increased in size considerably and it shows a different form in the different orders of Teleosts. It may grow high up as a solid mass, as is often the case in *Acanthopterygii* (fig. 11), or it remains more or less flat; it may be situated above the fourth ventricle as in *Gadidae*, or it may bend in frontal direction above the tectum opticum as in *Siluridae*.

Also the *eminentia granularis* varies greatly in development. This all has been described by FRANZ for a great number of Teleosts.

I only will call attention here to the relation met with in *Anguillidae* (fig.

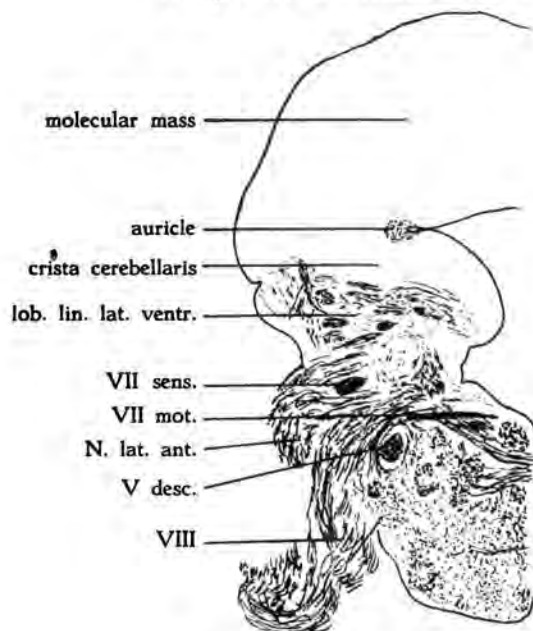


Fig. 9. *Osmerus eperlanus*.

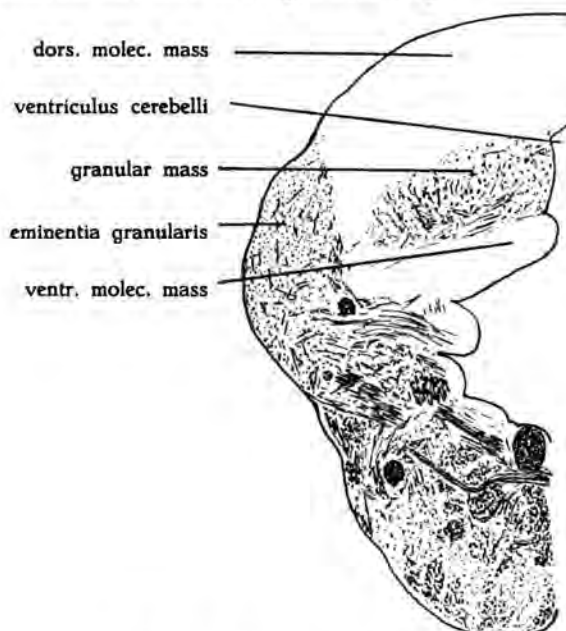


Fig. 10. *Osmerus eperlanus*.

12). Here the granular layer reaches the lateral surface along the whole length of the cerebellum. Also the granular mass consists clearly of two layers, the ventral one of which is in connection with the eminentiae granulares. These two layers are separated by a furrow on the lateral surface. According to FRANZ this is a primitive condition and it proves, that the cerebellum of Teleosts has developed from a plate-like state by curving upwards. This should correspond to a selachian cerebellum being so much flattened in fronto-caudal direction, that the ventricle should have quite disappeared. Only in some cases as in *Anguilla*, a limit between the dorsal and ventral granular layer should be visible.

In my opinion the cerebellum of *Anguilla* must be explained as follows: The eminentiae granulares are greatly developed and extend along the whole length of the cerebellum. Also the granular layer, which otherwise in Teleosts connects the two eminentiae only in the frontal part of the cerebellum, has enlarged in caudal direction. In this way two granular layers are visible externally over the total length of the cerebellum, the ventral one

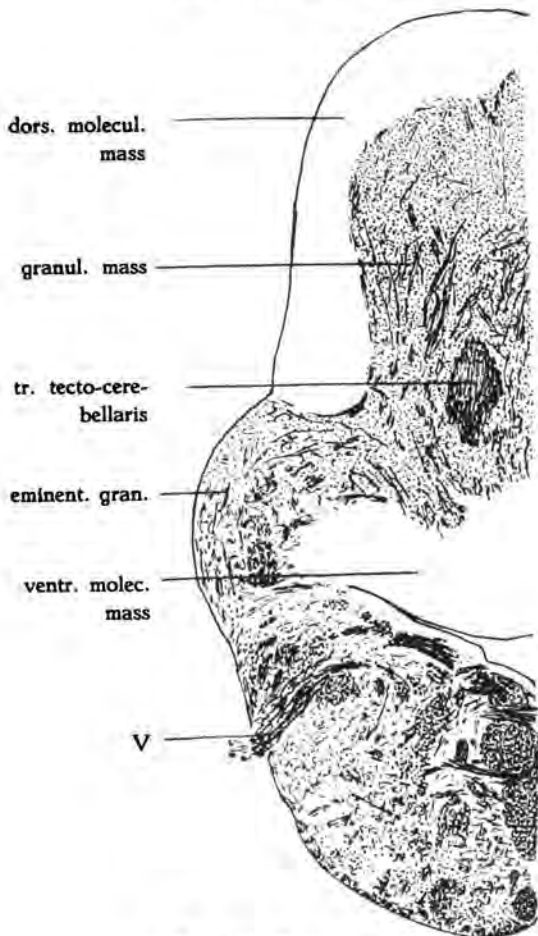


Fig. 11. *Trachinus draco*.

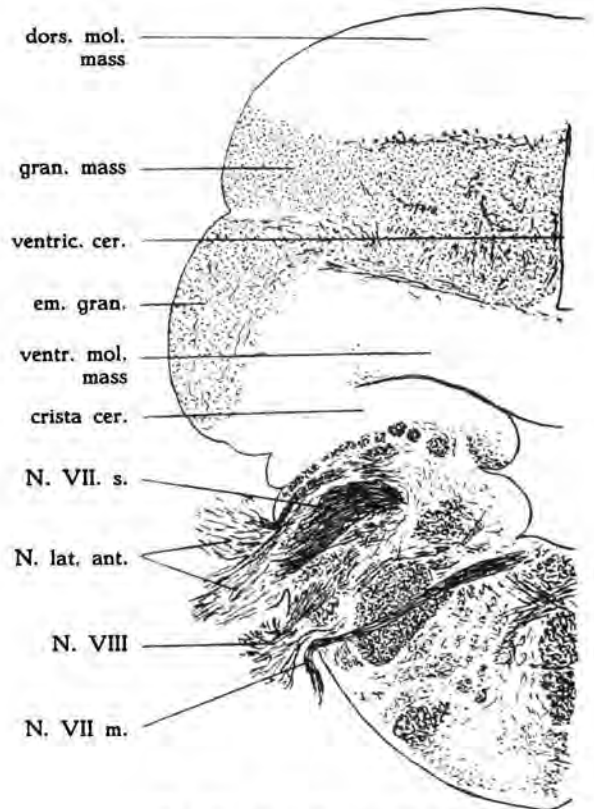


Fig. 12. *Anguilla anguilla*.

belongs to the eminentiae granulares, the dorsal one is the real granular substance of the corpus cerebelli. Also the latter granular substance reaches the surface in Anguillidae in contradistinction to the other Teleosts, and this may be in relation with the great depression of the cerebellum.

Finally I may show, that the ventriculus cerebelli in *Amia* and different primitive Teleosts, is not homologous to the ventriculus cerebelli in Selachians. In Teleosts this ventricle is a very narrow sagittal fissure, being a last remnant of the bilateral origin of the cerebellum as described by SCHAPER. If the opinion of FRANZ were correct, we might expect a horizontal or a transverse fissure instead of a sagittal one. The cerebellum of Selachians arises by folding upwards of a plate-like rudiment which is found in embryo's. So the ventriculus cerebelli in these animals is a part of the fourth ventricle separated from the rest by the folding upwards of the cerebellum. The only part of this ventricle which may be compared with the ventriculus cerebelli of Teleosts is the sagittal fissure between the two granular ridges.

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Chemistry. — "*On the Crystalstructure of Germanium-tetraiodide*".
By Prof. Dr. F. M. JAEGER, Dr. P. TERPSTRA and Mr. H. G. K.
WESTENBRINK.

(Communicated at the meeting of September 26, 1926).

§ 1. In the following the results of the determination of the crystal-structure of *Germaniumtetraiodide*: GeI_4 are published, of which a small quantity was kindly presented to us by Prof. DENNIS¹⁾. At the same time a small quantity of the corresponding optically-uniaxial *Di-iodide*: GeI_2 was received, the crystals of which were, however, unsuitable for an investigation in its full extent. We hope, however, yet to be able within a short time to compare the structures of both these compounds in connection with the results of a study of some derivatives isomorphous with GeI_2 .

In the first instance a number of diffraction-images were obtained after the method of HULL and DEBIJE, the source of radiation in this case being a copper-anticathode. The type of ROENTGEN-tube used was a dismantable gas-tube of cylindrical shape of the form used in Sir W. H. BRAGG's laboratory, and provided with an aluminium-window. The radiation used (at 50 K. V.; current: in mean 9 m.Amp.) consisted of copper-*K*-radiation of the wave-lengths: $\lambda_\alpha = 1,537$ A.U. and $\lambda_\beta = 1,388$ A.U., $\frac{\lambda_\alpha}{\lambda_\beta} = 1,107$. Occasionally a nickelfilter was made use of; however, afterwards this was dropped, because of the weakening of intensity, especially, as it appeared that the diffraction-images which belonged to each of these wave-lengths, could easily be discerned from each other. In these experiments the very finely powdered iodide was smeared upon a thin silk thread stretched along the axis of the cylindrical camera.

As an instance the values are given in the following table, measured by means of a comparator on one of the best films (N^o. 18) obtained in this way; the radius of the camera was 24,76 m.M.

Evidently the line N^o. 1 is the β -line corresponding to N^o. 2; N^o. 3 that corresponding to the β -line N^o. 4; N^o. 6 the β -line of N^o. 7; N^o. 8

that corresponding to the α -line N^o. 9. Moreover, $\frac{\sin^2 \frac{\theta}{2}}{\Sigma(h^2)}$ is, for λ_α equal to: 0,00418 and for λ_β equal to: 0,00341; these numbers are, indeed, to each other in the proportion of $\left(\frac{\lambda_\alpha}{\lambda_\beta}\right)^2$. Although, if the two first values

¹⁾ L. M. DENNIS, Journ. Amer. Chem. Soc., **44**, 2856, (1922).

are not considered, the indices: (111), (200), (220), (311), (222), (331), (240) and (224) may be calculated directly from these measurements, it will become clear from the following determinations, that the line N⁰. 4 corresponds to the *second* order reflection on {111}. If the values N⁰. 1 and N⁰. 2 are also taken into account, it follows from these, that $\Sigma(h)^2$ for them is equal to 6, and the other forms observed will then obtain the values indicated in the table; evidently the images N⁰. 1 and 2 represent the first order images on {112}, line N⁰. 13 thus being the fourth order of them. In this connection it may be remarked also, that on Film N⁰. 12 a rather intense line was found for $\theta/2 = 28^\circ 17'$, on Film N⁰. 7a one for $\theta/2 = 25^\circ 16'$, corresponding to the third order reflections on {112} for λ_α en λ_β ; the theoretical angles are here: $28^\circ 22'$, resp.: $25^\circ 24'$. On the contrary. the corresponding images of the second order were nowhere observed with certainty.

Analysis of Film N ⁰ . 18.								
Number of the lines from the centre	Distance l of the images on both sides in m.m.	Wave-length	Estimated intensity	2θ	$\theta/2$	$\sin \theta/2$	$\sin^2 \theta/2$	Indices
1	$l/2 = 7.17$	λ_β	extremely weak	$\theta = 16^\circ 36'$	$8^\circ 18'$	0.1444	0.0208	(112)
2	$l/2 = 7.88$	λ_α	very weak	$\theta = 18^\circ 14'$	$9^\circ 7'$	0.1584	0.0251	(112)
3	20.29	λ_β	5	$47^\circ 16'$	$23^\circ 48'$	0.203	0.0412	(222)
4	22.49	λ_α	10	$52^\circ 4'$	$26^\circ 2'$	0.225	0.0506	(222)
5	26.00	λ_α	7	$60^\circ 12'$	$30^\circ 6'$	0.260	0.0676	(400)
6	33.31	λ_β	3	$77^\circ 8'$	$38^\circ 44'$	0.333	0.1089	(440)
7	37.11	λ_α	9	$85^\circ 56'$	$42^\circ 58'$	0.366	0.1340	(440)
8	39.33	λ_β	1	$91^\circ 4'$	$45^\circ 42'$	0.387	0.1497	(622)
9	43.85	λ_α	8	$101^\circ 32'$	$50^\circ 46'$	0.429	0.1840	(622)
10	$l/2 = 22.97$	λ_α	3	$106^\circ 20'$	$53^\circ 10'$	0.448	0.2007	(444)
11	59.18	λ_α	3	$137^\circ 0'$	$68^\circ 30'$	0.563	0.3169	(662)
12	60.92	λ_α	3	$141^\circ 4'$	$70^\circ 42'$	0.577	0.3329	(480)
13	67.64	λ_α	2	$156^\circ 36'$	$78^\circ 18'$	0.631	0.3981	(448)

From these measurements it can be deduced, that here a cubic space-lattice is present in the structure: from $\frac{\lambda_\alpha^2}{4a^2} = 0.00418$ and $\frac{\lambda_\beta^2}{4a^2} = 0.00341$, the edge a of the elementary cubic cell is calculated:

$$a = 11.89 \text{ A.E.}$$

As the volume V of this cell is $1679 \text{ cubic A.U.} = 1679 \cdot 10^{-24} \text{ ccm.}$, and as DENNIS¹⁾ determined the specific weight d of the crystals (in sulphuric acid) at 26° C. on: 4,3215, the number N of the molecules GeJ_4 ($M=580,18$) in this cell is calculated as: $N = \frac{V \cdot d}{M \cdot 1,64 \cdot 10^{-24}} = 7,63$; evidently, therefore, the cell contains 8 molecules GeJ_4 , and the true specific weight²⁾ of the crystals must be: $d_{40} = 4,534$.

Besides the films mentioned here, also some photographs were prepared after HULL's method on flat films; although very faint, also in this case the lines of $\{112\}$ were observed here. One of these radiograms proved, moreover, without any doubt, that the line $N^0. 3$ is indeed no other than the line for λ_{β} , corresponding to $N^0. 4$.

Film $N^0. 18$ was tested, moreover, by the aid of a photometer-arrangement with a thermoelectrical cell and mirror-galvanometer with respect to its differences in intensity. In fig. 1 the results of these measurements on one half of the film are plotted graphically. Besides the images already mentioned above, the presence of the images of the first order (for α - and β -radiation): $\{111\}$, $\{221\}$, $\{421\}$, $\{411\}$, $\{432\}$, $\{731\}$, etc., although comparatively weak, was revealed, as well as that of those of $\{112\}$.

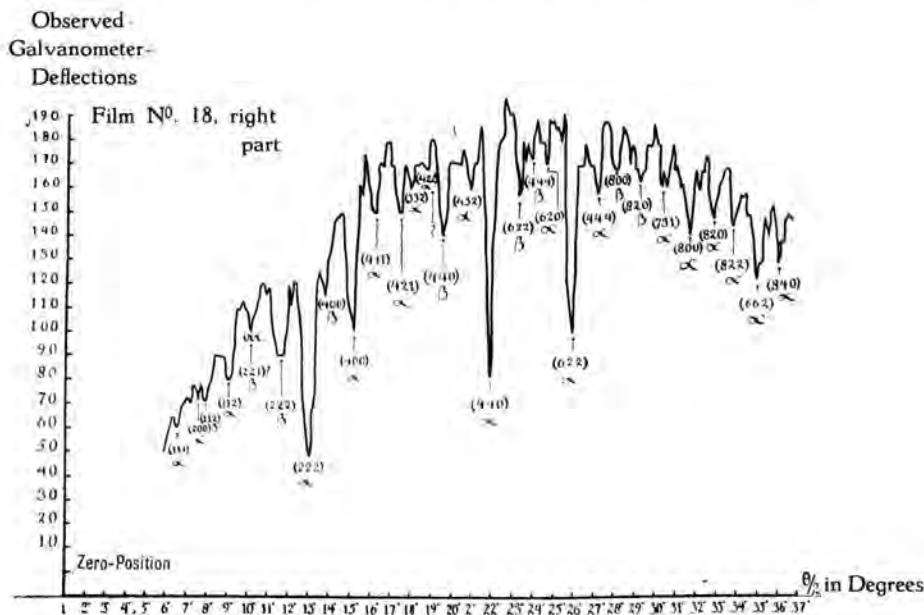


Fig. 1. Photometrical curve of Film $N^0. 18$.

1) Loc. cit., p. 2856. As GeJ_4 in contact with solvents is extremely easily decomposed, so it is probable, that in reality no solvents will be without action upon this substance, — the deviations in d thus being explicable.

2) From the measurements on the other films a value for a is deduced, not appreciably deviating from 12 A.U. In this case, d_{40} would be: 4,405.

Because of the general veil superimposed upon all these lines, it is, however, impossible to determine the absolute intensity of these lines. The most intense lines correspond to $\{111\}$, $\{331\}$ and $\{311\}$ in the *second* order; to $\{100\}$, $\{110\}$ and $\{210\}$ in the *fourth* order; to $\{100\}$ in the *eighth* order etc.

Further confirmation of this was again obtained by means of a rotation-radiogram, a perpendicular to the edge of one of the triangular octahedron-planes being chosen here as vertical axis of revolution. Besides some other images, those of $\{222\}$, $\{444\}$, $\{622\}$, $\{440\}$ and $\{662\}$ appeared to be present upon it; but there was, for instance, no indication of $\{100\}$ or $\{110\}$.

§ 2. For the purpose to obtain full certainty about the orders of the diffraction-images mentioned above, measurements were made on a plate parallel to $\{111\}$, after BRAGG's spectrographic method. The crystalplates parallel to $\{111\}$ were obtained by slow evaporation of a solution of the iodide in carbondisulphide in a vacuum. The very thin triangular plates thus obtained were mounted carefully on thin glass-plates, put upon the *X*-ray-spectrometer and given a slow oscillating motion along the axis of the instrument by means of a clock-work. To determine accurately the distance between the crystal-plate and the central spot on the photographic plate, two photograms were made on the same film, this being placed in parallel positions at two different distances a_1 and a_2 . The shift $a_2 - a_1 = w$ was measured very accurately; by measuring also on the film the distances s_1 and s_2 of two corresponding lines, e.g. that of the lines for λ_x of λ_3 , in both cases, the distance x , where the plate stood in the first experiment, can be easily calculated; for:

$$\frac{x}{x+w} = \frac{s_1}{s_2}.$$

If θ is the glancing angle, at which the diffraction takes place, then evidently $\tan 2\theta = \frac{s_1}{2x}$, so that, θ being now determined, the spacing $d_{(111)}$ of the reticular planes may be calculated from the formula: $2d_{(111)} \sin \theta = n \cdot \lambda$.

In this way for $x = 45,82$ mm. and for $\lambda_x = 1,54$ A.U.¹⁾, s_1 was found to be: 44,10 mm.; therefore, $\theta_x = 12^\circ 51'$; in the same way, for $\lambda_3 = 1,389$ A.U. and $x = 45,40$ mm., s_1 was found to be: 39,09 mm., θ_3 thus being: $11^\circ 39'$. If these spectra be *second* order spectra, $d_{(111)}$ becomes: 6,924 A.U., resp.: 6,879 A.U., in mean: 6,901 A.U. Indeed, if in a cubic space-lattice the edge a be really equal to 11,9 A.U., $d_{(111)} = \frac{1}{3} a \sqrt{3}$ must be: 6,90 A.U. The intensive image N⁰. 4 film 18 thus corresponds really to (222). The spectrum of the fourth order must,

¹⁾ Actually in the *K*-radiation of copper; $\lambda_{x_1} = 1,537$ A.U. and $\lambda_{x_2} = 1,543$ A.U.; on an average therefore, $\lambda_x = 1,540$ A.U. For λ_3 the value: 1,389 A.U. was used; θ is here equivalent to $\theta/2$ in the table above.

therefore, be situated at a distance from the central spot (for λ_x), equal to: 60,34 mm., when x again is 45,82 mm. ($2\theta = 52^\circ 48'$). With an exposure during 10 minutes (8 to 10 milli-Amp.), this image was really found at its right place on the films X and X', and that very intensive. For the spectrum of the first order, the distance to the central spot for λ_x should be: 10,38 mm. and for λ_3 : 9,31 mm. Indeed, both these spectra could be stated, be it extremely faint, on film III; their intensities are incomparably fainter than those of the second and fourth order¹⁾. Even if (on film III') the spectrum of the first order was exposed during 37 minutes, that of the second order during only 5 minutes, the intensity of the first image appeared to be very much smaller than that of the last image.

Finally these experiments were executed once more with a silver-anticathode, which gives a radiation of $\lambda = 0,565$ A.U. Now the spectrum of the second order appeared at: $2\theta = 9^\circ 24'$; the distance of both images to the central spot now being: 7,52 mm., with $x = 45,5$ mm. ($s_1 = 15,1$ mm.); in the same way the spectrum of the fourth order appeared at a distance from the central spot of: 15,52 mm. ($s_1 = 31,4$ mm.) and with an appreciable intensity ($2\theta = 18^\circ 50'$). The spectrum of the third order must be found at: $2\theta = 39^\circ 6'$, i. e. at a distance from the central spot of: 36,97 mm., if copper-radiation of $\lambda 1,540$ A.U. be used; its distance from the second order spectrum (see above) therefore being: $36,97 - 22,05 = 14,9$ mm. The experiment was made in such a way, that the spectrum of the second order was exposed only 5 minutes, but that of the third order 30 minutes (film VI), and notwithstanding this, an extremely faint image appeared to be hardly visible in the calculated place.

By all these experiments it is convincingly proved, that on (111) diffraction occurs in such a way, that the spectra of the first and third order are extremely faint, those of the second and fourth order, however, very intensive.

§ 3. In trying to solve the problem: to which of the 230 space-groups do the crystals of GeI_4 really belong?, — it is necessary also to keep in mind, that the specific diffracting influence of the I -atoms, which are four times as numerous, is very different from that of the Ge -atoms, and also, that the absorption of ROENTGEN-rays is very different for both²⁾.

¹⁾ During the preparation of film III the aluminium-window of the tube appeared to be gradually covered with volatilized copper. Because of the unequal absorption thus taking place, the lines corresponding to λ_3 appeared now to be more intensive than those for λ_x .

²⁾ The strong absorptive power of iodine in this salt, manifested itself also in preparing the radiograms after VON LAUE: it was only possible to get them, if extremely thin plates were made use of.

A first step towards this solution of the problem was the determination of the crystallographical symmetry. With some small crystals obtained from a solution in benzene, a number of very small facets were observed at the corners of one of the planes of the octahedron. The crystal was measured by means of a goniometer with two circular divisions; the plane (112) being taken as polar facet. The following reflexes were localised:

Face	φ	ρ	Kind of reflection:	Index of Crystal-plane
α	0°	19° 38'	sharp	(111)
β	129	23 57	very sharp	(102)
γ	0	90 10	sharp	(111)
δ	34	34	faint	(211)
ε	25	57	very faint	(210)
ζ	184	69	very faint	(112)
η	204	56 35	sharp	(102)
θ	209	27	very faint	?
ι	294 $\frac{1}{4}$	42 37	sharp	(021)
κ	330	35	very faint	(121)
λ	34	32	faint	(211)
μ	124	37	faint	?
ν	114	62 15	sharp	(111)
\omicron	182	34 59	very sharp	(001)
σ	313	65	very faint	(010)
τ	34	31	very faint	(211)
τ , μ and δ are parts of the same facet; $\varphi = (112)$				

A stereographic projection of the forms observed is reproduced in Fig. 2. Evidently is a combination present of an *octahedron* {111}, a *hexahedron* {100}, an *icositetrahedron* {211} and a *pentagonal dodecahedron* {210}; the zonal relations in the projection-figure make this sufficiently clear.

The symmetry of the crystals can, therefore, only be that of the *tetrahedral-pentagonal dodecahedral* class ($3A_2$; $4L_3$; $0L_2$; $0II_4$; $0P$; $0C$), or that of the *dyakis dodecahedral* class ($3A_2$; $4L_3 (= \bar{L}_6)$; $0L_2$; $3II_2$; $0P$; C).

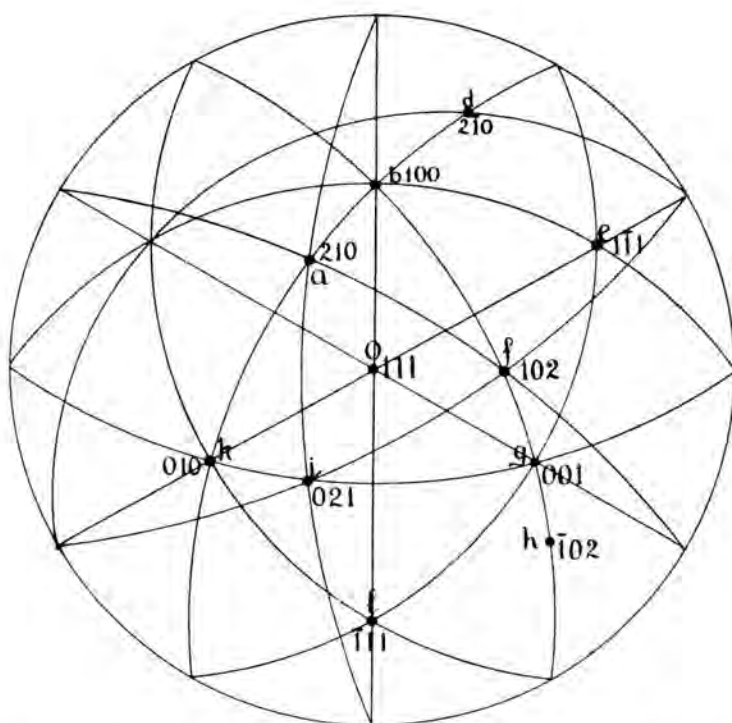


Fig. 2. Stereographical Projection of the observed Forms on a plane of $\{111\}$.

§ 4. It is *a priori* excluded to make a final choice between these two classes of symmetry by means of a LAUE-photograph of a crystal-plate cut parallel to (111); other plates were, moreover, not at our disposition. For, as one of us¹⁾, in collaboration with H. HAGA, was able to prove formerly, such LAUE-radiograms must always show the same symmetry as a similarly orientated plate of a crystal, whose symmetry is that of the crystal under investigation after a centre of symmetry has been added to it. But as in both classes mentioned *no* axes of twofold symmetry perpendicular to the faces of the rhombododecahedron do occur, these faces can *never* appear as planes of symmetry in the LAUE-radiogram on (111), if a centre of symmetry is thought to be added to the tetrahedral-pentagonaldodecahedral symmetry, nor will this be the case with a dyacisdodecahedral crystal, because this does already possess such a centre of symmetry. The LAUE-radiogram obtained by radiation perpendicular through a plane of (111) can, therefore, in both cases only show an axis of threefold symmetry, *without* any symmetrical arrangement of its spots with respect to three planes intersecting along this axis under 120° (60°). Notwithstanding this fact, such a LAUE-radio-

¹⁾ H. HAGA and F. M. JAEGER, These Proceedings 17, 18, 19.

gram was yet prepared, because it seemed of interest for the further determination of the crystalstructure. A very thin plate parallel to (111) was for this purpose stuck to a thin glass-plate and a diffraction-image made in the usual manner by means of a MÜLLER-gas-tube with a platinum-anticathode and an osmotic pressure-regulation (60 K. V.). The glass-plate was orientated as accurately as possible by means of a goniometer-arrangement; the time of exposition was 5 hours (with 4 milli-Amp.). The image appeared, however, yet to be not completely symmetrical, as a consequence of a slight deviation in the direction of the X -rays from the normal on (111); notwithstanding this, however, it could be clearly shown, that the LAUE-radiogram was undoubtedly symmetrically built with respect to three diameters intersecting at 120° (60°). The cause of this abnormal behaviour must doubtlessly be attributed to the great differences in diffracting power, already mentioned, of the numerous iodine-atoms on the one hand, in comparison with that of the germaniums-atoms on the other hand, which are four times as scanty, in connection with a particular kind of mass-distribution of both atomic species throughout the structure as a whole. Here, indeed, is found a

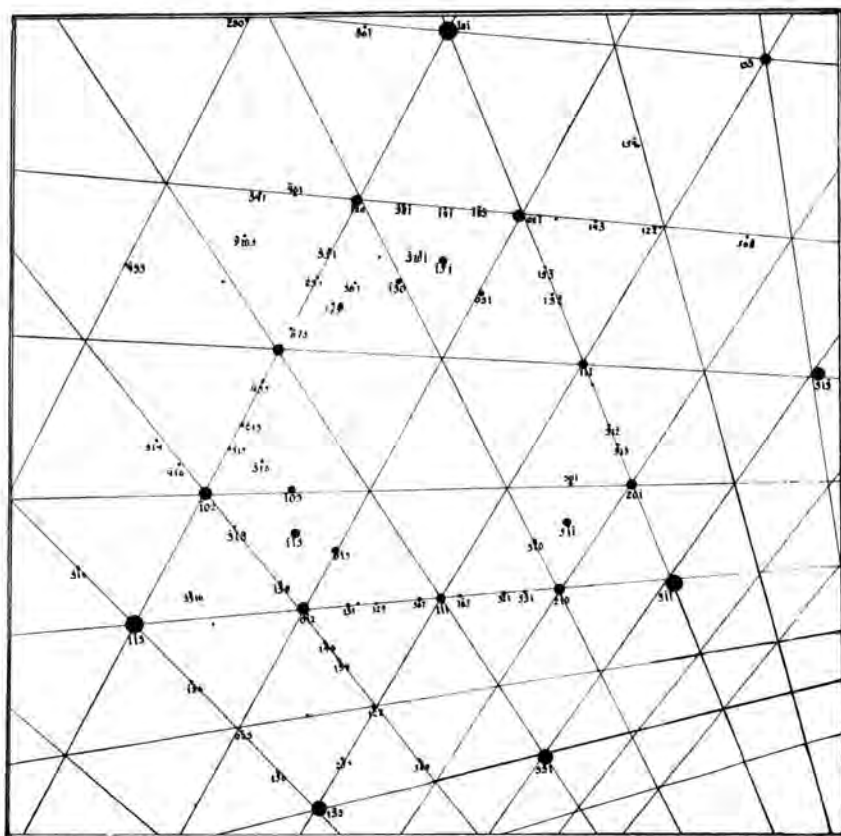


Fig. 3. Gnomonic Projection of the LAUE-radiogram on $\{111\}$.

new instance of the already known phenomenon, that the symmetry of such LAUE-radiograms can occasionally be deceptive in so far, as symmetry-elements may be apparently present, which are incompatible with the proper crystallographical symmetry, but only manifest themselves as a consequence of accidental peculiarities of the atomic arrangement.

A gnomonic projection of this LAUE-radiogram is reproduced in Fig. 3. The distance l of the spots from the central one and that ($s = 4$ c.m.) of the film and the crystal-plate being known, — the indices of the diffracting planes and the sinus of the angles θ could be calculated from the relation: $l = s \cdot \operatorname{tg} 2\theta$; at the same time the intensities of these spots were approximately estimated. As the edge a of the cubic cell ($= 11.89$ A.U.) is known, the distances d between the diffracting planes (hkl) can be directly calculated ¹⁾ in A.U. and by these values for d it is possible to determine the product $n \cdot \lambda$ in the formula: $2d \cdot \sin \theta = n\lambda$ or in

$$\frac{2a \cdot \sin \theta}{\sqrt{h^2 + k^2 + l^2}} = n\lambda. \text{ Now the voltage of the gas-tube in these experi-}$$

ments was 60 K.V.; the maximal intensity of the polychromatic platinum-radiation, therefore, must be situated in the neighbourhood of 0.4 or 0.5 A.U. ²⁾ On this supposition it appears possible, by comparison of the relative intensities, to estimate with a high degree of probability the values of n , i. e. of the orders of the observed spots: inversely, the sequence of the intensities ³⁾ for each value of λ thus calculated, gives a control with respect to the right choice of the multipliers n . In this way the data could be obtained, which are collected in the table on page 756.

If the estimated intensities are graphically plotted against the deduced wave-lengths ⁴⁾, a graph is obtained as reproduced in Fig. 4. The sequence of the observed, relative intensities for the faces of the same form $\{hkl\}$ appears really to be just the same, as might be expected in connection with the shape of the curve for the energy-distribution in the ROENTGEN-spectrum, if a voltage of 60 K.V. be applied to the tube.

¹⁾ R. W. G. WYCKOFF, *The Structure of Crystals*, (1924), p. 452; P. P. EWALD, *Ann. der Physik*, **44**, (1914), p. 257. Also here ζ is equivalent to $\zeta/2$ in the above.

²⁾ In WYCKOFF's book is given a graph of the intensity-distribution for the different wave-lengths λ of the tungstene-spectrum, as shown on the photographic plate, if a voltage of 60 K.V. is applied. The intensity increases from the shorter wave-lengths rapidly until a maximum at about 0.484 A.E., this being the characteristic limit of absorption for silver. As platinum in the periodic table is close to wolframium, the energy-distribution in the platinum-spectrum under 60 K.V. will *grosso modo* show great analogy with that of the other metal. It is this supposition, which is made use of in the determination of the numbers n of the spots considered.

³⁾ It need hardly to be said again, that the estimations of the relative intensities (10 for the most intensive, 1 for the faintest spots) can have no other significance than as rough indications of the existing differences. The numbers attributed to the spots only will express, that one spot is darker than another.

⁴⁾ R. W. G. WYCKOFF, *Amer. Journal of Science*, **50**, (1920), 318, P. P. EWALD, *Krystalle und Roentgenstrahlen*, p. 115.

Table of Diffraction-spots in the LAUE-radiogram

Distance of the Spot from the centre in m.m.:	Index of the diffracting planes:	$\sin \theta$	$n \cdot \lambda$ in A.U.	Orders n :	λ in A.U.	Estimated intensity:
32.5	(111)	0.335	4.65	8	0.58	5
26.0	($\bar{1}\bar{1}\bar{1}$)	0.284	3.94	8	0.49	6
34.5	($\bar{1}\bar{1}\bar{1}$)	0.348	4.83	8	0.60	4—5
25.2	(201)	0.278	2.98	4	0.74	5—6
22.5	(012)	0.253	2.71	4	0.68	6—7
18.0	(120)	0.210	2.25	4	0.56	6 (+)
26.0	(210)	0.284	3.04	4	0.76	5—6
20.0	($\bar{1}$ 02)	0.230	2.47	4	0.62	7 (—)
20.0	(02 $\bar{1}$)	0.230	2.47	4	0.62	6—7
27.8	($\bar{1}$ 51)	0.300	1.40	2	0.70	4—5
36.0	(5 $\bar{1}\bar{1}$)	0.359	1.66	2	0.83	4 (—)
29.0	($\bar{1}$ 15)	0.310	1.43	2	0.71	5 (—)
13.3	($\bar{1}$ 13)	0.158	1.14	2	0.57	10
17.5	(3 $\bar{1}\bar{1}$)	0.206	1.50	2	0.75	8
11.0	($\bar{1}$ 31)	0.134	0.97	2	0.49	10
40.0	(301)	0.383	2.91	4	0.73	2
35.1	(013)	0.353	2.68	4	0.67	3—4
30.4	(130)	0.320	2.43	4	0.61	3
41.5	(310)	0.391	2.96	4	0.74	2
32.4	($\bar{1}$ 03)	0.335	2.55	4	0.64	3—4
33.5	(03 $\bar{1}$)	0.342	2.59	4	0.65	3
15.2	(586)	0.181	0.39	1	0.39	1
13.2	(568)	0.158	0.34	1	0.34	1 (—)
9.8	(133)	0.120	0.66	2	0.33	6
12.0	(133)	0.145	0.80	2	0.40	8 (—)
13.6	(331)	0.162	0.89	2	0.45	8
12.0	(313)	0.145	0.80	2	0.40	7—8

This result may serve as an argument for the correctness of the calculated values of λ for each spot, and consequently for those of the numbers n . All the sections of curves in this graph are evidently parts

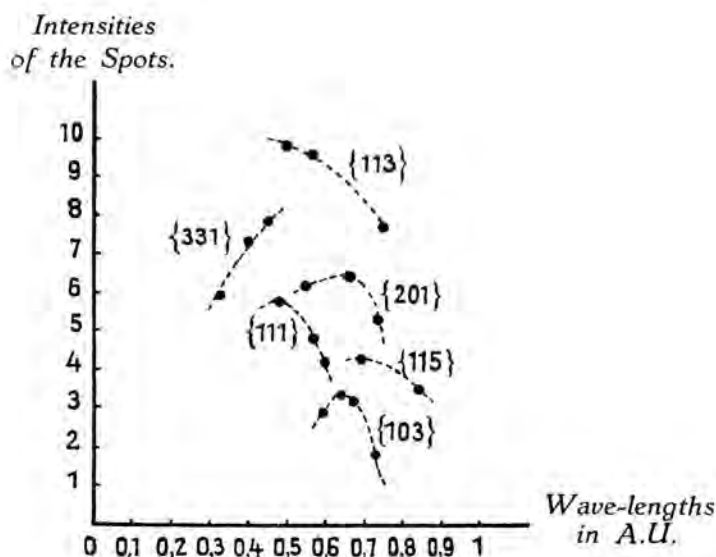


Fig. 4. Distribution of Intensities in the LAUE-radiogram.

of intensity-curves showing a maximum in the vicinity of 0.5 A.U. In connection with this, it may be, moreover, remembered, that in the DEBIJE-films the image of {201} has indeed but an appreciable intensity in the *fourth* order; also {331} appears in it only in the *second* order with a measurable intensity. By the BRAGG-method it was found, that {111} only shows a considerable intensity for *even* orders, while {113} has the greatest intensity as well in the DEBIJE- as in the LAUE-radiogram, etc. Moreover, the results obtained in the rotation-radiogram mentioned before, are also in best concordance with all this,

§ 5. If now it be considered that in the powder-radiograms a faint image of {111} and of {112} of the first order was found, as well, although very faint, of {221}, {441} and {432}, while it appears now from the discussion just given, that among the spots of the LAUE-image there is present also a first order image of {586}, — then it must be clear, that images of the *first* order are possible in this structure of planes having *three* odd, *two* odd, or *two* even indices. This fact, — combined with the evidence brought in the foregoing pages, that the spectra on {111} are very intensive in the second and fourth, but very faint in the first and third order, — enables us with a high degree of probability to make our choice between the twelve space-groups, which only are compatible with the two symmetries possible in this case.

If the three fundamental translation-groups (BRAVAIS' space-lattices) of the space-groups considered are discerned as follows: I'_c for the simple cubic, I''_c for the body-centred, and I'''_c for the face-centred cubic space-lattice, — then the twelve space-groups here only of interest, can be tabulated as follows ¹⁾:

Symbol of the Space-groups of dyacisdodecahedral and of tetrahedral-pentagonal-dodecahedral symmetry	Corresponding translation-group:	Number of points equivalent to each point of the Space-group:
T_1	Γ_c	12
T_2	Γ'_c	48
T_3	Γ''_c	24
T_4	Γ_c	12
T_5	Γ''_c	24
T_h^1	Γ_c	24
T_h^2	Γ_c	24
T_h^3	Γ'_c	96
T_h^4	Γ'_c	96
T_h^5	Γ''_c	48
T_h^6	Γ_c	24
T_h^7	Γ'_c	48

In the last column the number of equivalent points is indicated, corresponding to each arbitrarily chosen point of the group. If through each of these corresponding equivalents molecular planes be passed parallel to each other, their sequence will appear to be such, that the diffraction-images of definite orders must be cut out by interference. It can be foreseen ²⁾, that:

a. if the fundamental translation-group is Γ_c , there will appear diffraction-images of *all three* kinds of planes $\{hkl\}$ in *all* orders;

b. if the translation-group is Γ'_c , there will appear in *odd* orders only images of planes $\{hkl\}$ with *three odd indices*;

c. if the translation-group is Γ''_c , there will appear in *odd* orders only

¹⁾ R. W. G. WYCKOFF, *The analytical Expression of the Results of the Theory of Space-groups*, p. 33 and 34.

²⁾ R. W. G. WYCKOFF, loc. cit., IV, (1922), p. 175, 181, 183; W. T. ASTBURY and K. YARDLEY, Phil. Trans. R. Soc. London, A **224**, (1924), p. 222.

images of planes $\{hkl\}$ with *two even* indices and one *odd* index; in all these cases *zero* being considered as *even* index.

With respect to the facts mentioned above, it must be clear now, that, as among the images of *odd* order such appear not only of $\{111\}$ and $\{731\}$, but also of $\{221\}$, $\{421\}$, $\{432\}$, $\{568\}$, and of $\{112\}$ and $\{411\}$, the fundamental translation-group can only be Γ_c , i. e. the *simple cubic space-lattice*. For Γ_c'' is excluded by the first order of $\{111\}$ and Γ_c' by that of $\{112\}$, while the presence of the first order spectrum of $\{568\}$ is in full agreement with the presence of Γ_c . Of the twelve space-groups mentioned, thus only *five*: T^1 , T^4 , T_h^1 , T_h^2 , and T_h^6 need to be further considered here.

For each of these five groups is the relation of the consecutive values of $\sin^2 \frac{\theta}{2}$ as follows ¹⁾:

For T_1 and T_h^1 : 1: 2: 3: 4: 5: 6: 8: 9: etc.
(100) (110) (111) (200) (201) (211) (220) (221)

For T_4 : 2: 3: 4: 5: 6: 8: 9: 10: etc.
(110) (111) (200) (201) (211) (220) (221) (301)

For T_h^2 : 2: 3: 4: 6: 8: 9: etc.
(110) (111) (200) (211) (220) (221)

For T_h^6 : 3: 4: 5: 6: 8: 9: etc.
(111) (200) (102) (211) (220) (221)

In the row of observed diffraction-images there are certainly absent those of the first order on (100) and (110); for this reason the four groups: T^1 , T_h^1 , T^4 and T_h^2 are excluded, — thus only T_h^6 remaining. For this group is true, that images of planes $\{h0l\}$, in which h is *even* and l is *odd*, or those of $\{0kl\}$, in which k and l are both *odd*, cannot appear in *odd* orders ²⁾. Indeed, among the observed images, that of $\{201\}$ is *not* present; in the LAUE-radiogram the *fourth* order spectra of $\{201\}$ and $\{102\}$ have about the same intensity, which indicates that the diffracting power of both these planes is about identical and explains also the absence of the first order of $\{102\}$, so that this absence needs not to be considered an argument against T_h^6 in this case. In favour of T_h^6 , on the other hand, it may be remembered, that besides the first order spectra on $\{100\}$ and $\{110\}$, also that of $\{031\}$ is absent, — which follows from the powder-radiogram, where the row of consecutive

$\sin^2 \frac{\theta}{2}$ was:

3 : 6 : 8 : 16 : 22 : 24 : 38 : 40 : 48;

¹⁾ Or of: $(h^2 + k^2 + l^2)$. Cf. i.a. P. NIGGLI, Zeits. f. Kryst. **57**, (1922), 261; *idem*, Geometrische Kryst. des Diskontinuums, Table X, p. 482.

²⁾ R. W. G. WYCKOFF, loc. cit., p. 183.

i.e. possesses even more scanty terms, as is postulated with respect to what has been said above.

It is now necessary to fit 8 molecules GeI_4 into the fundamental cell with its edges of 11.89 A.V., i.e. 8 Ge-atoms and 32 J-atoms. With respect to their *structural* function, these 32 J-atoms, although chemically equivalent, need *not* be all in the same condition: in general, the possible cases would be either that they have all (32) the same structural function, or that such is the case with 16 on the one hand and 16 on the other; moreover, it is possible to discern 16 atoms of one kind, 8 of a second kind and 8 of a third function in spatial respects; or to have 24 atoms of one and 8 of a second kind; or finally, there would be possible four groups of 8 atoms, each group differing from the others by its spatial relation in the space-group considered. But, as is seen from the table on page 758, the number of equivalent points in each of the five here possible space-groups can be no other than 12 or 24; in no case will it be possible, therefore, that the 32 J-atoms will have identical functions¹⁾ in the structure of GeI_4 , and neither will it be possible that 16 atoms of one and 16 atoms of a second kind are present in this structure. Moreover, groups of 8 equivalent atoms cannot be present in the space-groups T_1 and T_4 ($n=12$); in T_h^1 , T_h^2 and T_h^6 an arbitrary number of 8 equivalent atoms of one kind and 24 of another kind may be present, but no group of 16 atoms. From this also follows, that T^1 and T^4 are excluded. T_h^1 also is highly improbable, because in this case $\sin^2\theta/2$ will be excluded from the series of values observed, while, as was shown, the number of missing values in this row appeared to be rather great in the powder-radiograms obtained. As the fundamental translation-group now is certainly I_c' , and not I_c'' , the 32 J-atoms cannot be present in the structure in any other way than as: $24+8$. Regarding all these arguments, there can, in every case, only be a choice between T_h^2 and T_h^6 ; and this choice can be fixed only by consideration of the lack of certain diffraction-images of odd order.

The forms $\{103\}$ and $\{301\}$ for instance, can in T_h^2 give spectra as well in the even, as in odd orders; in T_h^6 , however, only in even orders. On no radiograms, indeed, occur images of these forms in the first or in the third order; but those of $\{602\}$ and $\{12.04\}$ are present. (Film XII). On the LAUE-radiograms also $\{12.04\}$ is present. This is in contradiction with T_h^2 , but in agreement with T_h^6 . In the same way $\{330\}$ is everywhere absent; but $\{440\}$ and $\{880\}$ are all observed together on the powder-radiograms. These facts also lead to the same conclusion with respect to the two space-groups considered here.

In T_h^2 the reflections on $\{201\}$ and $\{102\}$ may only occur in even orders, in T_h^6 however, those on $\{201\}$ only in even, but those of $\{102\}$ as well in even as in odd orders, as was already emphasized. The fact,

¹⁾ R. W. G. WYCKOFF, *The analytical Expression*, etc., p. 176.

that neither on $\{201\}$, nor on $\{102\}$ diffraction-images of odd orders are met with on the different photographs, need *not* be considered here as an argument against T_h^6 , if the LAUE-radiogram be also taken in account. Summarizing all evidences, we think it highly probable, that GeI_4 has a structure¹⁾ corresponding to T_h^6 .

§ 6. The most simple supposition with respect to the arrangement of the eight GeI_4 -molecules, which can be made in concordance with all data acquired, leads to the structure reproduced in Fig. 5.

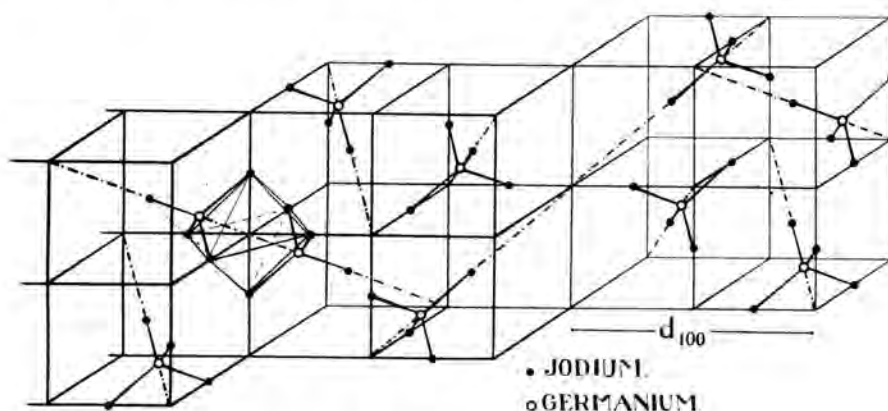


Fig. 5. The Crystal-structure of Germaniumtetraiodide.

Each Ge-atom in it appears as surrounded by four I -atoms, situated in the corners of a regular tetrahedron; from this it may be easily proved, that of the 32 I -atoms in each cell really 24 have equivalent positions in the structure and 8 a somewhat other structural function. For two GeI_4 -groups on each cube-diagonal of the fundamental cell can every time be thought to be combined in pairs, situated at equal distances of the centre to both sides of it; in such pairs evidently 6 I -atoms are always in equivalent positions with respect to each other, while 2 others have a somewhat different position, being directed more to the outsides of the combination. The I -atoms of such a pair are placed in the corners of a steep rhombohedron, the axis of which is a diagonal of the cubic cell; the nearest Ge-atoms, however, are then situated in the corners of an obtuse rhombohedron, coaxial with that of the I -atoms. In the combined pair of molecules both the Ge-atoms are placed in the centra of two diametrically opposed tetrahedra, the corners of which are occupied by the I -atoms. In the direction of a cube-diagonal planes of I -atoms alternate with such as are occupied by Ge-atoms in the way indicated in Fig. 6. Of course, this placing of the GeI_4 -molecules is somewhat

¹⁾ R. W. G. WYCKOFF, *The analytical Expression of the Results of the Theory of Space-Groups*, p. 127; P. NIGGLI, *Geom. Kryst. des Diskontinuums*, p. 367.

arbitrary, because the J -atoms may be thought shifted more or less along the cube-diagonal; in this case again 5 variable parameters must be

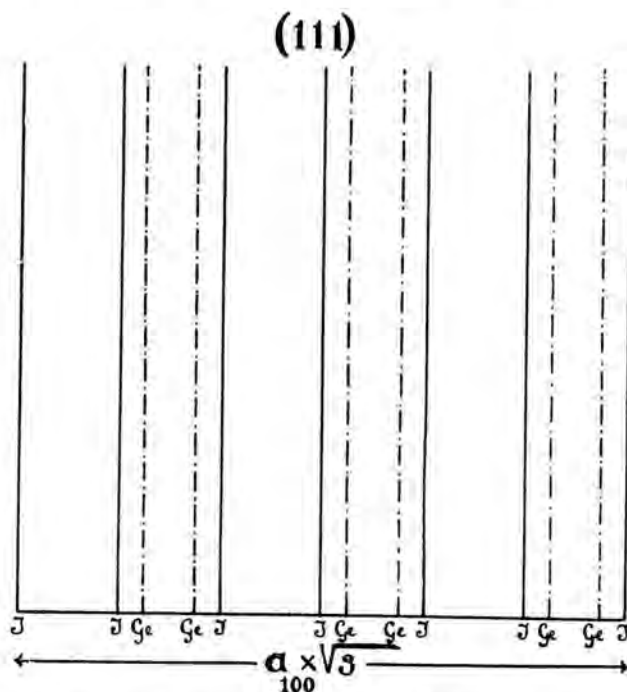


Fig. 6. Successive molecular Planes along a Perpendicular to $\{111\}$.

determined by comparison of observed and calculated intensities of the diffraction-images, — a task, which may safely be considered to be impracticable. In how far the here adopted structure can be considered to be in agreement with the observed relative intensities of the diffraction-images for the different planes on the DEBIJE-radiograms, may be seen from the data in the following table, in which the results are reviewed of the calculated values for a number of important crystal-planes.

If in the formula for the intensities:

$$I = \frac{1 + \cos^2 \theta}{2 \cos \theta/2 \cdot \sin^2 \theta/2} \cdot n \cdot |S|^2,$$

in which n is the number of planes of the crystal form $\{hkl\}$ and $|S|$ is the absolute value of the structural factor, the function preceding $n \cdot |S|^2$ be called: $f(\theta/2)$, then the value of this function for different forms $\{hkl\}$ and for successive orders, may be immediately read from the existing tables¹⁾. Moreover, for Ge and I in the formula for $|S|$

¹⁾ L. WEBER, Zeitschr. f. Kryst. 57, 402, (1923).

are taken the atomic numbers 32 and 53 respectively ¹⁾ while the coordinates of the $24 + 8$ *J*-atoms and of the 8 *Ge*-atoms are the following:

I. 32 <i>J</i> -atoms; <i>x</i> , <i>y</i> , <i>z</i> and <i>v</i> -along the cube-edges.											
a. the 24 equivalent atoms:											
0	0	1/4	1/2	1/2	-1/4	0	1/2	1/4	1/2	0	3/4
1/4	0	0	-1/4	1/2	1/2	1/4	0	1/2	3/4	1/2	0
0	1/4	0	1/2	-1/4	1/2	1/2	1/4	0	0	3/4	1/2
0	0	-1/4	1/2	1/2	1/4	0	1/2	3/4	1/2	0	1/4
-1/4	0	0	1/4	1/2	1/2	3/4	0	1/2	1/4	1/2	0
0	-1/4	0	1/2	1/4	1/2	1/2	3/4	0	0	1/4	1/2
b. the 8 equivalent atoms: $v = 1/4$.											
1/4	1/4	1/4	3/4	1/4	-1/4	-1/4	3/4	1/4	1/4	-1/4	3/4
-1/4	-1/4	-1/4	1/4	3/4	1/4	1/4	1/4	3/4	3/4	1/4	1/4
II. 8 <i>Ge</i> -atoms; $v = 1/8$.											
1/8	1/8	1/8	5/8	3/8	-1/8	-1/8	5/8	3/8	3/8	-1/8	5/8
-1/8	-1/8	-1/8	3/8	5/8	1/8	1/8	3/8	5/8	5/8	1/8	3/8

If these values for *p*, *q* and *r* for all ($= m$) atoms within the fundamental cell be substituted in:

$$S = \sum_m \left(A_n \cdot e^{2i\pi(p_m h + q_m k + r_m l)} \right),$$

and if it be taken into account, that for the group T_h^6 all terms containing sinuses are equal to zero in the structural factor, — then it is possible to calculate directly for all planes $\{hkl\}$ the intensities of the diffraction-images for all orders.

These values are given in the table on the next page.

It will be clear from this, that there is a fairly good agreement between the calculated and observed intensities from a qualitative point of view, especially if the difficulty be taken into account of avoiding the attribution of a too great relative value in the estimation of the intensities of images, which eventually are excelling by their distinctness.

For it is easily seen, that the estimated intensities in the last column are placed in all cases in just the same sequence of increase, as occurs

¹⁾ Instead of *Ge* and *J*, also the values for *Ge*^{IV} and *J*^I might have been taken; the differences, however, are not very appreciable in this case.

Table of calculated Intensities

Indices:	Order:	Structural-amplitudines:			Absolute value of $ S ^2$	Intensities	
		1st kind I -atoms:	2nd kind I -atoms:	Ge-atoms:		Calculated:	Estimated on DEBIJE-Film No. 18:
(111)	1	0	0	$64, \frac{1}{2}$	0.8	1.6	— *)
(111)	2	— 1272	— 424	0	287.6	42.08	10
(111)	3	0	0	$-64, \frac{1}{2}$	0.8	0.05	absent
(111)	4	1272	424	— 256	207.4	6.3	3
(111)	5	0	0	$64, \frac{1}{2}$	0.8	0.01	absent
(111)	6	— 1272	— 424	0	287.6		—
(011)	1	0	0	0	0	0	—
(011)	2	— 424	+ 424	0	0	0	absent
(011)	3	0	0	0	0	0	„
(011)	4	1272	424	256	381.0	28.1	9
(011)	5	0	0	0	0	0	absent
(011)	6	— 424	+ 424	0	0	0	„
(001)	1	0	0	0	0	0	—
(001)	2	424	— 424	0	0	0	absent
(001)	3	0	0	0	0	0	„
(001)	4	1272	424	— 256	207.4	16.7	7
(112)	1	0	0	— 128	1.6	1.5	very faint
(112)	2	— 424	424	0	0	0	absent
(112)	3	0	0	— 128	1.6	0.1	„
(112)	4	1272	424	256	381.0	15.2	2
(311)	1	0	0	$-64, \frac{1}{2}$	0.8	0.4	absent
(311)	2	— 1272	— 424	0	287.6	29.0	8
(331)	1	0	0	$64, \frac{1}{2}$	0.8	0.2	absent
(331)	2	— 1272	— 424	0	287.6	14.5	3

*) If the line was situated outside the efficient part of the film, this is indicated by — in the last column.

with the calculated values; and everywhere the calculated intensities are equal to zero or to extremely small values, if among the observed intensities they were zero in reality. The here adopted structure, therefore, evidently completely accounts for all characteristics of the ROENTGEN-photograms of these crystals.

With respect to the intensity-distribution of the spots in the LAUE-image, which gives the illusion of an apparent symmetry after the planes of $\{110\}$, — it may be remarked that in the adopted structure three planes of $\{110\}$ containing each time 8 *J*-atoms and 2 *Ge*-atoms intersect along each cube-diagonal. In each of these planes the diffractive power of the *J*-atoms strongly dominate that of the *Ge*-atoms. In the structure as a whole, the other *J*-atoms are situated, moreover, symmetrically with respect to these three planes, which is not the case with the *Ge*-atoms, and for the last reason, therefore, the $\{110\}$ -planes are, in reality, no true symmetry-planes of the structure. But just because the diffractive power of the symmetrically distributed *J*-atoms is so strongly predominant in comparison with that of the much more scanty *Ge*-atoms, the influence of the last is practically lost in the LAUE-radiogram. It is for this circumstance, that the LAUE-image on $\{111\}$ appears to be symmetrical after three planes of $\{110\}$ and is, therefore, deceptive as a criterion for the symmetry-determination of the crystal.

Finally, we wish to draw attention to the fact, that the results here obtained are in full agreement with R. G. DICKINSON's determinations ¹⁾ of the also dyacisdodecahedral *Tintetraiodide*: SnI_4 . According to GROTH's measurements this substance, which is isomorphous with GeI_4 , crystallizes from carbondisulphide in octahedral crystals, showing a combination of: $\{111\}$, $\{210\}$, $\{211\}$, $\{100\}$, and smaller: $\{110\}$, $\{120\}$ and a dyacisdodecahedron of the zone $[(210):(111)]$, which could not be determined more precisely. Also NORDENSKJÖLD ²⁾ and RETGERS ³⁾ investigated this compound; the last author observed in crystals from a solution in methylene-iodide also a pentagonal-dodecahedron $\{210\}$. The structure deduced by DICKINSON is completely analogous to that adopted here for GeI_4 ; even the dimensions of the fundamental cell (12,23 A.U.) are wholly comparable with those for GeI_4 . According to the American author a yet better agreement between calculated and observed intensities may be obtained in the case of SnI_4 , by a slight shift of the *Sn*- and *J*-atoms along a cube-diagonal.

On the contrary, the determinations of MARK and WEISSENBERG ⁴⁾ must be considered as quite insufficient. They also observed in their LAUE-radiograms a symmetry with respect to $\{110\}$ and, moreover, to $\{100\}$;

¹⁾ R. G. DICKINSON, Journ. Amer. Chem. Soc., **45**, 958, (1923).

²⁾ P. GROTH, *Chemische Kristallographie*, **1**, p. 231.

³⁾ N. G. NORDENSKJÖLD, Bihang K. Vet. Akad. Förh. Stockholm, **2**, N^o. 2, (1874).

⁴⁾ J. W. RETGERS, Zeits. f. Kryst., **22**, 270, (1894).

⁵⁾ H. MARK and K. WEISSENBERG, Zeits. f. Physik, **16**, 18, (1923).

for this reason, they exclude the space-group T_1^h . In the above we have discussed the cause of the appearance of those symmetry-planes parallel to $\{110\}$ and emphasized, that care must be taken not to be misled by this fact, as the phenomenon is solely a consequence of the predominant diffractive influence of the numerous *I*-atoms, symmetrically arranged with respect to $\{110\}$, in comparison with the much less powerful diffraction by the not symmetrically situated *Ge*-atoms. The authors also have taken a value for the cube-edge *a*, which is only half the true one: we have fully discussed, why the fundamental distance *a* needs to be taken twice as great. The measurements and determinations of both investigators are, therefore in full disagreement with the symmetry of Sn I_4 , as determined by GROTH and others; in accordance with our experiences in the case of Ge I_4 , there is no reason to doubt the exactness of these older crystallographical data.

Although there is no complete certainty as to the question, whether in the case of Ge I_4 there is present a structure formed by ions or not, — it is of interest, however, to draw attention to the fact, that throughout the whole structure tetrahedral groups (Ge—I_4) can clearly be discerned as more or less autonomous units in it. In this respect a very recent investigation of HANTZSCH and CARLSOHN¹⁾ may also be quoted here, in which paper the authors, by demonstrating a number of additive relations between the meltingpoints of the halogenides of the elements in the fourth group of the periodic table, also arrive at the result, that in the crystals of these compounds not the ions, but the molecules themselves are the real structural units.

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physical Chemistry of the University.*

¹⁾ A. HANTZSCH and CARLSOHN, Ber. d. d. chem. Ges., **58**, 1741, (1925).

Physics. "*On the Excitation of Spectrum Lines by Collisions of Electrons*".

By Dr. G. HERTZ. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of October 27, 1923).

According to the theory of quanta it is to be expected that by the collision with an electron an atom is enabled to emit a definite spectrum line only when the kinetic energy of the electron is greater than a certain threshold value, characteristic of the line in question. The potential which an electron must pass through freely to acquire this kinetic energy will be called the excitation potential dependent on the nature of the system emitting the light. In the simplest case of PLANCK's oscillator, the excitation potential is determined by the frequency, and expressed by the equation $Ve = h\nu$. According to BOHR's atomic theory, the work required for the excitation of a definite line, is equal to the energy which must be performed to transfer the atom from its normal state into the highest of the two stationary states between which a transition must take place to give the emission of the spectrum line in question. Hence the excitation potential of a definite spectrum line is given by the equation $Ve = Ie - hT$, in which I represents the ionisation potential, and T the smallest of the two terms characteristic of the spectrum line.

So far the existence of an individual excitation potential has, experimentally, only been shown for the resonance lines of the alkali and earth-alkali metals, and of the metals that are in the same group of the periodic system with these ¹⁾. Also the value of the excitation potential was found to be in agreement with that which is to be expected according to the theory of quanta. This furnished a proof of the quantous character of this phenomenon directly from the experiment: but the results found could teach us nothing about BOHR's atomic model, because for all absorption lines of the atom in its normal state, hence also for the resonance lines, the excitation tension can be derived from the frequency (through the $h\nu$ relation) both when BOHR's atomic model and when PLANCK's oscillator was taken as starting-point. To decide experimentally whether the terms of a series must really be taken as definite values of the energy, as is the case

¹⁾ J. FRANCK and G. HERTZ, Verh. D. Phys. Ges. **16**, 512, 1914.

J. C. MC LENNAN and HENDERSON, Proc. Roy. Soc. **91**, 485, 1915.

J. C. MC LENNAN and H. I. C. IRETON, Phil. Mag. **36**, 461, 1918.

P. D. FOOTE, W. F. MEGGERS and F. L. MOHLER, Phil. Mag. **42**, 1002, 1921;
Astroph. Journ. **55**, 145, 1922; Phil. Mag. **43**, 659, 1922.

according to BOHR's theory, it is necessary to make observations of the excitation of the higher lines of the spectrum series. The possibility that by collisions of electrons not only quanta of energy corresponding to the frequency of the resonance lines can be transferred, but also such as correspond to the transition of the atom to higher stationary states, has been experimentally shown by J. FRANCK and E. EINSPOHN¹⁾ for mercury, and by J. FRANCK and P. KNIPPING²⁾ for helium. As the energy quanta observed here are in very good agreement with the values calculated according to BOHR's theory from the terms of the series, it was very probable that also the emission of the lines corresponding to these terms, will start at the excitation potentials observed. Remarkably enough, however, almost all the observers who of late have investigated directly spectroscopically the excitation of spectrum lines through collisions of electrons, have come to another result. RAU³⁾, indeed, found already before, that in helium the excitation potentials become greater for the different terms of a series with ascending number. Likewise RICHARDSON and C. B. BAZZONI⁴⁾ found different excitation potentials for different lines. On the other hand in their experiments on the excitation of light in metal vapours P. D. FOOTE and W. F. MEGGERS⁵⁾ come to the conclusion that the resonance lines from a definite excitation potential (given by the $h\nu$ -relation) can be excited without the other part of the spectrum being excited at the same time, but that all the higher lines of the series together do not make their appearance until the ionisation potential is reached. A. C. DAVIES⁶⁾ arrives at the same result for helium and G. DÉJARDIN for helium and mercury⁷⁾. Under these circumstances it seemed to me of interest once more to investigate the excitation of spectrum lines through collisions of electrons by the aid of an arrangement through which surces of error were prevented as much as possible.

The method used was in principle the same as is often applied in investigations in this region. The electrons emitted by an incandescent cathode are accelerated by an electric field, and pass through a metal gauze into a fieldfree space, in which they collide with the atoms of the gas or the metal vapour; then it is examined in what way the spectrum of the light emitted in consequence of the collisions depend on the potential which gives the electrons their acceleration. One of the first requirements is that the electrons have as

¹⁾ E. EINSPOHN, *Zeitschr. f. Phys.* 5, 208, 1921.

²⁾ J. FRANCK and P. KNIPPING, *Zeitschr. f. Phys.* 1, 320, 1920.

³⁾ H. RAU, *Sitzungsber. Phys. Med. Gesellsch. Würzburg* 1914, pag. 20.

⁴⁾ O. W. RICHARDSON and C. B. BAZZONI, *Nature* 98, 5, 1916.

⁵⁾ P. D. FOOTE and F. W. MEGGERS, *Bur. Standards Scientif. Paper* Nr. 386, 1920.

⁶⁾ A. C. DAVIES, *Proc. Roy. Soc.*, 100, 599, 1922.

⁷⁾ G. DÉJARDIN, *C. R.* 175, 952, 1922.

much as possible the same velocity. As the excitation potentials for the different lines often differ only a few tenths of a Volt, a comparatively small irregularity in the velocity is already sufficient to render its determination impossible. Sources of errors which may have an injurious influence in this respect, are: 1. Potential differences between different points of the source of the electrons (gradient of the tension in the incandescent wire). 2. Wide grating instead of a fine gauze. 3. Disturbance through space charges in the observation space in consequence of the use of too great densities of the current. 4. The possibility that the pure electron discharge changes into an arc discharge, to which there is a tendency chiefly in potentials in the neighbourhood of the ionisation potential. These sources of errors are not independent of each other. Thus e.g. the transition to an arc discharge is promoted by the use of a wide grating, whereas on the other hand the appearance of the arc discharge partially renders the error in consequence of too great gradient of the tension in the incandescent wire ineffectual, because such a low tension arc always takes up a position at a definite point of the incandescent wire. When the spectrum [of a low tension arc is observed, it is found that under favourable circumstances we have

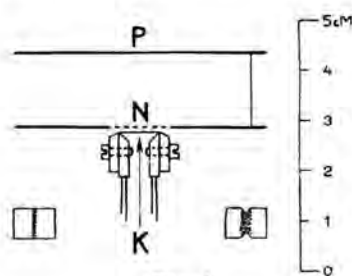


Fig. 1.

to do with electron velocities which are pretty equal inter se; they are, however, evidently not yet sufficient to bring out the small differences in the excitation tensions of the higher terms in the series.

To avoid these errors as much as possible an arrangement was used as represented in fig. 1. The incandescent cathode *K*, a thin platinum strip 6 mm. wide provided with a spot of barium-oxide on the

upper side, is placed before a gauze *N*, at a distance of about half a mm. The plate *P* is in conducting connection with *N*. In some experiments the space between *N* and *P* was enclosed on all sides with metal walls, with the exception of one slit, in order to obtain a perfectly fieldfree space; the simpler form represented in the figure has, however, also appeared to be sufficient. With this arrangement there was no danger of the transition to an arc charge, even at tensions above the ionisation tension, at the pressures applied, when the meshes of the gauze were taken sufficiently fine and the distance between the incandescent cathode and the gauze sufficiently small. In order to prevent any injurious influence of the gradient of the tension in the incandescent cathode, care was taken that only a narrow strip at right angles to the direction of the heating current emitted electrons, so that there were no potential differences of more than 0.1 Volt between the different points of the source of the electrons. In some experiments this effect was reached in this way that the oxide was added in the form of a transverse strip only $\frac{1}{2}$ mm.

broad on the platinum band. The application of such a strip being, however, difficult, the experiment was afterwards made with a larger spot, and a shape was given to the platinum band as drawn in the figure at the bottom on the right. In consequence of the increased current density in the middle a pretty sharp maximum of the temperature is obtained there. In view of the exceedingly great dependence of the electron emission on the temperature this entails that practically the emission issues only from a narrow strip lying in the region of maximum temperature.

To avoid disturbances through space charges the strength of the current was never chosen higher than 10 amp. This is particularly necessary when rare gases are examined, in which case higher pressures must be worked with than with metal vapours on account of the slighter efficiency of the unelastic collisions. Already at small current densities the electrons which are innumerable times knocked to and fro by the gasatoms, cause a considerable space-charge, from which ensues that the space is no longer fieldfree, so that the electrons have different velocities at different places. That this is actually the case may be clearly seen when a tension is applied which is just above the excitation tension of the lines appearing first. Then the space-charge betrays itself by a dark space in the neighbourhood of the greatest density of the electrons (immediately before the gauze). For here the electrons have a smaller velocity than corresponds to the applied tension as a consequence of the negative space-charge.

In experiments where an intensity as great as possible is aimed at, this injurious influence of the space-charges may be obviated by the addition to the gas under examination of a small quantity of another rare gas or metal vapour of which the ionisation tension lies below the lowest excitation tension of the gas under examination. If this is done, there are always some positive ions present, which are just able to compensate the space-charge of the electrons. Of course the pressure of the added gas must not be too great, because else the positive space-charge would become too great and too many electrons would cede their energy to the atoms of the added gas, instead of to that of the gas under examination. It has appeared that mercury vapour with the vapour tension which it has at room temperature, added to neon of a pressure of about 0.8 mm. gives exactly the required effect. In such a tube filled with neon and mercury it is possible to work with currents of some milliampères without being hampered by the space-charge, and then a sufficient intensity is reached to enable us to perform the experiment also by way of demonstration. Particularly suitable for this purpose is a tube filled with a mixture of neon and helium, to which mercury has been added, because such a tube enables us to observe the successive appearance of the lines of mercury, neon, and helium at the corresponding excitation tensions. Also the appearance of the resonance line

of mercury at about 5 Volt can be shown with such a tube, as the appearance of this ultra-violet line becomes visible through the fluorescence of the glass wall. In the investigation mentioned the experiment was made without addition of mercury, and the strength of the current was chosen sufficiently small to prevent disturbances through space-charge, this to avoid possible secondary effects, as e.g. action of excited atoms of one kind on those of the other kind. Then the intensity of the excited radiation was comparatively small; the spectrum observations reproduced required an exposure of from 6 to 12 hours.

Already a cursory visual observation taught that all the examined lines of the arc-spectrum of mercury, neon, and helium behave in accordance with the theory of BOHR, as they appear from definite excitation tensions characteristic of the separate lines or groups of lines. Accurate measurements of the excitation tensions have not yet been carried out. For this it is necessary to make measurements about the dependence of the intensity of the lines on the velocity of the electrons. Such measurements are in preparation. In the strongest lines the excitation tension could be measured with the accuracy of some tenths of a Volt, by determining the tension at which these lines suddenly appear. Though the results obtained thus agree very well with the values that can be derived from the values of the terms, yet this method of measurement cannot be considered as reliable in every respect.

Also without measurements of the intensity the successive appearance of the lines can be shown by exciting different tensions smaller than the ionisation tension, and examining the corresponding spectrum. Then, only those lines will be observed of which the excitation tension lies below the excited tension. If this tension is increased by a definite amount, the newly occurring lines must all be lines with higher excitation tension.

As in all measurements on collisions of electrons, the difficulty is also here to know the absolute value of the tension which gives its velocity to the electrons; here too this tension can only be indicated with an accuracy of about 0.5 Volt. For the measurement of the excitation tension the best method is therefore to test the apparatus by means of a gas, the excitation tensions of which can be calculated from the spectrum series, as this has been done more than once in measurements of excitation tensions by the electric method. On account of this uncertainty in the absolute values, the values of the tension that corresponds with the actual velocity of the electrons have been derived in what follows from the calculated excitation tensions of the occurring resp. missing lines. The difference between the indicated values and the tensions read on the Voltmeter was between 1.5 Volt and 2 Volt in all cases; it was accordingly really found through direct measurements of the velocity of the electrons (application of a retarding electric field in vacuum) that the correction to be applied must lie between these limits. It may, therefore, be concluded from the data communicated below that the absolute values

agree with an accuracy of 0,5 Volt with those which are calculated from the ionisation tension and the values of the terms according to BOHR.

In the figures 2, 3, and 4 a series of spectra have been reproduced excited in mercury, helium, and neon through the collisions of electrons with different velocities. The times of exposure in mercury and helium have been chosen so that the strongest lines, which also appear already at lower tensions, have about the same intensity on the two representations. The values which are put after the wave-lengths between brackets denote the excitation tensions calculated from the ionisation tension and the values of the terms. The observations with mercury (fig. 2) have been made at a pressure of about 0,03 mm. (the vapour tension at

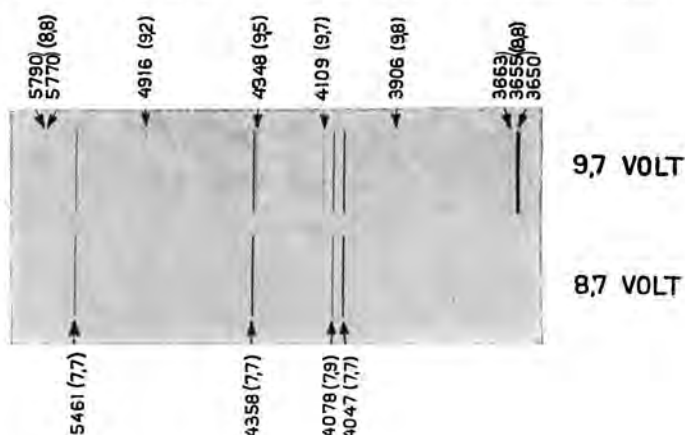


Fig. 2.

about 60°). It is seen that at lower tension only lines with an excitation tension smaller than 8 Volt appear, the lines that make their appearance on increase of the tension all having a higher excitation tension. Particularly striking is the behaviour of the strong line 3650, which is by

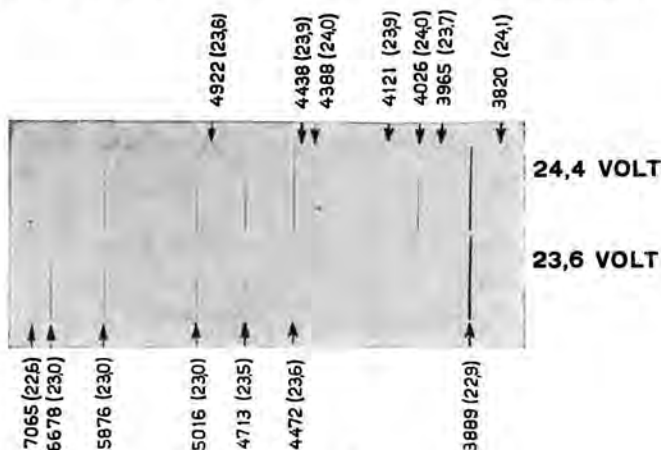


Fig. 3

far the strongest line at the higher tension, and is entirely wanting at the lower tension.

The helium lines behave in the same way (fig. 3). The reproduced spectrum photographs have been made for a pressure of 0,8 mm. From experiments made since then it has appeared that it is more profitable to work with lower pressures; and it seems that to effect a sharp excitation of the lines, still smaller current densities should be used in helium than e.g. in neon. It is impossible that here the formation of metastable helium atoms still plays a part. With sufficiently small current densities the different lines can be made to appear successively also in helium, in correspondence with the successive order of their excitation tensions. Hence here too there is a very good agreement with the values calculated according to BOHR, as appears from the spectrograms.

In neon the pressures worked with were between 0.5 and 1 mm. Fig. 4

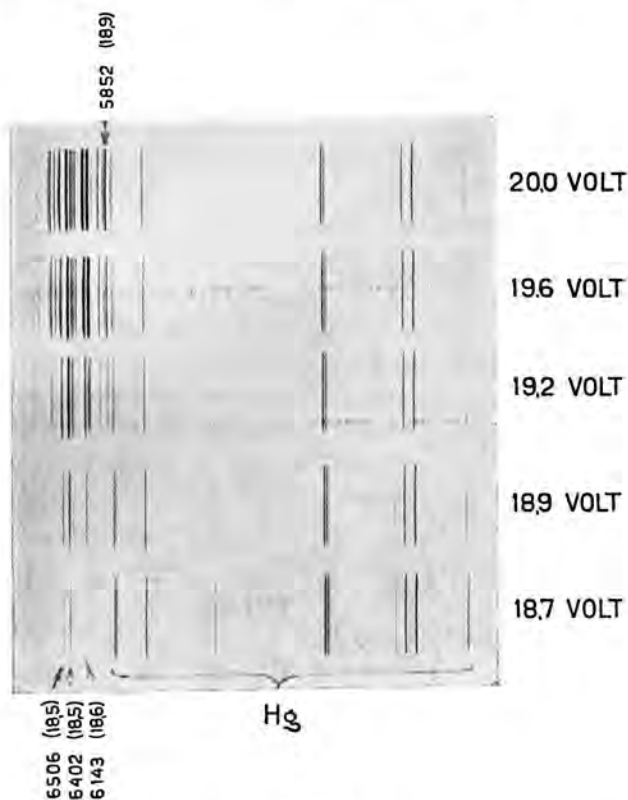


Fig. 4.

gives a series of photographs which show the development of the group of the red neon lines on increasing velocity of the colliding electrons. These observations were made in the presence of a drop of mercury in the tube, but the phenomenon is exactly the same without mercury. Special attention should be given to the behaviour of the yellow neon

line 5852, which under normal circumstances is by far the strongest line of the neon spectrum. According to the scheme of the series, as given by PASCHEN ¹⁾ for neon, this line must have an excitation tension which is 0.4 Volt higher than that of the lines 6143, 6402 and 6506; and the yellow line is, indeed, entirely absent at the lowest tension required to excite the said lines; only on increase of the tension by some tenths of a Volt does it make its appearance, and on further increase it soon exceeds the other lines in intensity.

Within the limits of the experimental errors the absolute value of the excitation tensions of these lines are in harmony with the values which can be calculated from the terms of the series and the values found by the writer of this paper for the ionisation tension ²⁾; thus the measurements of the excitation and the ionisation tensions are confirmed by the observations on the excitation of the spectrum lines.

Similar observations were also made with zinc and thallium vapour, which, however, bear a preliminary character. In order to avoid the difficulties met with, when the whole apparatus is brought to a high temperature, a method was applied in which the apparatus could remain at room temperature. For this purpose the apparatus was filled with helium and neon of a pressure of some mm., after which the metal under investigation was brought to evaporation in the fieldfree space between the plates. Thus the result was reached that both the electrons and the metal atoms diffuse through the rare gas, and finally arrive on the surface of the metal after numerous collisions. In this the circumstances can be chosen so that the number of collisions between electrons and metal atoms is great enough to bring about such an intensity of the light excited by these collisions that it can be observed with the spectroscope. So far these experiments have remained restricted to subjective observations with the spectroscope. With a suitable choice of the tension a spectrum could be obtained from zinc consisting only of the triplet 5680, 4722, 4811, while the strong red line 6362 did not make its appearance until the tension had been raised by 1 Volt.

In thallium 3.5 Volt was measured as excitation tension of the green line. This confirms that in thallium the $2p_2$ state is the normal condition, as also GROTRIAN ³⁾ has succeeded in showing by means of absorption measurements.

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¹⁾ F. PASCHEN, Ann. d. Phys. **60**, 405, 1919.

²⁾ G. HERTZ, These Proceedings **25**, 179; Zeitschr. f. Phys. **18**, 307, 923.

³⁾ W. GROTRIAN, Zeitschr. f. Phys. **12**, 218, 1922.

Botany. — "*The connection between lightgrowthresponse and phototropical curvature of seedlings of Avena sativa.*" By C. VAN DILLEWIJN. (Communicated by Prof. F. A. F. C. WENT).

(Communicated at the meeting of September 26, 1925).

According to the theory of BLAAUW the phototropical curvature of a unilaterally illuminated organ is the result of the difference in lightgrowthresponse induced in the various parts of that organ.

If, for instance, a coleoptile of Avena is subjected to the action of onesided light, there will be a decrease in the quantity of light from the lighted to the unlighted side. As every quantity of light induces a certain lightgrowthresponse, the various parts of the coleoptile will respond differently, causing a phototropical curvature.

As the greatest difference in the quantity of light is found between the proximal and distal sides, these sides will also show the greatest difference in growthresponse, and will be of the greatest importance for the appearance of the phototropical curvature.

BLAAUW¹⁾ examined a number of objects and proved that organs which exhibit a phototropical curvature also show a typical lightgrowthresponse when subjected to omnilateral illumination, while organs which do not respond to unilateral illumination show no lightgrowthresponse.

The sporangiophore of Phycomyces and the hypocotyl of Helianthus belong to the first, the roots of Avena and Raphanus to the second group. The lightgrowthresponse of Avena was first examined by VOGT²⁾ and later by SIERP³⁾, LUNDEGÅRDH⁴⁾ and KONINGSBERGER⁵⁾.

For all these objects it has been demonstrated that phototropical sensibility and lightgrowthresponse go together.

If the theory of BLAAUW is correct it must be possible to deduce the phototropical curvature from the lightgrowthresponse of proximal and distal sides.

¹⁾ BLAAUW, A. H., Licht und Wachstum I Zeitschr. f. Bot. 6, 1914.

" " " II " " " 7, 1915.

" " " III Mededeelingen van de Landbouwhoogschool Wageningen 15, 1918.

²⁾ VOGT E., Über den Einfluss des Lichtes auf das Wachstum der Koleoptile von Avena sativa. Zeitschrift f. Botanik 7, 1915.

³⁾ SIERP, H., Untersuchungen über die durch Licht und Dunkelheit hervorgerufenen Wachstumsreaktionen bei den Koleoptilen von Avena sativa u.s.w. Zeitschr. f. Botanik 13, 1921.

⁴⁾ LUNDEGÅRDH, H., Ein Beitrag zur Analyse des Phototropismus. Arkiv f. Botanik 1922.

⁵⁾ KONINGSBERGER, V. J., Tropismus und Wachstum, Rec. des Trav. bot. Néerl. XIX 1922.

BLAAUW¹⁾ demonstrated this for the hypocotyl of *Helianthus* and found that the real phototropic curvature corresponds with the curvature deduced from the lightgrowthresponse.

VAN DE SANDE BAKHUYZEN²⁾ has tried to do the same for the coleoptile of *Avena*. He used the lightgrowthresponses found by VOGT and SIERP. He assumed rather arbitrarily the proportion of 4:1 for the quantities of light acting on the proximal and distal sides and then calculated the curvatures which would appear on unilateral illumination. He compared these with the curvatures found by ARISZ.

It will be proved afterwards that the distal side receives far less than $\frac{1}{4}$ of the light received by the proximal side.

The connection between lightgrowthresponse and phototropic curvature for *Avena* was examined experimentally by LUNDEGARDH, who opposes BLAAUW's theory because of the results he obtained.

SIERP, who especially studied the lightgrowthresponse, has also considered the connection between lightgrowthresponse and phototropic curvature and with RENNER³⁾ declares himself in favour of BLAAUW's theory.

BRAUNER⁴⁾ compared the course of phototropic curvature with the course of the lightgrowthresponse of the proximal side. It will be evident afterwards that the response of the distal side has a great influence on the nature of the curvature and may not be neglected.

I have determined the lightgrowthresponse to a number of different quantities of light and also the lightgrowthresponse to $\frac{1}{30}$ of these quantities which corresponds to the quantity of light received by the distal side. In each case I compared the curvature deduced from the combination of these two lightgrowthresponses with the phototropic curvature found by ARISZ⁵⁾.

A brief account of the main results is given below. For further details I refer to a publication which will appear later.

The distribution of light.

The distribution of light in the coleoptile was determined with the photographic method, also used by BLAAUW in his study of the hypocotyls of *Helianthus*: an oblique sagittal section is placed on a sensitive photographic plate and illuminated from above.

¹⁾ BLAAUW, A. H., Licht und Wachstum II. Zeitschrift f. Botanik 7, 1915.

²⁾ BAKHUYZEN, H. L. VAN DE SANDE, Analyse der fototropische stemmingsverschijnselen, Diss. Utrecht 1920.

³⁾ RENNER, O., Die Wachstumsreaktionen bei Licht- und Schwerkraftreizung. Zeitschrift f. Botanik 14, 1922.

⁴⁾ BRAUNER, L., Lichtkrümmung und Lichtwachstumsreaktion. Zeitschrift f. Botanik 14, 1922.

⁵⁾ ARISZ, W. H., Untersuchungen über den Phototropismus. Rec. des Trav. bot. Néerl. 12, 1915.

The decrease of light for *Avena* appeared to be far greater than for *Helianthus*. The distal side receives only $1/30$ of the quantity of light received by the proximal side.

This is mainly due to the presence of the primary leaf, which absorbs the greater part of the light. (Fig. 1).

More light passes through where this leaf ends (about $1/2$ mm from the apex). In this part the distribution

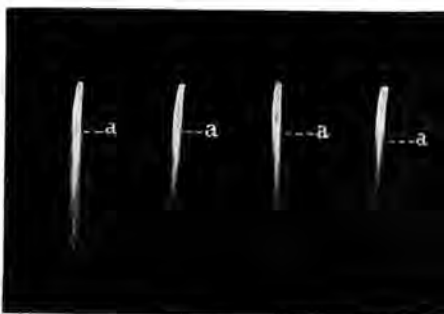


Fig. 1. The sections from left to right are illuminated by increasing quantities of light. It is obvious that a fair amount of light passes when only the coleoptile is present. Most of the light is absorbed in the part where the primary leaf is present.

a indicates the place where the section begins.

of light is very complicated, which is mainly due to the paraboloid form of the apex. I have assumed the light proportion of 30:1 for the whole coleoptile in my experiments. If further investigations should prove that the influence of the apex may not be neglected, I will have to compare the phototropic curvatures calculated from the lightgrowthresponse with the curvatures of the coleoptile in the apex of which the light proportion of 30:1 has been caused artificially. This can be achieved by bringing a smoked piece of glass in a median incision in the apex.

Everywhere in these coleoptiles there will actually be a lightproportion of 30:1.

The lightgrowthresponse.

The lightgrowthresponse was determined with the auxanometer of KONINGSBERGER ¹⁾ by which the growth is recorded automatically while the plant grows in the dark. As a source of light a PHILIPS "Argenta" electric lamp was fixed above the plant. The light was reflected onto the coleoptile by three mirrors which were placed at an angle of 45°. The coleoptile was protected against direct light from above by a round piece of card-board between lamp and coleoptile. The temperature of the darkroom was 20° C. The relative humidity varied between 65 % and 70 %. The growth was recorded for a few hours and only after the growth remained constant for an hour or more the coleoptile was illuminated.

Four series of lightgrowthresponses were determined, three with the intensity of 2400 M. C. and 80 M. C. and one with 80 M. C. and

¹⁾ KONINGSBERGER, V. J., *Tropismus und Wachstum*. Rec. des Trav. Bot. Néerland. Vol. XIX 1922.

2.5 M. C. The lightgrowthresponse was determined for each quantity of light about 6 times and the average taken.

15 min. \times 2400 M.C.

15 min. \times 80 M.C.

Graph *a* in fig. 2 gives the lightgrowthresponses to these quantities. In all the graphs the great period is taken into consideration and only changes in the rate of growth, as result of the illumination, are reproduced. In graph *a* both reactions are about the same; a minimum of growth is reached after about half an hour and a maximum after about 50 min. The responses differ however in the rate of growth. On illuminating with 2400 M.C. the growth remains constantly less than on illuminating with 80 M.C. If this is applied to a coleoptile illuminated unilaterally with 15 min. \times 2400 M.C., the distal side will grow quicker than the proximal side, and we may expect a positive curvature.

ARISZ actually found a positive curvature for this quantity (2.160.000 M.C.S.).

90 sec. \times 2400 M.C.

90 sec. \times 80 M.C.

These quantities give about the same result as the first. The only difference is that the minimum and maximum are reached sooner owing to the shorter period of illumination. This difference becomes even greater in the following experiments, where the coleoptile was illuminated during 10 sec. Graph *b* shows that the lightgrowthresponse to 2400 M.C. is greater than the response to 80 M.C. As the difference is even greater than in the first experiment we may expect a stronger positive curvature.

ARISZ did not determine the curvature for the same quantity of light (216000 M.C.S.) In the case of 162000 M.C.S. and 240.000 M.C.S. he found a positive curvature.

10 sec. \times 2400 M.C.

10 sec. \times 80 M.C.

Graph *c* illustrates the responses to these quantities. This experiment shows that the response to 2400 M.C. is totally different from the response to 80 M.C., whereas in the first two experiments there was only a difference in the rate of growth.

The response to 2400 M.C. is about the same as in the previous experiments except that the minimum is reached sooner (after 23 min.) owing to the shorter period of illumination. The response to 80 M.C. is quite different; the rate of growth decreases slowly and only reaches a minimum after 78 minutes. The maximum growth is attained after 108 minutes. The proximal side of a coleoptile subjected to a unilateral illumination of 10 sec. \times 2400 M.C. will give a "short" growthresponse, the distal side a "long" response. The result will be a faint positive curvature, which changes into a stronger negative one after $\frac{1}{2}$ hour.

It is also possible that the difference in the rate of growth during the first half an hour is not great enough to cause a noticeable positive

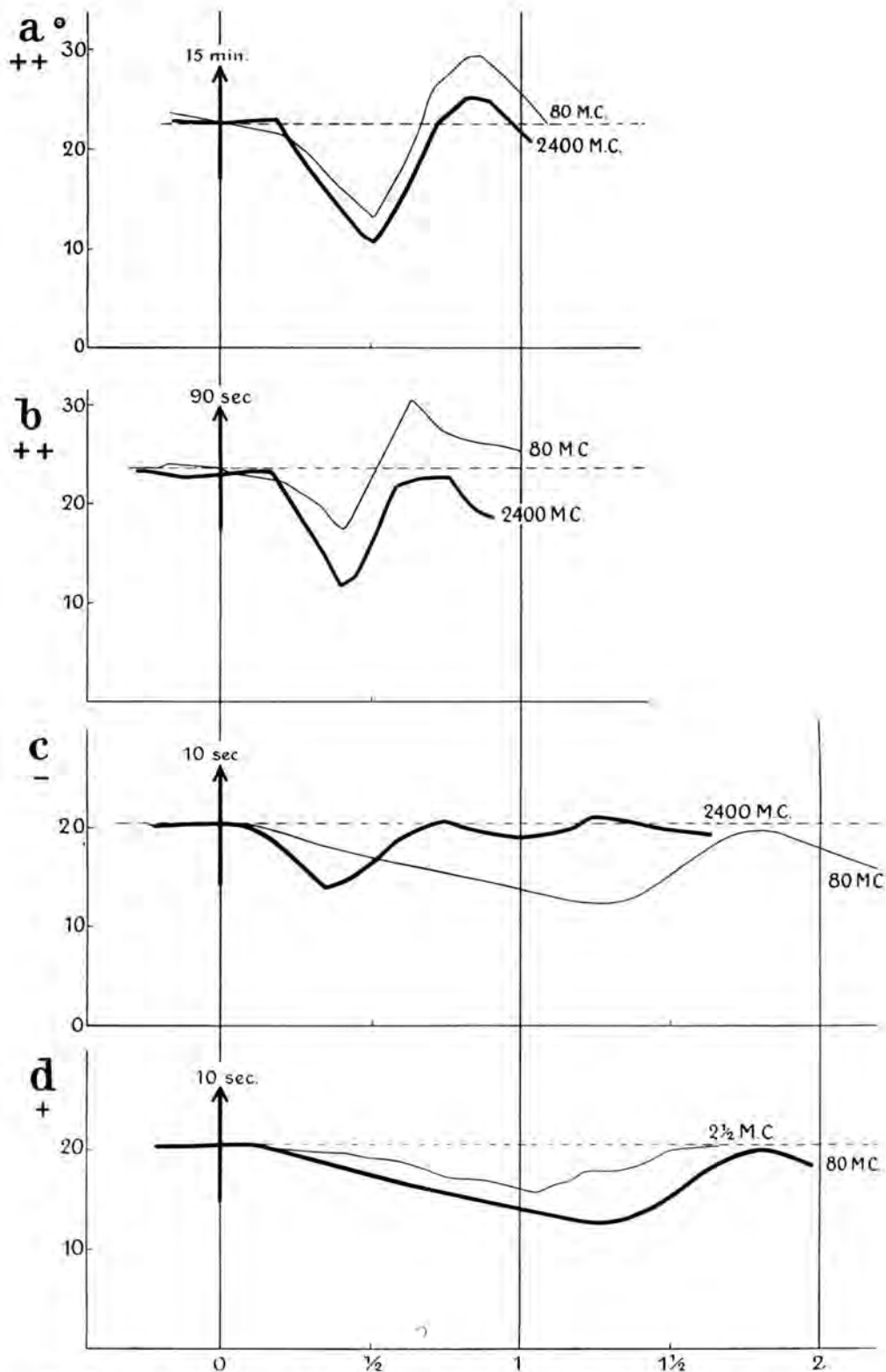


Fig. 2. In the above graphs abscissa represent time in hours and the ordinates rate of growth in μ pro minute. The intensity of light is indicated in M.C.

+ means the area of the first positive curvature

- that of the negative and ++ that of the second positive curvature.

The arrow indicates the moment of illumination.

curvature, and hence only the negative curvature would be visible. ARISZ found negative curvatures in response to 13500 M.C.S. and 27000 M.C.S. With the same quantities of light but with very high intensities he found a positive instead of a negative curvature. This is easily explained as my experiments demonstrated that the "long" response only occurs with low intensities. The distal side will also show a "short" response to high intensities and a positive curvature as in graph *a* and *b* would occur.

10 sec. \times 80 M.C.

10 sec. \times 2.5 M.C.

Both quantities give a "long" response but the response to 80 M.C. is greater than the response to 2.5 M.C. Hence a coleoptile illuminated unilaterally with 10×80 M.C. will show a positive curvature. ARISZ actually found a positive curvature in response to this quantity.

On examining the responses in fig. 2 it will be obvious that the curvature deduced from them must be positive with the smallest quantity of light (*d*), negative with greater quantities (*c*), and when the quantity increases again positive (*b*) gradually becoming fainter as the quantity is further increased (*a*). ARISZ in his research about the phototropic curvature of *Avena* also found three areas of curvatures: one of the first positive curvature, one of the negative curvature, and one of the second positive curvature, according to the increasing quantity of light.

Hence the curvatures deduced from the lightgrowthresponse of proximal and distal sides correspond with the real curvatures observed by ARISZ.

ARISZ found a peculiarity in the phototropic curvatures which he could not explain. He observed that no negative curvature is obtained with low light intensities, no matter how long the illumination lasts. This fact is easily explained by means of the lightgrowthresponse, as low intensities call forth a "long" response of the proximal and distal sides (graph *d*) causing a positive curvature. A negative curvature only appears when the proximal side gives a "short" response and this is obtained only with a certain intensity. No negative curvature will occur below this intensity.

Utrecht, September 1925.

Botanical Laboratory.

Physics. — "*On the Relation of the Internal Latent Heat of Evaporation to the Molecular Surface Energy, in Connection with the Modified Law of the Corresponding States*". By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of September 26, 1925).

I.

These Proceedings, 28, p. 356 contain an interesting article by Mr. VAN URK on the limiting value of the above relation at the absolute zero, for which he theoretically finds the value 4 for simple substances. For oxygen, argon and nitrogen this value is about confirmed; for the values found for these substances are resp. 3,75, 4,0 and 3,9. But for hydrogen 2,6 is found, and for Helium a still smaller value, i.e. 1,8, would have been found. And for the large category of the so-called „ordinary” substances everywhere values are found in the neighbourhood of 5,3 (as against 7 for $T = \frac{1}{2}T_k$). These values already indicate that the relation in question is by no means constant, but that in a way, which will be more closely defined later, the value will depend on the *family* of substances that is considered, and which is characterized by the value of the *parameter* γ , i.e. of the reduced coefficient of direction of the straight line between $\frac{1}{2}d_0$ en d_k , when d_0 and d_k represent the reduced liquid densities resp. at $T=0$ and $T=T_k$.

It is, indeed, easy to derive a general formula for the ratio $\lambda:\mu$, from which it will then appear that this ratio with close approximation will be $=f$ for $T = \frac{1}{2}T_k$, f being the so-called vapour-pressure factor at this temperature in the well-known vapour pressure formula

$$\log \frac{p_k}{p} = f \left(\frac{T_k}{T} - 1 \right),$$

and that this ratio approaches to $\frac{1}{2}f_0$ at $T=0$, in which f_0 is the extrapolated limiting value of f at $T=0$. (For hydrogen to 0,8 f_0).

II.

We start from the relation (valid for temperatures, at which the vapour density may be neglected in comparison with the liquid density) for the surface tension σ :

$$\sigma = \frac{a}{v^2} u,$$

III.

Let us now calculate the values of λ and μ from known formulae. From the general relation

$$L = T(v_2 - v_1) \frac{dp}{dt} = T v_2 \frac{dp}{dt},$$

when the liquid volume v_1 may be neglected by the side of the vapour volume v_2 , follows

$$L = \frac{T}{p} \frac{dp}{dt} \cdot p v_2 = RT \cdot \frac{T}{p} \frac{dp}{dt},$$

because at lower temperatures also $p v_2 = RT$; so that

$$\lambda = RT \left[\frac{T}{p} \frac{dp}{dt} - 1 \right], \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

is found for

$$\lambda = L - p(v_2 - v_1) = L - p v_2 = L - RT.$$

Now from

$$\log \frac{p_k}{p} = f \left(\frac{T_k}{T} - 1 \right),$$

in which f is a slight function of the temperature, follows immediately (cf. also Zust.gl., p. 228 et seq.):

$$-\frac{1}{p} \frac{dp}{dt} = -\frac{f T_k}{T^2} + \left(\frac{T_k}{T} - 1 \right) \frac{df}{dt}.$$

Hence

$$\frac{T}{p} \frac{dp}{dt} = f \frac{T_k}{T} - \left(\frac{T_k}{T} - 1 \right) T \frac{df}{dt},$$

or with $T : T_k = m$ and $\frac{df}{dt} = \frac{1}{T_k} \frac{df}{dm}$:

$$\frac{T}{p} \frac{dp}{dt} = \frac{f}{m} - \left(\frac{1}{m} - 1 \right) m \frac{df}{dm} = \frac{f}{m} - (1-m) f'_m.$$

As $T : m = T_k$, (4) becomes therefore:

$$\lambda = RT_k [(f-m) - m(1-m) f'_m] \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Further we have according to the well-known equation of EÖTVÖS:

$$\mu = \varphi (T_k - T) = \varphi T_k (1-m), \quad . \quad . \quad . \quad . \quad . \quad (6)$$

so that equation (3) passes into

$$x(1+\theta) = \frac{\lambda'}{\mu'} = \frac{R}{\varphi} \frac{(f-m) - m(1-m) f'_m}{1-m} \cdot \frac{1}{N^{1/3}}, \quad . \quad . \quad . \quad (7)$$

in which φ generally lies in the neighbourhood of 2. At low tempera-

tures the value of x will therefore be chiefly determined by f , which value — as we remarked above — will be *different for every category of substances*, dependent on the value of the parameter γ ¹⁾.

IV.

We will now further reduce the above formula. For R we may write $83,17 \cdot 10^6$ Ergs/Gr.mol., while $N^{1/3} = \sqrt[3]{0,6060 \cdot 10^{24}} = 0,8462 \cdot 10^8 = 84,62 \cdot 10^6$, so that $R : N^{1/3}$ becomes $= 1 : 1,0175$.

For *ordinary* substances on an average 2,10 is found for φ (benzene 2,104, CHCl_3 2,013, CCl_4 2,105, Ether 2,172, etc.), while on an average 1,98 is found for argon, nitrogen, and oxygen (argon 2,02, N_2 2,002, O_2 1,917). Hence φ (except for H_2 and He) may be put at 2,04, and as $(1 : 1,0175) : 2,04 = 0,48 = 0,5$, we may write:

$$x(1 + \theta) = \frac{\lambda'}{\mu'} = 0,5 \frac{(f-m) - m(1-m)f'_m}{1-m} \quad (7a)$$

in which the factor 0,5 passes into 0,76 for H_2 , where $\varphi = 1,294$.

We shall now examine this formula more closely for the case $m = 1/2$ ($T = 1/2 T_k$) and for $m = 0$ ($T = 0$).

a. $m = 1/2$. That the formula for this case leads to good results, may appear from what follows.

1. In *benzene*, a member of the extensive family of the *ordinary* substances, $f'_m = T_k f'_t$ lies in the neighbourhood of $562 \times (-0,0038) = -2,1$ for $m = 0,5$ (8°C.) (See Zust. Gl. p. 222), so that $m(1-m)f'_m$ becomes $= -0,5$. Consequently the numerator becomes $= f - 0,5 + 0,5 = f$, and therefore

$$\frac{\lambda'}{\mu'} = 0,5 \frac{f}{0,5} = f \text{ (ordinary substances)} \quad (8)$$

According to the table in Zust. Gl. p. 222 the value of f is equal to 6,8 for $m = 1/2$.

If λ is calculated directly from the vapour pressures²⁾ — which calculation must of course also be made according to (4) or (5), in which at higher temperatures $p(v_2 - v_1)$ must be substituted for RT — then 6,7 is obtained (see the table in Z. Gl. p. 259). The small difference is owing to this, that in formula (7) φ for benzene is not $= 2,04$ but $= 2,1$, so that 6,8 will become somewhat smaller, and that besides a slight error in f'_t appears augmented in f'_m through multiplication by T_k .

2. For *argon* (Z. Gl. p. 227) the value of f'_t (extrapolated) is clearly

¹⁾ Compare about this — in extension of what VAN DER WAALS wrote about this already before — my Papers in These Proc. 16 (1914), p. 808, and Zust. Gl. p. 128 et seq. and 140 et seq. There the whole development of this important subject will be found.

²⁾ I have repeated these calculations, and also those with $m = 0$ in V with the greatest accuracy.

2. For *argon* ($\gamma = 0.75$), *oxygen*, and *nitrogen* ($\gamma = 0.8$) the value $x_0 = \frac{1}{2} \times 5$ to $5.4 \times 1.5 =$ from 3.75 to 4, with $a : a_k = 1.5$ and $f_k = 6$ to 6.4. From the values of λ the following values are actually found: 3.9 for argon, 4.0 for nitrogen and 3.75 for oxygen. These values are, accordingly, close to 4, but this is in my opinion to be attributed more to purely accidental circumstances than to a theoretical property.

3. For in *hydrogen* everything is again different. Here with $\gamma_{rh} = 0.61$ the value of $(\gamma + 1)^2 : 4\gamma = 1.06$, hence $x_0 = 0.76 \times 1.06 \times 3.88 \times 0.9$, as $f_k = 8\gamma = 4.88$, and $a_0 : a_k = 0.9$ or still slightly less, as for hydrogen the value of a below T_k at first remains about constant when the temperature becomes lower, whereas at lower temperatures it gradually decreases. (For Helium $a_0 : a_k$ is already < 0.7 ; see Z.Gl. p. 249 and 250). Accordingly we find at most $x_0 = 2.8$. From the extrapolated value of λ_0 is found 2.6, which is again somewhat lower (see above). But at any rate not 4.

Recapitulating all this, we get the following survey, in which the values of $\lambda' : \mu'$ at T_k have been determined from the values of λ in the neighbourhood of T_k given by VAN URK, and as regards benzene, from these calculated by me in Z.Gl. p. 259.

	$T = 0$	$T = \frac{1}{2} T_k$	$T \text{ somewhat } < T_k$
Ordinary substances	$\lambda' : \mu' = 5.3$	7	± 50
Argon etc.	3.9	5.3	± 30
Hydrogen	2.8	($<$) 4.4	± 10

It follows from all this that there can be no question of a general limiting value 4 at $T = 0$ (Compare also the *Appendix*).

V.

Some Experimental Data.

From the equation of the straight diameter $d_1 + d_2 = d_0 - 2\gamma m$, when at lower temperatures d_2 may be neglected compared with d_1 , follows $d_1 = d_0 - 2\gamma m$, or with $d_1 = v_k : v$ (for d_1 is the reduced liquid density):

$$\frac{1}{v} = \frac{1}{v_0} - \frac{2\gamma}{v_k} m = \frac{1}{v_0} \left(1 - 2\gamma \frac{v_0}{v_k} m \right).$$

But $v_k : v_0 = d_0$, and $d_0 = 2(1 + \gamma)$, hence:

$$\frac{1}{v} = \frac{1}{v_0} \left(1 - \frac{\gamma}{1 + \gamma} m \right).$$

[That $d_0 = 2(1 + \gamma)$, follows immediately from the equation for the

straight diameter, which becomes $2d_k = d_0 - 2\gamma$ for $m = 1$, hence because $d_k = 1$, d_0 will be $= 2(1 + \gamma)$.

If a were constant, $\frac{a}{v}$ would also be $\frac{a}{v} = \frac{a}{v_0} \left(1 - \frac{\gamma}{1+\gamma} m\right)$, but since a is always $< a_0$ (except for H_2 and He), we get:

$$\frac{a}{v} = \frac{a_0}{v_0} \left(1 - \varepsilon \frac{\gamma}{1+\gamma} m\right),$$

in which ε is a factor > 1 , except for H_2 and He , where ε will be slightly < 1 . And since $\lambda = \frac{a}{v} (1 + \theta)$, in which $\theta = 0$ for $m = 0$ and positive for $m > 0$ (negative for H_2 and He , see § 2), it follows that with $\frac{a_0}{v_0} = \lambda_0$:

$$\frac{\lambda}{1 + \theta} = \lambda_0 \left(1 - \varepsilon \frac{\gamma}{1+\gamma} m\right),$$

or

$$\lambda = \lambda_0 \left(1 - \varepsilon' \frac{\gamma}{1+\gamma} m\right),$$

in which ε' will be somewhat smaller than ε (for H_2 and He somewhat larger).

a. From the experimental results for benzene (Z.Gl. p. 259) follows with $T_k = 561,6$:

$$\lambda = 12770 - 17 T = 12770 (1 - 0,001332 T),$$

hence also

$$\lambda = 12770 (1 - 0,748 m) \text{ (in gr. kal. per gr. mol.)}$$

Now $\gamma = 0,973$, hence $\gamma : (1 + \gamma) = 0,493$, so that the value 1,52 is found for the factor ε' , which corresponds to the variability of a with t .

For μ holds:

$$\mu = 2,104 \times 561,6 (1 - m) = 1182 (1 - m),$$

so that $\left(\frac{\lambda}{\mu}\right)_{0,5} = \frac{7990}{591} = 13,53$ is found for $m = 0,5$.

Now $\frac{\lambda'}{\mu'} = \frac{\lambda}{\mu} : N^{1/3}$ (see § 2), so that we must still divide by $84,62 \cdot 10^6$ (see § 4). But in order to reduce Gr. cal. to ergs we must multiply by $41,863 \cdot 10^6$; hence we must finally divide by 2,0212. Therefore we find for benzene:

$$\left(\frac{\lambda'}{\mu'}\right)_{1/2} = \frac{13,53}{2,021} = 6,69 = 6,7.$$

And for $m = 0$ $\left(\frac{\lambda'}{\mu'}\right)_0$ will become:

$$\left(\frac{\lambda'}{\mu'}\right)_0 = \frac{12770}{1182} : 2,021 = 5,34 = 5,3.$$

b. From the data of VAN URK follows for argon:

$$\lambda \text{ (per gr.)} = 58,06 - 0,2655 T = 58,06 (1 - 0,004573 T),$$

which becomes with $T_k = 150,65$:

$$\lambda \text{ (per gr. mol.)} = 58,06 (1 - 0,689 m) \times 39,95.$$

With $\gamma = 0,745$ we get $\gamma : (1 + \gamma) = 0,427$, hence $\epsilon' = \underline{1,61}$.

For μ may be written:

$$\mu = 2,02 (145,44 - T) = 293,8 (1 - 1,036 m).$$

For $m = 0,5$ (about 75° , hence below the triple point at 84°) the equation becomes:

$$\left(\frac{\lambda'}{\mu'}\right)_{1/2} = \frac{38,06}{141,6} \times 39,95 : 2,021 = 5,31 = 5,3.$$

And for $m = 0$ we find:

$$\left(\frac{\lambda'}{\mu'}\right)_0 = \frac{58,06}{293,8} \times 39,95 : 2,021 = 3,91 = 3,9.$$

c. For oxygen we find:

$$\lambda \text{ (per gr.)} = 69,86 - 0,269 T = 69,86 (1 - 0,003856 T),$$

which becomes with $T_k = 154,17$:

$$\lambda \text{ (per gr.mol.)} = 69,86 (1 - 0,595 m) \times 16.$$

With $\gamma = 0,793$ $\gamma : (1 + \gamma)$ becomes $= 0,442$, hence $\epsilon' = \underline{1,35}$.

Further

$$\mu = 1,917 (153,77 - T) = 294,8 (1 - 1,003 m).$$

Hence we have for $m = 0,5$:

$$\left(\frac{\lambda'}{\mu'}\right)_{1/2} = \frac{49,08}{147,0} \times 16 : 2,021 = 5,29 = 5,3.$$

And for $m = 0$:

$$\left(\frac{\lambda'}{\mu'}\right)_0 = \frac{69,86}{294,8} \times 16 : 2,021 = 3,75.$$

d. For nitrogen we find:

$$\lambda \text{ (per gr.)} = 72,20 - 0,3857 T = 72,20 (1 - 0,005342 T),$$

or with $T_k = 125,96$:

$$\lambda \text{ (per gr. mol.)} = 72,20 (1 - 0,673 m) \times 14,008.$$

With $\gamma = 0,813$ $\gamma : (1 + \gamma)$ becomes $= 0,448$, so that $\epsilon' = \underline{1,50}$.

We find for μ :

$$\mu = 2,002 (124,29 - T) = 248,8 (1 - 1,013 m).$$

This yields for $m = 0,5$:

$$\left(\frac{\lambda'}{\mu'}\right)_{1/2} = \frac{47,90}{122,8} \times 14,01 : 2,021 = 5,40 = 5,4.$$

And with $m=0$:

$$\left(\frac{\lambda'}{\mu'}\right)_0 = \frac{72,20}{248,8} \times 14,01 : 2,021 = 4,02 = 4,0.$$

e. In conclusion *hydrogen*. Here

$$\lambda \text{ (per gr.)} = 114,4 - 1,27 T = 114,4 (1 - 0,01110 T).$$

With $T_k = 33,18$ this becomes:

$$\lambda \text{ (per gr. mol.)} = 114,4 (1 - 0,3683 m) \times 2,0154.$$

Further $\gamma_{th} = 0,6$, hence $\gamma : (1 + \gamma) = 0,375$, through which ε' becomes $\underline{= 0,98}$ (slight decrease of a when t becomes lower).

For μ is found:

$$\mu = 1,294 (34,49 - T) = 44,63 (1 - 0,962 m).$$

For $m=0,5$ we get therefore:

$$\left(\frac{\lambda'}{\mu'}\right)_{1/2} = \frac{93,34}{23,16} \times 2,0154 : 2,0212 = 4,02 = 4,0.$$

And with $m=0$:

$$\left(\frac{\lambda'}{\mu'}\right)_0 = \frac{114,4}{44,63} \times 2,0154 : 2,0212 = 2,56 = 2,6.$$

And these values for benzene, argon etc. have been mentioned in § 4 for a comparison with the values, calculated from our formula for λ with f and f_0 .

July 1925.

Tavel sur Clarens (Suisse).

VI.

Appendix.

After I had written the foregoing paper, it has appeared to me that the quantity $x = l : u$ occurring in (1), which at the absolute zero (extrapolated) is about 5 for ordinary substances, 4 for argon etc., 3 for hydrogen, is $\underline{= 14}$ for all melted alkali-haloids. I shall discuss this more at length in a paper which will shortly appear in the *Zeitschr. f. anorg. u. allg. Ch.* (the third of a series of three papers on the substances mentioned ¹⁾), and will give here only the principal results.

With $l : u = x$ the formula

$$\mu = \sigma v^{2/3} = \frac{1}{x} \frac{a}{v} \frac{1}{N^{1/3}}$$

follows, as we saw in § 1 (formula (1)), from $\sigma = \frac{a}{v^2} u$, since $l = (v : N)^{1/3}$.

In this formula v is the molecular volume $M : D$. (M = molecular

¹⁾ I in 146, p. 263—280, II in 148, p. 235—255, III in 149, p. 324—352 (all in 1925).

weight, $D = \text{density}$). As the quantity μ , i.e. the *molecular* surface-tension has an almost *linear* course from $T=0$ to almost T_k (the difference between the point of intersection of this straight line with the temperature-axis and the real value of T_k is possibly about 10° , so that the error for the said salts will be about $10^\circ : 3000^\circ = \frac{1}{300}$), the coefficient of the temperature θ will be given with great approximation by

$$\theta = \frac{\mu_0}{T_k} = \frac{1}{x_0} \frac{a_0}{v_0} \frac{1}{N^{1/3}} : \frac{8}{27} \lambda \frac{1}{R} \frac{a_k}{b_k}.$$

With $\lambda = \frac{27}{28}$, which is the value of this correction quantity in the formula for T_k for substances where γ is about $= 1$ (Zustandsgl. p. 140), θ becomes:

$$\theta = \frac{1}{x_0} \frac{7}{2} \frac{a_0}{a_k} \frac{b_k}{b_0} \frac{R}{N^{1/3}},$$

or with $R = 83,17 \cdot 10^6$ (Ergs), $N = 0,6060 \cdot 10^{24}$, hence $N^{1/3} = 0,8462 \cdot 10^8 = 84,62 \cdot 10^6$, so that $R : N^{1/3}$ becomes $= 1 : 1,0175$:

$$\text{(ordinary substances)} \quad \theta > \frac{3,44}{x_0} \frac{a_0}{a_k} \frac{b_k}{b_0} \dots \dots \dots (a)$$

With $x_0 > 5$, as we have found for ordinary substances, $a_0 : a_k = 1,6$ (Zust.gl. p. 250—255), $b_k : b_0 = 2\gamma = \text{from } 1,8 \text{ to } 2$, we therefore get for ordinary substances:

$$\theta = \frac{10,5}{x_0} = \underline{2,1},$$

2,1 being also found as mean value ¹⁾.

But it follows from $x_0 = l_0 : u_0 = 5$, that $u_0 = l_0 : 5 = \frac{2}{5} r$, as for ordinary substances the radius of the molecule r will be about $\frac{1}{2} l$ for cubic distribution of the molecules. (For it is known that for these substances $(v - b) : v = m : f$, so that for $m = \frac{1}{2} (T = \frac{1}{2} T_k)$ the value $(v - b) : v$ is already $= \frac{1}{2} : 7 = \frac{1}{14}$, hence $(l - r) : l = \frac{1}{42}$). For $T=0$ the value r is strictly $= \frac{1}{2} l$.

Now it appears, however, that not only for ordinary substances, but also for the *melted alkalihaloids*

$$u_0 = \frac{2}{5} r, \dots \dots \dots (b)$$

in which now r is, however, much smaller than $\frac{1}{2} l$, as for ordinary substances. If $l_0 = 2r'$ is written, in which r' would therefore be the radius of the molecule if, as for ordinary substances, the elementary cubes are entirely filled with the molecule (thought spherical), (a) becomes quite generally:

$$\theta = 3,44 \frac{\frac{2}{5} r}{2r'} \frac{a_0}{a_k} \frac{b_k}{b_0} = 0,69 \frac{a_0}{a_k} \frac{b_k}{b_0} \frac{r}{r'}.$$

¹⁾ For H_2 (with $x_0 = 2,8$, $a_0 : a_k = 0,9$, $b_k : b_0 = 1,2$) θ would become $= 1,3$, which again is in harmony with the value found.

The melted salts are all *electrolytically dissociated*. The values of μ used in practice are, however, calculated from the values determined experimentally by multiplication (see above) by $v^{2/3} = (M:D)^{2/3}$, in which the so-called "normal" value is taken for M , i.e. on the supposition that there is no electrolytic dissociation. (for KCl e.g. = 74.6). But (for total dissociation) this is, in fact, twice too great, as M should not have been taken for the whole molecule, but the mean value $1/2 M$ for each of the ions. In general M has been taken $(1 + \alpha)$ -times too great, hence μ and θ both $(1 + \alpha)^{2/3}$ -times too great. The above formula must, therefore, still be multiplied by $(1 + \alpha)^{2/3}$ in order to find the "conventional" value of θ . (This is, therefore, found too great with dissociation, too small with association). In consequence of this we get quite generally:

$$\theta = 0.7 \frac{a_0}{a_k} \frac{b_k}{b_0} \frac{r}{r'} (1 + \alpha)^{2/3}, \quad \dots \dots \dots (c)$$

and this for all cases where $u_0 = 2/5 r$. That the latter is also fulfilled with the melted alkali-haloids, as with the ordinary substances, follows from this that for the completely dissociated cesium salts $\theta = 0.8$, so that, with $a_0 = a_k$ (as a has been found almost independent of the temperature for the great values of the valency attractions; cf. Zustandsgl. p. 325), $b_k : b_0 = 2\gamma = 1$ (as according to the third paper in the Z. f. anorg. Ch. cited the melted salts behave as boundary substances, where $\gamma = 1$) and $(1 + \alpha)^{2/3} = 2^{2/3} = 1.59$, is found:

$$0.8 = 0.7 \times 1 \times 2 \times \frac{r}{r'} \times 1.6,$$

from which follows $r : r' = 0.8 : 2.2 = 1 : 2.75 = 1 : 2.8$. This latter (see below) has actually been found by LORENZ-BORN¹⁾, so that the supposition $u_0 = 2/5 r$ appears to be correct.

But then $x_0 = l_0 : u_0 = 2r' : 2/5 r = 5 (r' : r)$ assumes also the value $5 \times 2.8 = 14$, as we already stated in the beginning. And this value is certainly very far from the "theoretic" value 4, which ought to be valid according to VAN URK (loc. cit.). We see clearly from all this, that in this and in allied problems a number of other factors play a part (as the values of $a_0 : a_k$, $b_k : b_0$, $r : r'$) than one would at first be inclined to suppose.

In passing we may just point out that in case of association (for ordinary substances) the factor $\left(\frac{1 + \beta}{2}\right)^{2/3}$ must be substituted in (c) for $(1 + \alpha)^{2/3}$, in which β is the degree of dissociation of the double molecules. Hence $\beta = 0$ with complete association, so that then the value must

¹⁾ Cf. RICHARD LORENZ's excellent book: Raumerfüllung und Ionenbeweglichkeit, p. 242—257.

be multiplied by $\left(\frac{1}{2}\right)^{2/3}$, i. e. *divided* by 1,6 — instead of multiplied, as with total electrolytic dissociation of the salt molecules.

With melted electrolytes this electrolytic dissociation would increase the value of the (conventional) temperature coefficient θ , but in consequence of the fact that $a_0 : a_k = 1$ instead of 1,6, and particularly in consequence of the *very low* value of $r : r'$ (2,8 times less than for ordinary substances) θ is not found greater, but on the contrary *much smaller* than the normal value 2,1 holding for ordinary substances — which latter also ensues from (c) with $a_0 : a_k = 1,6$, $b_k : b_0 = 1,9$, $r : r' = 1$ and $\alpha = 0$.

That for the alkali-haloids really

$$\underline{r' : r = 2,8}, \dots \dots \dots (d)$$

appears from what follows. The following values are e. g. calculated for $\nu_0 = M : D_0$ for the kations of the alkali-haloids (the values of D_0 have been calculated by me in the first paper in the *Z. f. anorg. Ch.* cited):

$$\nu_0 = \frac{6,94}{0,559} \quad \frac{23,00}{1,024} \quad \frac{39,10}{0,904} \quad \frac{85,45}{1,631} \quad \frac{132,8}{2,035},$$

or

$$\nu_0 = 12,41 \quad 22,24 \quad 43,25 \quad 52,39 \quad 65,26 \quad (\text{roughly } 1 : 2 : 4 : 5 : 6),$$

resp. for *Li*, *Na*, *K*, *Rb*. and *Cs*. Division by $N = 0,606 \cdot 10^{24}$ yields, therefore, for the volume of the elementary cubes:

$$\omega = 20,48 \quad 36,70 \quad 71,37 \quad 86,45 \quad 107,7 \cdot 10^{-14},$$

hence

$$l = \sqrt[3]{\omega} = 2,74 \quad 3,32 \quad 4,15 \quad 4,42 \quad 4,76 \cdot 10^{-8},$$

or

$$r' = \frac{1}{2} l = 1,37 \quad 1,66 \quad 2,07 \quad 2,21 \quad 2,38 \cdot 10^{-8}.$$

If now really $r' : r = 2,75$, the following values must be found for r : 0,498, 0,604, 0,755, 0,804, 0,865, i. e.

$$r = 0,50 \quad 0,60 \quad 0,75 \quad 0,80 \quad 0,87 \cdot 10^{-8},$$

while LORENZ-BORN (loc. cit.) found:

$$r = 0,45 \quad 0,51 \quad 0,69 \quad 0,77 \quad 0,83 \cdot 10^{-8},$$

adding that these values are all somewhat too small. The conformity could not be better; particularly striking is the almost perfect identity of the value for *Na*, i. e. 0,604 found by us, with the value 0,605 calculated by LANDÉ (loc. cit. p. 251) from the quantum theory for the sodium atom.

If in (c) the values 0,55 (which is found as average value for the lithium haloids), 0,68 (*Na*-salts), 0,74 (id. *K*), 0,80 (id. *Rb*) and 0,82 (id. *Cs*), are substituted, it appears that resp.

$$(1 + \alpha)^{2/3} = 1,086 \quad 1,314 \quad 1,434 \quad 1,551 \quad 1,590,$$

hence

$$1 + \alpha = 1,13 \quad 1,51 \quad 1,72 \quad 1,93 \quad 2,00,$$

so that for the degree of dissociation α of the said salts resp. the values

$$\alpha = 0,13 \quad 0,51 \quad 0,72 \quad 0,93 \quad 1,00$$

are found.

Accordingly the melted *Li*-salts are dissociated only for about $\frac{1}{8}$, the sodium salts about half, the potassium salts for about $\frac{3}{4}$, and the rubidium and the cesium salts completely or almost completely.

By the discussion of the said relations for melted salts ($u_0 = \frac{2}{5} r$, $r' : r = 2,8$ etc.) and by the derivation of the general formula (c) for θ (about which so far nothing was known), I hope to have been of use to some scientists interested in this subject.

August 1925.

Chemistry. — "*An observation on the growth of crystals*". By P. TERPSTRA. (Communicated by Prof. F. M. JAEGER).

(Communicated at the meeting of September 26, 1925).

In his paper „Wachstum und Auflösung der Kristalle” J. J. P. VALETON¹⁾ discusses a. o. the following case: A very little crystal is placed in the centre of a spherical quantity of its slightly supersaturated solution. There is a device which cares that the concentration on the surface constantly remains C_2 , whereas the concentration very near the growing crystal is C_1 . Putting for the radius of the little crystal r_1 , for the radius of the solution r_2 , VALETON finds the concentration in any point:

$$C = -\frac{1}{r} \frac{r_1 r_2}{r_2 - r_1} (C_2 - C_1) + C_2 + \frac{r_1}{r_2 - r_1} (C_2 - C_1).$$

This question has its analogy in the discipline of electrostatics, viz. in the case of a spherical condenser. If the spheres have radii a and b and potentials V_a and V_b , the potential V in any point between the spheres appears to be:

$$V = -\frac{1}{r} \frac{ab}{b-a} (V_b - V_a) + V_b + \frac{a}{b-a} (V_b - V_a).$$

This analogy suffices to demonstrate that VALETON wrongly endeavours to deduce from his formula the so-called „Kristallisationshof-bildung”. Just as in the case of the spherical condenser a „Hof” is out of the question, so in the case under discussion this phenomenon cannot appear in the neighbourhood of the growing crystal.

The formula for the velocity of crystal-growing which VALETON deduces from his theory is one of great value. A little crystal is supposed to be placed in a slightly supersaturated solution, which now, however, in contrast with the former case, is stirred thoroughly. Even then, it may be assumed that in the very neighbourhood of the crystal there is a layer of liquid with thickness s , which remains in a state of rest. At the surface of the crystal the solution has a concentration C_1 , which is different at the different faces of the crystal, but is always a little more than the concentration of saturation C_0 . The velocity of growing G of a face of the crystal can be put $k (C_1 - C_0)$, in which k is a constant

¹⁾ Ztschr. f. Kryst. Bnd. 59, 135; 335 Bnd. 60, 1.

which is characteristic for the crystal-face. Putting the concentration of the stirred solution C_2 , VALETON deduces $G = R (C_2 - C_0)$. If the lines of diffusion are parallel to one another, as very approximately the case will be in points which lie opposite the middle-part of a crystal-face,

$$R = \frac{k \frac{D}{s}}{k + \frac{D}{s}} \quad (D = \text{the constant of diffusion of the solution}).$$

This formula shows very clearly that the velocity of growing of the various crystal-faces and in consequence their relative importance is not only a function of the crystal itself, as f.i. in the case of the property of cleavage: the properties of the solution also play a part.

To demonstrate in which manner the quantities k and $\frac{D}{s}$ produce the factor R of the observed velocity of growing, a graphical method may be applied which J. PLATEAU used in his work on two soap-bubbles in contact¹⁾. We are supposed to be given three right lines intersecting in

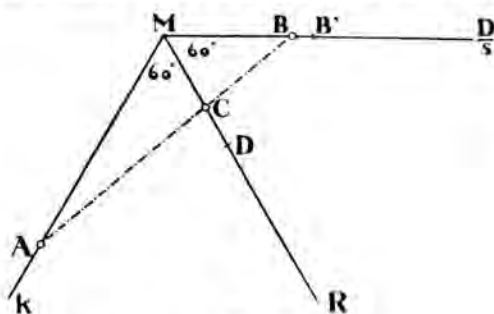


Fig. 1.

the point M at angles of 60° . Now if we choose two points A and B so that $MA = k$ and $MB = \frac{D}{s}$, the line connecting the points A and B intersects the third line in a point C , so that $MC = R$. The figure illustrates that if one of the quantities k or $\frac{D}{s}$ is very great

with respect to the other the value of R approaches to that of the latter. The crystal-faces which have their characteristic constant k greater than MA have all a R value, which is between MC and MD ($MD = MB$). So there is a possibility that while the characteristic constants k are very different, yet the observed velocities of growing differ but little, so that they may cause the formation of convex-curved parts in the surface of the crystal. In most cases, however, these curved parts have no chance to develop, because they are effaced by the faces which grow slowly. In this connection one might think of some cases among the minerals and of the explosive cubes which grow from a saturated solution of ammonium-chloride, to which had been added a little quantity of $CdCl_2$. These cubes, which are rather strongly endowed with the property of double refraction, have planes which are very obviously curved.

In the neighbourhood of the margins of a crystal-face the lines of

¹⁾ J. PLATEAU: *Statique expérimentale et théorique des liquides* (1873) Vol. I pag. 299.

diffusion form a convergent system of lines. The formula of the velocity of growing takes the form:

$$G = \frac{k \cdot \epsilon \cdot \frac{D}{s}}{k + \epsilon \frac{D}{s}} (C_2 - C_0) \text{ in which } \epsilon > 1.$$

This means that in the figure with the margin of a crystal-face a point B' corresponds, that lies a little farther to the right than B , so that the line AB' cuts the third line in a point C' . MC' being slightly

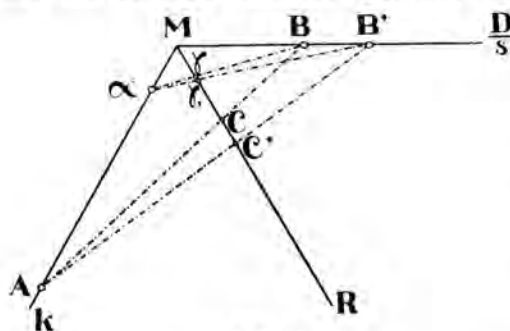


Fig. 2.

greater than MC , the diagram shows that in the case of a crystal that grows in a thoroughly stirred solution, there may be on the margins of a crystal-face a velocity of growing which is slightly greater than that velocity of the central part of that face. This increase of the velocity of growing will be relative

small if k is small relative to $\frac{D}{s}$, whereas $\frac{MC'}{MC}$ approaches to $\epsilon \left(= \frac{MB'}{MB} \right)$

if k becomes great relative to $\frac{D}{s}$ (cf. Fig. 2).

Notwithstanding the above mentioned effect, the faces which are growing slowly have, therefore, the greater chance to remain plane to the margin.

Mathematics. — "*On treating Skew Correlation*". By Prof. M. J. VAN UVEN. (Communicated by Prof. W. KAPTEIJN).

(Communicated at the meeting of September 26, 1925).

Biological Statistics — founded by QUETELET and GALTON — deal with sets of similar individuals (for instance: adult men of the same race, trees of the same kind in the same wood). In whatever point the individuals of such a set may agree with another, yet they are not quite equal; for instance: all the trees of the same kind in the same wood are not equally thick. Nevertheless the similitude of the individuals of such a set is typified i.a. by the fact that the amount of such a measurable characteristic (length of body, thickness of the trunk) varies comparatively little among the individuals, at least so little that it is reasonable to speak of a typical value, a standard value, round which the amounts, found in the different individuals, oscillate.

The quantity the amount of which is measured in the different individuals being denoted by x , and the concrete values observed in determinate individuals being expressed by $\xi_1, \xi_2, \dots, \xi_n$, these ξ_k are partly larger, partly smaller than a certain standard value X , whence the deviations $v_k = \xi_k - X$ turn out to be partly positive, partly negative.

The total number N of individuals being large, the determinate value ξ_k will appear more than once, say Y_k times. This number Y_k is called the *frequency* of ξ_k . Evidently $\sum_{k=1}^n Y_k = N$.

As a rule the frequency Y_k of ξ_k is stated to be larger according as ξ_k differs less from the standard value X , that is to say: according as the absolute value of v_k be less, so that Y_k and ξ_k seem to be functionally related to each other. In a good many cases this relation is stated to be satisfactorily expressed by the GAUSSIAN exponential law of error, viz: Being chosen as standard value the arithmetical mean

$\bar{\xi} = \frac{1}{N} \sum_{k=1}^n Y_k \xi_k$ of the observed values ξ_k , and being formed the differences $u_k = \xi_k - \bar{\xi}$, the deviations from that mean, then the frequency Y_k is proportional to $e^{-h^2 u_k^2}$, where h is a constant, the so-called "modulus of precision", which is connected with the "mean error" $\varepsilon = \sqrt{\overline{u^2}} = \sqrt{\frac{\sum Y_k u_k^2}{N}}$ by the well-known relation $h\varepsilon\sqrt{2} = 1$.

The exponential law, more precisely expressed, runs:

The probability W_a^b , that x is found between a and b , is

$$W_a^b = \frac{h}{\sqrt{\pi}} \int_a^b e^{-h^2(x-\bar{\xi})^2} dx.$$

In this expression there appear besides the limits a and b two independent constants, viz. $\bar{\xi}$ and h . So, to construct the law of error, which is supposed to agree with a given frequency series, these two constants are to be derived from the given quantities $\xi_k, Y_k (k=1, 2 \dots n)$ by means of the relations

$$\bar{\xi} = \frac{\sum_1^n Y_k \xi_k}{N}, \quad h = \frac{1}{\varepsilon \sqrt{2}}, \quad \varepsilon^2 = \overline{u^2} = \frac{\sum_1^n Y_k u_k^2}{N} = \frac{\sum_1^n Y_k (\xi_k - \bar{\xi})^2}{N},$$

Usually the observed ξ_k form an arithmetic progression. The successive values being $\xi_1, \xi_2, \dots, \xi_n$, then

$$\xi_{k+1} - \xi_k = c;$$

c is called the class-interval.

The values ξ_k often being obtained by estimation, and accordingly being rounded results of measuring, the frequency Y_k really expresses that it is stated Y_k times that x is found between $\xi_k - \frac{c}{2}$ and $\xi_k + \frac{c}{2}$, whence the theoretical probability of ξ_k amounts to

$$W_k = \frac{h}{\sqrt{\pi}} \int_{\xi_k - \frac{c}{2}}^{\xi_k + \frac{c}{2}} e^{-h^2(x-\bar{\xi})^2} dx, \quad , \quad , \quad , \quad , \quad , \quad (1)$$

For the given frequency series to agree exactly with this exponential law of error, the relation

$$W_k = \frac{Y_k}{N}$$

must appear to hold good.

Thus by comparing the empirical values of the quotients $\frac{Y_k}{N} = y_k$ (relative frequencies) with the theoretical values W_k , we can examine whether the given frequency series really agrees or not with the "normal" law of frequency.

We are also able to experiment further on this agreement by tests which are the more valuable as they embrace the whole material of observations. They are founded on the following considerations:

1°. Theoretically the mean absolute value of u , viz. $|\overline{u}| = \eta$ must equal $\sqrt{\frac{2}{\pi}} \times \varepsilon$; thus $\eta_{\text{theor.}} = \sqrt{\frac{2}{\pi}} \cdot \varepsilon = 0.79788 \dots \varepsilon$.

2°. Theoretically the mean third power of u must be zero, or $\overline{u^3} = 0$.

3°. Theoretically the mean fourth power of u must equal $3\varepsilon^4$, in other words: $\overline{u^4} = 3\varepsilon^4$.

In order to become independent from the unit, in which x (and so $u = x - \xi$, and ε) is expressed, we form the expressions

$$S = \frac{\overline{u^3}}{\varepsilon^3} \quad \text{and} \quad E = \frac{\overline{u^4}}{\varepsilon^4} - 3,$$

resp. called Skewness and Excess.

Now, for the empirical value of $\eta: \eta_{\text{emp.}} = \frac{\sum Y_k |u_k|}{N}$ there being found a value little different from $\sqrt{\frac{2}{\pi}} \cdot \varepsilon$ and for $S_{\text{emp.}} = \frac{\sum Y_k u_k^3}{N\varepsilon^3}$ and $E_{\text{emp.}} = \frac{\sum Y_k u_k^4}{N\varepsilon^4} - 3$ very small numbers, these statements suggest the idea that the given frequency distribution substantially answers to the normal (exponential) law of frequency, and that the remaining small discrepancies between y_k and W_k may be imputed to accidental perturbations.

In the theory of correlation each individual of a statistical manifoldness is considered with regard to two or more measurable characteristics: x, x', x'', \dots ; for instance: among adult men of the same race: length of body, circumference of the chest, eye distance, \dots ; among trees of the same kind in the same wood: thickness of the trunk, height, volume of the trunk, \dots

Arranging the observed values of x according to ascending magnitude $\xi_1, \xi_2, \dots, \xi_n$ (where usually $\xi_{k+1} - \xi_k = c$ is constant), and, equally, the observed values of x' : $\xi'_1, \xi'_2, \dots, \xi'_n$ (where, as a rule, $\xi'_{l+1} - \xi'_l = c'$), and so on with regard to the other variables, each individual of the manifoldness will then furnish a set $\xi_k, \xi'_l, \xi''_m, \dots$. The number N of the individuals being very large, such a set of concrete measured values will occur more than once, say $Y_{klm\dots}$ times. We should then establish a functional relation between $Y_{klm\dots}$ on one hand and $\xi_k, \xi'_l, \xi''_m, \dots$ on the other.

By expanding the GAUSSIAN exponential law of error to more than one variable, BRAVAIS¹⁾ established a chance formula, according to which the probability $W_{klm\dots}$ of the set $\xi_k, \xi'_l, \xi''_m, \dots$ is proportional to $e^{-f(u_k, u'_l, u''_m, \dots)}$, where $f(u, u', u'', \dots) \equiv A u^2 + B u u' + C u'^2 + D u u'' + E u' u'' + F u''^2 + \dots$ is a positive definite homogeneous quadratic function of the variables

¹⁾ A. BRAVAIS. „Analyse mathématique sur les probabilités des erreurs de situation d'un point". Paris: Mémoires présentés par divers savants à l'Académie royale des sciences de l'Institut de France; T. 9 (1846) p. 255.

$u = \xi - \bar{\xi}$, $u' = \xi' - \bar{\xi}'$, $u'' = \xi'' - \bar{\xi}''$, ... If the coefficients B , D , E , ... of the products uu' , uu'' , $u'u''$, ... are different from zero, we may then conclude that the probability of a certain u , say u' , depends on the accompanying u , u'' , ...; so the quantities x , x' , x'' , ... mutually affect their values, or, in other words, the quantities x , x' , x'' , ... cannot vary independently from each other, or, again: there exists a mutual connection, a "correlation" between them.

Thus: among the trees of the same kind in the same wood, the highest will, in the main, also be the thickest and have the largest volume of trunk.

In the present paper we shall exclusively confine ourselves to two variables, x and x' . In this case the chance formula runs:

$$W_{kl} = \frac{h h' \sqrt{1-\gamma^2}}{\pi} \int_{x=\xi_k-\frac{c}{2}, x'=\xi'_l-\frac{c'}{2}}^{\xi_k+\frac{c}{2}, \xi'_l+\frac{c'}{2}} e^{-(h^2 u^2 - 2\gamma h h' u u' + h'^2 u'^2)} du du'. \quad (2)$$

Taking a determinate value of u' , say u'_i , the average concurring quantity u appears to be $(\bar{u})_i = \gamma \frac{h'}{h} u'_i$. So this average value is proportional to u'_i , whence $(\bar{\xi})_i - \bar{\xi} = \gamma \frac{h'}{h} (\xi'_i - \bar{\xi}')$, that is to say: $(\bar{\xi})_i$ is a linear function of ξ'_i . On account of this property in the above case the connection is called: linear correlation.

Being $u_k = \xi_k - \bar{\xi}$, $u' = \xi'_l - \bar{\xi}'$, the probability formula (2) contains, besides the class-intervals c and c' , which occur in the limits, five constants, viz. the two averages $\bar{\xi}$, $\bar{\xi}'$, the two "moduli" h , h' and the so-called coefficient of correlation γ , the last having always its absolute value ≤ 1 .

If $\gamma > 0$ the correlation is said to be positive, if $\gamma < 0$ to be negative.

Now from (2) follows

$$\mu = \bar{\epsilon^2} = \bar{u^2} = \frac{1}{2h^2(1-\gamma^2)}, \quad \mu' = \bar{\epsilon'^2} = \bar{u'^2} = \frac{1}{2h'^2(1-\gamma^2)}, \quad \lambda = \overline{u u'} = \frac{\gamma}{2h h'(1-\gamma^2)}.$$

Hence the five constants mentioned above may be found empirically from

$$\bar{\xi} = \frac{\sum Y_{kl} \xi_k}{N}, \quad \bar{\xi}' = \frac{\sum Y_{kl} \xi'_l}{N}, \quad \mu = \frac{\sum Y_{kl} u_k^2}{N}, \quad \mu' = \frac{\sum Y_{kl} u_l'^2}{N}, \quad \lambda = \frac{\sum Y_{kl} u_k u'_l}{N},$$

where the sums are taken over k from 1 to n , over l from 1 to n' .

In order to control whether a given two-dimensional frequency scheme ξ_k , ξ'_l , Y_{kl} agrees satisfactorily with the formula (2) or not, we might make some tests, e.g. by making use of the following theoretical relations:

$$\overline{u^3} = 0, \quad \overline{u^2 u'} = 0, \quad \overline{u u'^2} = 0, \quad \overline{u'^3} = 0;$$

$$\overline{u^4} = 3\epsilon^4, \quad \overline{u^3 u'} = 3\gamma \epsilon^3 \epsilon', \quad \overline{u^2 u'^2} = (1+2\gamma^2) \epsilon^2 \epsilon'^2, \quad \overline{u u'^3} = 3\gamma \epsilon \epsilon'^3, \quad \overline{u'^4} = 3\epsilon'^4,$$

where, as above, the notation $\overline{f(u, u')}$ always expresses the average value of $f(u, u')$, so that its empirical value is

$$\{\overline{f(u, u')}\}_{\text{emp.}} = \frac{\sum Y_{kl} f(u_k, u'_l)}{N} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Desiring to get rid of the influence of the units of x and x' (so of u and u' and of ε and ε'), it is preferable to construct the following expressions, which are analogous to the Skewness and the Excess in the case of one variable:

$$S = \frac{\overline{u^3}}{\varepsilon^3}, \quad S_1 = \frac{\overline{u^2 u'}}{\varepsilon^2 \varepsilon'}, \quad S_2 = \frac{\overline{u u'^2}}{\varepsilon \varepsilon'^2}, \quad S' = \frac{\overline{u'^3}}{\varepsilon'^3},$$

$$E = \frac{\overline{u^4}}{\varepsilon^4} - 3, \quad E_1 = \frac{\overline{u^3 u'}}{\varepsilon^3 \varepsilon'} - 3\gamma, \quad E_2 = \frac{\overline{u^2 u'^2}}{\varepsilon^2 \varepsilon'^2} - 1 - 2\gamma^2, \quad E_3 = \frac{\overline{u u'^3}}{\varepsilon \varepsilon'^3} - 3\gamma, \quad E' = \frac{\overline{u'^4}}{\varepsilon'^4} - 3.$$

All these expressions are theoretically equal to zero.

If their empirical values are very small, one may be convinced that the given frequency scheme — apart from accidental perturbations — corresponds to the two-dimensional exponential chance formula (2).

We now return for a moment to the frequency distribution with only one variable.

However often the frequency distribution offered by practice may even be represented by the normal law of distribution, yet it often happens that a given frequency distribution shows deviations from the normal law of distribution too striking and too systematic to be considered a normal distribution accidentally disturbed. On drawing a diagram of such a frequency distribution by plotting an ordinate Y_k above each point ξ_k of the x -axis, it is impossible to draw a normal frequency curve through the points thus obtained, but a skew frequency curve can be drawn.

The investigation of skew frequency curves has already been carried on on all sides. Besides the work of the Biometric school of KARL PEARSON, which aims at deducing a set of formulae giving account numerically for the frequency distributions occurring in practice, no attempts have been wanting to explain the origin of skew frequency distributions. A start has usually been made from the GAUSSIAN normal law of error. Several — among others the Danish astronomer T. N. THIELE¹⁾, the Swedish astronomer C. V. L. CHARLIER²⁾ and the English statistician F. Y. EDGEWORTH³⁾, are especially worth mentioning — in deducing a more

¹⁾ T. N. THIELE. Theory of observations. London 1903. Ch. 8 E. Layton.

²⁾ C. V. L. CHARLIER. Ueber das Fehlergesetz. Arkiv för Matem., Astr., och Fysik Bd. N^o. 8 (1905). Researches into the theory of Probability. Lunds Univ. Årsskrift. N.F. Afd. 2, Bd. 1 N^o. 5, Lund 1906.

³⁾ F. Y. EDGEWORTH. The Law of Error. Transactions of the Cambridge Phil. Soc. Vol. XX (1908), pp. 36 and 113.

general law of error have attached themselves to the methods of LAPLACE and POISSON, broadening the basis of their theory. So the formula

$$e^{-h^2u^2} (A + Bu^3 + Cu^4 + \dots)$$

is established, which is derived by several authors, and is called by CHARLIER: the law of frequency type A. CHARLIER¹⁾ too has deduced quite a different formula (law of frequency type B) starting from the POISSON law of distribution.

It is, however, possible to start from another point of view. Both the above mathematician EDGEWORTH²⁾ and the Dutch astronomer J. C. KAPTEYN³⁾ have pointed to the possibility that the normal law of frequency may be maintained in the most general case, provided it be granted, that the quantity which is normally distributed is not necessarily the 'directly observed quantity x , but rather a function $f(x)$ of this quantity. EDGEWORTH admitted that this function answers to the form $f(x) = A + Bx + Cx^2$. On the other hand KAPTEYN, in his first publication: „Skew Frequency Curves in Biology and Statistics“, has adopted the form $f(x) = (x + \kappa)^q$. The special merits of KAPTEYN are — in my opinion — that he derived the normal distribution of a function of x from very simple suppositions concerning the growth conditions of the x directly observed, viz. by admitting that the elementary increment of x depends on the value already reached.

While both EDGEWORTH and KAPTEYN, in tracing the function $f(x)$ which is really distributed normally, have confined themselves to a concrete type of function, the present writer⁴⁾ has tried, in the 2nd part of KAPTEYN's "Skew Frequency Curves", to determine this function without any premised supposition with regard to its analytic structure. It was only necessary — in order to make the problem determinate — to introduce some simplifying suppositions upon finiteness, continuity, etc. By modifying some of these suppositions it moreover appeared to be possible to account for particular irregularities in several frequency distributions⁵⁾.

Since the method of treating skew correlation (i. e. non-normal frequency schemes of two, or more, variables) suggested in the following paper will depend on the method of analysing skew frequency curves,

1) C. V. L. CHARLIER: Die zweite Form des Fehlergesetzes. Arkiv för Matem., Astron., och Fysik. Bd. 2 N^o. 15 (1905). Researches (see above).

2) F. Y. EDGEWORTH: On the Representation of Statistics by Mathematical Formulae. Journal of the R. Statistical Society. Vol. 61 (1898) p. 670, Vol. 62 (1899) p. 125, p. 373 and p. 534, Vol. 63 (1900) p. 72.

3) J. C. KAPTEYN. Skew Frequency Curves in Biology and Statistics. Groningen, 1903, Noordhoff.

4) J. C. KAPTEYN and M. J. VAN UVEN: Skew Frequency Curves in Biology and Statistics. 2nd Paper. Groningen, 1916, Noordhoff.

5) M. J. VAN UVEN. Skew Frequency Curves. These Proceedings 19, p. 670.

last mentioned, this method will be sketched here in its principal outlines, referring the reader for further details to the original paper.

Given the frequency scheme ξ_k, Y_k ($\sum_1^n Y_k = N$), the meaning is, that Y_k values of x lie between $\xi_k - \frac{c}{2}$ and $\xi_k + \frac{c}{2}$, or, putting

$$\xi_k + \frac{c}{2} = x_k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

between x_{k-1} and x_k .

So, with $Y_1 + Y_2 + \dots + Y_k = \sum_{i=1}^k Y_i$ individuals x lies beneath x_k .

The theoretical lower limit x_0 ought not to be equal to $\xi_1 - \frac{c}{2}$. but may be smaller, since the theoretical frequencies may sink beneath the empirical minimum value 1. For the same reason the theoretical upper limit x_n may surpass $\xi_n + \frac{c}{2}$.

We next consider a function $z = f(x)$ normally distributed round the mean 0 and unimodular (i. e. with $h = 1$), and require that the corresponding intervals $x_0 \rightarrow x_k$ and $z_0 = f(x_0) \rightarrow z_k = f(x_k)$ be equally probable.

Besides, we admit — as a simplifying supposition — that the (unimodular) variable z is a continuous, univalent, ever increasing function of x . Then z_0 is the theoretical lower limit of the variable z normally distributed, thus $z_0 = -\infty$; likewise we have $z_n = +\infty$. So the z_k conjugate to x_k is determined by

$$p_k = \frac{Y_1 + Y_2 + \dots + Y_k}{N} = \frac{\sum_{i=1}^k Y_i}{N} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{z_k} e^{-z^2} dz = \Theta(z_k) \quad . \quad . \quad (5)$$

The values x_0 and x_n , conjugate to $z_0 = -\infty$ and $z_n = +\infty$ being indeterminate, we obtain $n-1$ equations $p_k = \Theta(z_k)$ ($k=1, 2, \dots, n-1$), thus $n-1$ pairs $(x_1, z_1), (x_2, z_2) \dots (x_{n-1}, z_{n-1})$. So $n-1$ values of the function $z = f(x)$ are known.

Representing the pairs (x, z) by the coordinates x, z , the problem, translated into geometrical language, runs: to draw a (curve) line through $n-1$ points.

Hence the problem proposed is indeterminate in a high degree. Nevertheless it is possible in a good many cases to draw a simple line (corresponding to a simple function $z = f(x)$) through these points.

Then the analytical expression of the curve is a suitable solution of the function required. In choosing $f(x)$ we also have particularly in mind the obtaining of a simple form for the so-called "reaction function"

$\eta = 1 : \frac{df(x)}{dx}$. If, in particular, the $n-1$ points lie in a straight line, we

may conclude from it that the given frequency distribution is a normal one. So this method furnishes a criterion for the being normal of a frequency distribution.

Likewise the frequency scheme of a set of two variables often shows deviations from the ideal distribution (according to (2)) so striking, that these deviations cannot reasonably be imputed to accidental perturbations of a linear correlation scheme.

On drawing a spatial diagram of such a non-normal two-dimensional frequency distribution by plotting above each point (ξ_k, ξ'_l) of the (x, x') -plane a third coordinate Y_{kl} , it is impossible to lay a normal frequency surface through these points, but a "skew surface" can be put.

The spine of the normal frequency surface having a rectilinear projection on the (x, x') -plane, the spine of such a skew frequency surface has a curvilinear projection on the (x, x') -plane. In this case the squares of the frequency table which contain the highest frequencies, lie in a curved row; hence we introduce the denomination "skew correlation".

Investigations on skew correlation are comparatively rare. An important one is due to N. R. JØRGENSEN¹⁾, who in his paper „Undersøgelser over Frequensflader of Korrelation", treats correlation of two variables, making use of CHARLIER's two types A and B.

The aim of this paper is to analyse skew correlation of two variables, x and x' according to the principle of EDGEWORTH-KAPTEYN, by reducing it to a linear correlation between two functions t and t' , which in general may depend on both x and x' .

$x \backslash x'$	ξ'_1	ξ'_2		ξ'_l		$\xi'_{n'}$
ξ_1	Y_{11}	Y_{12}		Y_{1l}		$Y_{1n'}$
ξ_2	Y_{21}	Y_{22}		Y_{2l}		$Y_{2n'}$
ξ_k	Y_{k1}	Y_{k2}		Y_{kl}		$Y_{kn'}$
ξ_n	Y_{n1}	Y_{n2}		Y_{nl}		$Y_{nn'}$

As we have already pointed out, we shall make use of the method, which in the case of one variable has given us an idea of the function $z = f(x)$ normally spread.

We may formulate the data in this way:

Both quantities x and x' are observed with each of N individuals. For x are found n ascending values: $\xi_1, \xi_2, \dots, \xi_k, \dots, \xi_n$, for x' n' ascending values: $\xi'_1, \xi'_2, \dots, \xi'_l, \dots, \xi'_{n'}$. The combination

¹⁾ N. R. JØRGENSEN. Undersøgelser over Frequensflader og Korrelation. København, 1916. Arn. Busck.

ξ_k, ξ'_l is stated Y_{kl} times. These frequencies are clearly summarized by the frequency scheme; of the variable x the ascending values are tabulated downwards, of the variable x' the ascending values run to the right.

Usually the values $\xi_1, \xi_2, \dots, \xi_k, \dots, \xi_n$ increase by the same interval c (so that $\xi_{k+1} = \xi_k + c$), the values $\xi'_1, \xi'_2, \dots, \xi'_l, \dots, \xi'_n$, by the same interval c' (so that $\xi'_{l+1} = \xi'_l + c'$).

By denoting the rounded numbers ξ_k, ξ'_l we really mean that x is found between $\xi_k - \frac{c}{2}$ and $\xi_k + \frac{c}{2}$, and that x' lies between $\xi'_l - \frac{c'}{2}$ and $\xi'_l + \frac{c'}{2}$.

So, representing x and x' by rectangular coordinates, the combination (ξ_k, ξ'_l) indicates, that the "point" (x, x') lies within a rectangle the sides of which are $x = \xi_k - \frac{c}{2}, x = \xi_k + \frac{c}{2}, x' = \xi'_l - \frac{c'}{2}$ and $x' = \xi'_l + \frac{c'}{2}$. Hence Y_{kl} points (x, x') are found within this rectangle. Only this proposition must be less positive at the extreme limits.

If $D(x, x')$ be the theoretical probability function, so that the chance that the point (x, x') lies within the infinitesimal domain $(\xi, \xi + dx, \xi', \xi' + dx')$ is

$$dW = D(\xi, \xi') dx dx',$$

then we have for the frequency Y_{kl} corresponding to the probability

$$y_{kl} = \frac{Y_{kl}}{N}$$

$$Y_{kl} = N \cdot y_{kl} = N \cdot \int_{x=\xi_k-\frac{c}{2}}^{x=\xi_k+\frac{c}{2}} \int_{x'=\xi'_l-\frac{c'}{2}}^{x'=\xi'_l+\frac{c'}{2}} D(x, x') \cdot dx \cdot dx' = N \int_{x=\xi_k-\frac{c}{2}}^{x=\xi_k+\frac{c}{2}} \int_{x'=\xi'_l-\frac{c'}{2}}^{x'=\xi'_l+\frac{c'}{2}} dW. \quad (6)$$

We have now to bring the probability function $D(x, x')$ into a form, which corresponds to a positive linear correlation between two unimodular functions $t(x, x')$ and $t'(x, x')$; that is to say; to determine two functions t and t' in such a way that

$$D(x, x') = \frac{\sqrt{1-\gamma^2}}{\pi} e^{-(t^2-2\gamma t t'+t'^2)} \frac{\partial(t, t')}{\partial(x, x')}. \quad (7)$$

being

$$\frac{\partial(t, t')}{\partial(x, x')} = \begin{vmatrix} \frac{\partial t}{\partial x} & \frac{\partial t}{\partial x'} \\ \frac{\partial t'}{\partial x} & \frac{\partial t'}{\partial x'} \end{vmatrix}$$

and γ the coefficient of correlation ($0 \leq \gamma \leq 1$).

It is easy to understand, and, moreover, it will appear from the following reasoning that the problem, put in full generality, is indeterminate.

We can therefore only succeed in solving it by introducing limiting (if possible simplifying) conditions.

We shall next transform the infinitesimal probability

$$dW = \frac{\sqrt{1-\gamma^2}}{\pi} e^{-(\alpha-2\gamma t t' + t'^2)} \frac{\partial(t, t')}{\partial(x, x')} \cdot dx \cdot dx' \rightarrow \frac{\sqrt{1-\gamma^2}}{\pi} e^{-(\alpha-2\gamma t t' + t'^2)} dt \cdot dt'$$

into a canonic form. This may be done in several ways:

1°. Putting

$$\sqrt{1-\gamma^2} \cdot t = z, \quad t' - \gamma t = \zeta,$$

so that

$$\frac{\partial(t, t')}{\partial(z, \zeta)} = \frac{1}{\sqrt{1-\gamma^2}},$$

we find

$$dW = \frac{1}{\pi} e^{-(z^2 + \zeta^2)} dz \cdot d\zeta = \frac{e^{-z^2}}{\sqrt{\pi}} dz \cdot \frac{e^{-\zeta^2}}{\sqrt{\pi}} d\zeta.$$

or, introducing

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^z e^{-v^2} dv = \Theta(z) = s, \quad \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\zeta} e^{-v^2} dv = \Theta(\zeta) = \sigma \quad (8)$$

$$dW = ds \cdot d\sigma \quad (I)$$

2°. Putting

$$\sqrt{1-\gamma^2} \cdot t' = z', \quad t - \gamma t' = \zeta',$$

we obtain

$$dW = \frac{1}{\pi} e^{-(z'^2 + \zeta'^2)} dz' \cdot d\zeta' = \frac{e^{-z'^2}}{\sqrt{\pi}} dz' \cdot \frac{e^{-\zeta'^2}}{\sqrt{\pi}} d\zeta',$$

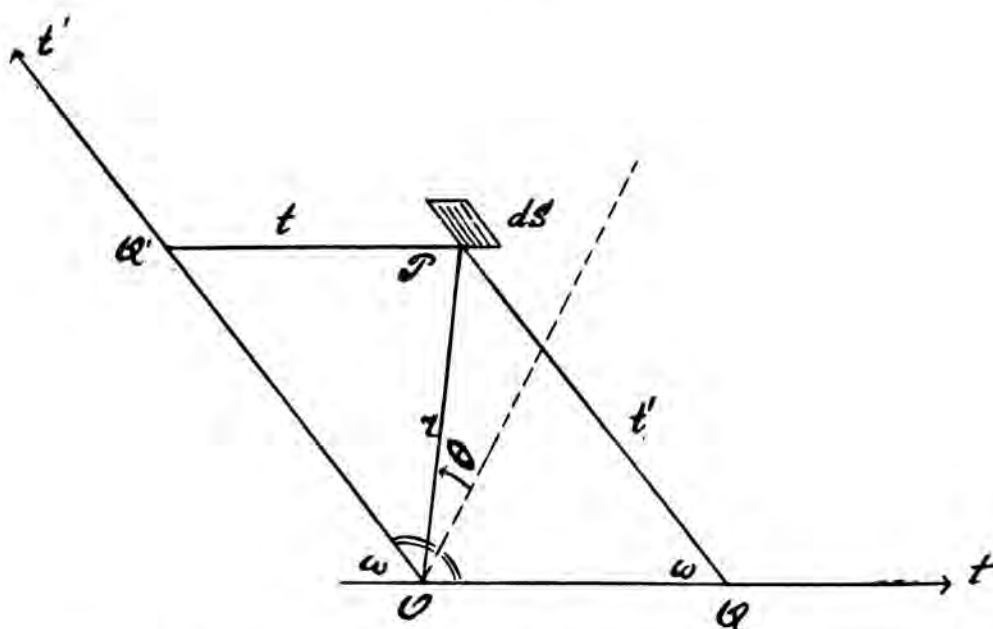
or, introducing

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{z'} e^{-v^2} dv = \Theta(z') = s', \quad \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\zeta'} e^{-v^2} dv = \Theta(\zeta') = \sigma',$$

$$dW = ds' \cdot d\sigma' \quad (II)$$

3. A third manner suggests itself by introducing t and t' as non-rectangular coordinates, the positive axes of which include an angle $\pi - \omega$, ω being given by

$$\cos \omega = \gamma.$$



Denoting the radius vector OP of the point (t, t') by r , we have

$$r^2 = t^2 - 2 \cos \omega \cdot t t' + t'^2 = t^2 - 2\gamma t t' + t'^2.$$

The element of area dS , i. e. the elementary parallelogram on dt, dt' , with included angle $\pi - \omega$, is found to be

$$dS = dt \cdot dt' \cdot \sin(\pi - \omega) = \sin \omega \cdot dt \cdot dt' = \sqrt{1 - \gamma^2} \cdot dt \cdot dt';$$

whence

$$dW = \frac{e^{-r^2}}{\pi} dS.$$

We next pass on to polar coordinates. The polar axis of the argument θ may coincide with the bisector of the positive axes (t) and (t') .

Then from

$$\angle POQ = \theta + \frac{\pi - \omega}{2} = \frac{\pi}{2} - \left(\frac{\omega}{2} - \theta \right),$$

$$\angle OPQ = \pi - \omega - \angle POQ = \frac{\pi}{2} - \left(\frac{\omega}{2} + \theta \right),$$

results

$$\frac{t}{\cos \left(\frac{\omega}{2} + \theta \right)} = \frac{t'}{\cos \left(\frac{\omega}{2} - \theta \right)} = \frac{r}{\sin \omega}$$

or

$$t = \frac{r}{\sin \omega} \cos \left(\frac{\omega}{2} + \theta \right), \quad t' = \frac{r}{\sin \omega} \cos \left(\frac{\omega}{2} - \theta \right).$$

Inversely from

$$t' - t = \frac{2r}{\sin \omega} \sin \frac{\omega}{2} \sin \theta = \frac{r \sin \theta}{\cos \frac{\omega}{2}} \quad \text{and} \quad t' + t = \frac{2r}{\sin \omega} \cos \frac{\omega}{2} \cos \theta = \frac{r \cos \theta}{\sin \frac{\omega}{2}}$$

we derive

$$\operatorname{tg} \theta = \frac{t' - t}{t' + t} \cot \frac{\omega}{2} = \frac{t' - t}{t' + t} \sqrt{\frac{1 + \gamma}{1 - \gamma}},$$

r being found from

$$r^2 = t^2 - 2\gamma t t' + t'^2.$$

At present the element of area comes out at

$$dS = r \cdot dr \cdot d\theta,$$

whence

$$dW = \frac{e^{-r^2}}{\pi} r \cdot dr \cdot d\theta,$$

or, putting

$$2 \int_0^r e^{-v^2} v \, dv = 1 - e^{-r^2} = \varphi, \quad \frac{\theta}{2\pi} = \psi,$$

$$dW = d\varphi \cdot d\psi \quad \text{. (III)}$$

So we have separated the two-dimensional differential dW in three different ways into a product of two one-dimensional differentials.

These three products not being equal to each other, the three differentials dW are no more equal. Yet each of them may be used as two-dimensional element of the chance W .

We meet the same state of things in expressing the element of area in different systems of coordinates. x, x' being a system of rectangular coordinates, r, θ a system of polar coordinates, we may note for the areal increment both $dx \cdot dx'$ and $r \cdot dr \cdot d\theta$, without being $dx \cdot dx' = r \cdot dr \cdot d\theta$.

We shall indicate this equivalency in representing the two-dimensional differential in a double integral by \rightleftharpoons . Thus $dx \cdot dx' \rightleftharpoons r \cdot dr \cdot d\theta$. The meaning of the latter is therefore

$$\frac{\partial (x, x')}{\partial (r, \theta)} = r.$$

So, from

$$dW = D(x, x') \cdot dx \cdot dx' \rightleftharpoons ds \cdot d\sigma \rightleftharpoons ds' \cdot d\sigma' \rightleftharpoons d\varphi \cdot d\psi$$

may be concluded

$$D(x, x') = \frac{\partial (s, \sigma)}{\partial (x, x')} = \frac{\partial (s', \sigma')}{\partial (x, x')} = \frac{\partial (\varphi, \psi)}{\partial (x, x')}.$$

If the frequency distribution were known to the minutest details, the function $D(x, x')$ would be wholly known in its dependency on x and x' .

So the frequency scheme can by no means furnish more than the function $D(x, x')$.

Admitting $D(x, x')$ to be known, the equation

$$\frac{\partial(s, \sigma)}{\partial(x, x')} = \frac{\partial s}{\partial x} \cdot \frac{\partial \sigma}{\partial x'} - \frac{\partial s}{\partial x'} \cdot \frac{\partial \sigma}{\partial x} = D(x, x'),$$

allows us still to dispose arbitrarily of one of the functions s and σ (save its being limited to the interval between 0 and 1). If, for example, s is chosen, then σ derives from the above differential equation; hence in determining σ , a certain freedom is still left.

Having so obtained s and σ , the functions z and ζ are known too. Then we must yet assume a value of γ for determining t and t' .

A similar reasoning may be held concerning s' and σ' , likewise with regard to φ and ψ . An unimodular set t, t' once being fixed, it is easy to derive a whole group of new unimodular sets t, t' , submitting t, t' to the transformation group leaving invariant the form $r^2 = t^2 - 2\gamma tt' + t'^2$ and the areal increment.

These transformations, interpreted in the above non-rectangular coordinates, just are the rotations about the origin, the point $P(r, \theta)$ being carried to the point $\mathfrak{P}(r, \vartheta)$ ($\vartheta = \theta + \tau$).

So we find

$$\frac{t}{\cos\left(\frac{\omega}{2} + \vartheta\right)} = \frac{t'}{\cos\left(\frac{\omega}{2} - \vartheta\right)} = \frac{r}{\sin \omega} \quad (\cos \omega = \gamma)$$

or

$$\frac{t}{\cos\left(\frac{\omega}{2} + \theta + \tau\right)} = \frac{t'}{\cos\left(\frac{\omega}{2} - \theta - \tau\right)} = \frac{r}{\sin \omega},$$

whence, by eliminating r and θ ,

$$T \begin{cases} t = \frac{\sin(\tau + \omega)}{\sin \omega} t - \frac{\sin \tau}{\sin \omega} t' \\ t' = \frac{\sin \tau}{\sin \omega} t - \frac{\sin(\tau - \omega)}{\sin \omega} t' \end{cases} \quad (9)$$

Thus: the functions t, t' may occasionally be transformed by the continuous group T having one parameter. Further we may apply the reflection $S\left(\frac{t=t'}{t'=t}\right)$ against the internal bisector of $\angle(tOt')$, likewise the reflection $S'\left(\frac{t=-t'}{t'=-t}\right)$ against the external bisector of $\angle(tOt')$, hence also their product $SS'\left(\frac{t=-t}{t'=-t'}\right)$ which effects a rotation of π about O . This rotation being also furnished by a transformation T

(with $\tau = \pi$), we may build up all the transformations considered out of the continuous group T and the finite (cyclic) group S of order 2.

In future we shall not make any use of this reflecting transformation, which only implies a change of names.

Thus it has been proved that — even if the function $D(x, x')$ were completely known — it is impossible to determine the functions t and t' without adding new arbitrary data. The question is now to choose these data in such a way that the solution should be of some practical value.

The following example shows clearly that "to establish a linear correlation" becomes an indeterminate problem as soon as functions of both variables are admitted.

If between two quantities t and t' there exists linear correlation, with the unimodular formula

$$dW = \frac{\sqrt{1-\gamma^2}}{\pi} e^{-(t^2 - 2\gamma t t' + t'^2)} dt \cdot dt',$$

then by substituting

$$t = \frac{T - T'}{\sqrt{2}}, \quad t' = \frac{T + T'}{\sqrt{2}}, \quad dt \cdot dt' \rightleftharpoons dT \cdot dT'$$

we obtain

$$\begin{aligned} dW &= \frac{\sqrt{1-\gamma^2}}{\pi} e^{-1/2[(T-T')^2 - 2\gamma(T^2 - T'^2) + (T+T')^2]} dT \cdot dT' = \\ &= \frac{\sqrt{1-\gamma^2}}{\pi} e^{-[(1-\gamma)T^2 + (1+\gamma)T'^2]} dT \cdot dT'. \end{aligned}$$

Hence between the new (not unimodular) variables T and T' there exists linear correlation with a coefficient of correlation zero; that is to say: T and T' are wholly independent. In this case no one will prefer the variables T and T' to t and t' , as the really existing correlation between the original variables t and t' suggests a dependence between these variables. It is just this property of suggesting a certain dependence that makes correlation so important.

If the original variables x and x' are not linearly correlated, the frequency scheme yet pointing to some dependence, we will firstly try to establish a linear correlation between a function t only of x , and a function t' only of x' . Should this prove to be impossible, we shall try to obtain at least one variable t (resp. t') depending on only one variable x (resp. x'). If this attempt also fails, we shall try to introduce one function t (resp. t') which varies but little by the influence of x' (resp. x), and, at the same time, to obtain a correlation as large as possible, since just a high degree of correlation in interpretation will give interesting results. Moreover it will appear from the following reasoning that, though we have found two functions of x and x' linearly correlated, we shall yet continue our investigations in order to obtain functions giving more palpable results in biological interpretation; at the same time we

shall be mindful of raising — as far as circumstances allow — the degree of correlation (measured by the value of the coefficient of correlation).

In discussing the canonic forms we have taken this point of view that $D(x, x')$ is fully known as function of x and x' . But in reality it is not so. The real data are several values of the integral

$$\int_{\xi_k - \frac{c}{2}}^{\xi_k + \frac{c}{2}} \int_{\xi'_l - \frac{c'}{2}}^{\xi'_l + \frac{c'}{2}} D \cdot dx \cdot dx' = y_{kl} = \frac{Y_{kl}}{N} \quad \dots \quad (6^a)$$

Thus we shall have to resort to these integral-values.

As we always have to operate with the class-limits, we shall introduce them into the notation. So we put

$$\xi_k + \frac{c}{2} = x_k, \quad \xi'_l + \frac{c'}{2} = x'_l, \quad \dots \quad (10)$$

hence

$$\xi_k - \frac{c}{2} = x_{k-1}, \quad \xi'_l - \frac{c'}{2} = x'_{l-1}.$$

It will be easy furtheron to designate the class-centres ξ_k, ξ'_l by broken indices. So we put at the same time

$$\xi_k = x_{k-1/2}, \quad \xi'_l = x'_{l-1/2} \quad \dots \quad (10^a)$$

The lower limit x_0 (resp. x'_0) need not coincide with $\xi_1 - \frac{c}{2}$,
 (resp. $\xi'_1 - \frac{c'}{2}$), nor the upper limit x_n (resp. $x'_{n'}$) with $\xi_n + \frac{c}{2}$,
 (resp. $\xi'_{n'} + \frac{c'}{2}$).

Hence

$$\int_{x_{k-1}}^{x_k} \int_{x'_{l-1}}^{x'_l} D(x, x') \cdot dx \cdot dx' = \frac{Y_{kl}}{N} \quad \dots \quad (6^b)$$

In order to arrive at an exponential function of the form $e^{-(r^2 - 2\gamma r r' + r'^2)}$ — starting from this rectangular integral —, we shall next examine the case of linear correlation.

Chemistry. — „Equilibria in systems in which phases, separated by a semipermeable membrane." XI. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of September 26, 1925).

Systems in which a substance different to water diffuses through the membrane.

Although the preceding considerations are valid generally, also when substance different to water is diffusing through the membrane, yet we shall consider a single case more in detail. Firstly we take the osmotic equilibrium

$$E = L_1 | L_2 \dots \dots \dots (1)$$

of two liquids; we shall represent the composition of L_1 by $x_1X + y_1Y \dots \dots + (1 - x_1 - y_1 \dots) W$, that of L_2 by substituting the index 1 by 2. If water (W) is the diffusing substance, then, when δn quantities of water diffuse from L_2 towards L_1 , the thermodynamical potential of L_1 increases with:

$$(\varphi_1)_W \cdot \delta n \text{ in which } (\varphi_1)_W = \left(\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \right)_1,$$

that of L_2 decreases with:

$$(\varphi_2)_W \cdot \delta n \text{ in which } (\varphi_2)_W = \left(\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \right)_2$$

and that of the total system increases, therefore, with:

$$[(\varphi_1)_W - (\varphi_2)_W] \cdot \delta n \dots \dots \dots (2)$$

If the component X is the diffusing substance, then, when δn quantities of X diffuse from L_2 towards L_1 , the thermodynamical potential of L_1 increases with:

$$(\varphi_1)_X \cdot \delta n \text{ in which } (\varphi_1)_X = \left[\zeta + (1 - x) \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \right]_1$$

that of L_2 decreases with:

$$(\varphi_2)_X \cdot \delta n \text{ in which } (\varphi_2)_X = \left[\zeta + (1 - x) \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \right]_2$$

so that the thermodynamical potential of the total system increases with:

$$[(\varphi_1)_X - (\varphi_2)_X] \cdot \delta n \dots \dots \dots (3)$$

If other components diffuse, corresponding equations are valid then, of course.

Previously we have seen that (2) defines in which direction the water diffuses in system (1); viz. the water goes towards that liquid which has the smallest φ . For that reason we have said that $(\varphi_1)_W$ and $(\varphi_2)_W$ define

the osmotic water-attraction (O.W.A.) of the liquids L_1 and L_2 and that the O.W.A. increases with decreasing φ . The same is also true for the osmose of the substance X .

If viz. $(\varphi_1)_X = (\varphi_2)_X$ then (3) is zero for all values of δn ; consequently system (1) is in osmotic equilibrium with respect to the substance X ; we may say, therefore, that the O.X.A. (osmotic X -attraction) of both liquids is equal.

If $(\varphi_1)_X > (\varphi_2)_X$ then, as the thermodynamical potential of the total system can become only smaller, δn in (3) must be negative; consequently X diffuses from L_1 towards L_2 . We may say, therefore, that the O.X.A. of liquid L_2 is greater than that of L_1 .

If $(\varphi_1)_X < (\varphi_2)_X$ then in (3) δn must be taken positive; consequently X diffuses from L_2 towards L_1 . Now we may say, therefore, that the O.X.A. of liquid L_1 is greater than that of L_2 .

Consequently, as the substance X diffuses towards that liquid, which has the smallest φ , we may say, therefore, that φ defines the O.X.A. of the liquid and that the O.X.A. of a liquid increases with decreasing φ .

If in the osmotic equilibrium:

$$E = L_1 L_2 \dots \dots \dots (4)$$

in which L and L_1 are two ternary substances, the component Y is the diffusing substance, then must be satisfied:

$$z - x \frac{\partial z}{\partial x} + (1 - y) \frac{\partial z}{\partial y} = \left[z - x \frac{\partial z}{\partial x} + (1 - y) \frac{\partial z}{\partial y} \right]_1 \dots \dots (5)$$

If we take in (4) a definite liquid for L_1 f.i. L_p , represented in fig. 1 by point p , then the second part of (5) has a definite value. The liquids L , which are isotonic with L_p with respect to the substance Y , are represented, therefore, by a curve $p_1 p p_2$ going through the point p . Consequently this curve is an isotonic curve with respect to the diffusing substance Y ; therefore, all liquids of those curves have the same O.Y.A. (osmotic Y -attraction). We shall call the isotonic curves with respect to the substance W the „isotonic W -curves” and those with respect to the substance Y the „isotonic Y -curves”.

If we take in (4) for L_1 the liquid L_q , represented by point q (fig. 1), then all liquids which are isotonic with L_q with respect to Y , are represented by a curve $q_1 q q_2$. All liquids of this curve have the same O.Y.A. therefore.

The same is true for the isotonic Y -curves, which go through other points f.i. through r or s .

Consequently all liquids of curve $p_1 p p_2$ are isotonic with respect to the substance Y ; the same is true for all liquids of curve $q_1 q q_2$, etc. Liquids of different curves are not isotonic, however, f.i. liquid p not with q or with r_1 or with s_2 etc.

In Communication II we have deduced several properties of the isotonic W -curves; they are true also for the isotonic Y -curves. Consequently we have:

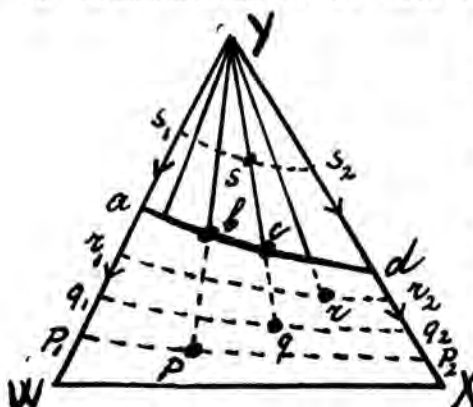


Fig. 1.

1. Each isotonic Y -curve has two ends; the one is situated on the side WY , the other on the side XY of the triangle.

2. Each straight line, drawn through the point Y , intersects the isotonic Y -curve in one point only.

3. Two different isotonic curves never can intersect or touch one another.

4. The isotonic Y -curves are straight lines in the vicinity of the point Y .

5. The O.Y.A. is equal in all liquids of an isotonic Y -curve; it is greater, however, the further this curve is remoted from point Y .

We have deduced the properties of the isotonic W -curves in Communication II with the aid of the ζ -surface; in exactly the same way follow the properties of the isotonic Y -curves, mentioned above. Of course they may be deduced also in another way. The O.Y.A. of a liquid L_q is viz. defined by:

$$\varphi = \left[\zeta - x \frac{\partial \zeta}{\partial x} + (1-y) \frac{\partial \zeta}{\partial y} \right]_q \quad (6)$$

The O.Y.A. of a liquid L'_q , the composition of which differs infinitely little from that of L_q is, therefore

$$\varphi' = \varphi + \Delta\varphi = \varphi + \frac{\partial \varphi}{\partial x} \Delta x + \frac{\partial \varphi}{\partial y} \Delta y \quad (7)$$

or:

$$\Delta\varphi = [-rx + (1-y)s]_q \Delta x + [-sx + (1-y)t]_q \Delta y \quad (8)$$

Of all liquids L'_q which differ infinitely little from L_q we now take that liquid which arises from L_q by solution of a little Y . If δn quantities of Y dissolve in one quantity of L_q , then we have:

$$\Delta x = -\frac{x \cdot \delta n}{1 + \delta n} = -x \cdot \delta n \quad \Delta y = \frac{(1-y) \cdot \delta n}{1 + \delta n} = (1-y) \cdot \delta n \quad (9)$$

so that (8) passes into:

$$\Delta\varphi = [x^2r - 2x(1-y)s + (1-y)^2t] \cdot \delta n \quad (10)$$

The stability requires that the coefficient of δn is positive; consequently $\Delta\varphi$ is also positive for positive values of δn . With solution of Y in the liquid L_q the φ of this liquid increases therefore and its O.Y.A. decreases.

In a similar way we may deduce the general rule:

if a little of a substance dissolves in a liquid, then its osmotic attraction with respect to this substance becomes smaller.

As is already said above, this rule is true, however, only for stable liquids. Later we shall see in systems, in which dimixtion into two or more liquids can occur, that this rule is valid no more for liquids, which are unstable, in itself.

Hence follows, in accordance with the rule, mentioned above sub 5, that the O.Y.A. of liquids of curve $q_1 q q_2$ is greater than that of curve $r_1 r r_2$ and smaller than that of curve $p_1 p p_2$. Consequently the O.Y.A. increases in the direction of the arrows, drawn in fig. 1 on the sides YW and YX.

We now assume that the diffusing substance Y can occur as solid phase; its saturation-curve is represented in fig. 1 by $abcd$. Consequently this is defined by

$$\zeta - x \frac{\partial \zeta}{\partial x} + (1-y) \frac{\partial \zeta}{\partial y} = \zeta_y \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which ζ_y represents the thermodynamical potential of the solid substance Y. As the O.Y.A. of an arbitrary liquid L_q is defined by (6), it follows from (11) that all liquids of curve $abcd$ have the same O.Y.A. This is in accordance with the rule, deduced in Communication II.

All liquids, which are saturated with a solid substance, are isotonic with respect to this substance.

The saturation-curve $abcd$ in fig. 1 is an isotonic Y-curve therefore; the isotonic Y-curves, in the vicinity of curve $abcd$, must have, therefore, a corresponding form.

Consequently the isotonic curves can have several forms, just as the saturation-curves. Let us take f.i. the saturation-curve $wcdv$ of the solid substance Y in fig. 3 Comm. III. We can represent the equilibria which occur at 4°5 in the system water + alcohol + nitril of succinic acid¹⁾ schematically by this figure, if W is water, X alcohol and Y the nitril of succinic acid. The isotonic curves of nitril of succinic acid will have in the vicinity of curve $wcdv$ a similar form with two points of inflexion.

Above we have seen that the O.Y.A. of the liquids of an isotonic Y-curve is greater, the further those curves are remoted from the point Y. We now see from fig. 1 that an unsaturated solution has a greater O.Y.A. and a supersaturated solution has a smaller O.Y.A. than a solution saturated with Y. This is in accordance with the meaning of: saturated, unsaturated and supersaturated solution.

We now take the osmotic system:

$$L_p \xleftarrow{\quad} L_c \quad \text{fig. 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

¹⁾ F. A. H. SCHREINEMAKERS, Zeitschr. f. Phys. Chem. 27, 144 (1898).

in which, as according to fig. 1, L_p has a greater O.Y.A. than L_r , the substance Y shall diffuse in the direction of the arrow. Consequently in fig. 1 L_p shifts from point p along the line pY towards Y and L_r from point r along the line Yr away from Y . The diffusion of the substance Y continues, till both liquids reach a same isotonic Y -curve f.i. curve $q_1 q q_2$.

In the osmotic system:

$$L_p \xleftarrow{\quad} Y + L_c \quad \text{fig. 1} \quad (13)$$

the substance Y diffuses in the direction of the arrow, as follows from fig. 1. Now is formed one of the osmotic equilibria:

$$E = L_b \mid Y + L_c . . . (14^a) \quad E = L'_p \mid L'_c (14^b)$$

If viz. a sufficient quantity of solid Y is present, then L_p of (13) passes into the saturated liquid L_b of (14^a); if in (13) there is too little solid Y , then arise the two unsaturated liquids of (14^b); if both liquids are situated f.i. on the isotonic curve $r_1 r r_2$ then L'_p is represented by the point of intersection of this curve with the line pY and L'_c by the point of intersection of this curve with the line Yc .

Consequently the disappearance of the solid substance Y from (13) when passing into (14^b) is here a consequence of the diffusion of the substance Y itself and not, as we have seen several times in the previous communications, a consequence of diffusion of water.

If we assume that the solid substance Y forms a hydrate H , then we may represent the saturation-curve of H by curve $wcdv$ of fig. 1 Communication IV. The dotted curves of this figure are isotonic W -curves. We have called in this Communication IV point w the finishing-point of this curve rich in water and point v the point poor in water. Then we have found the rule:

The O.W.A. of a liquid of a saturation-curve of a hydrate is greater, the further this liquid is remoted from the finishing-point of this curve rich in water.

Consequently the O.W.A. of the liquids must increase in the direction of the arrows along this curve. We may call point w the finishing-point of curve $wcdv$ poor in Y and point v the point rich in Y . Then we find the rule:

the O.Y.A. of the liquids of a saturation-curve of a hydrate of Y is greater according this liquid being situated further from the finishing-point of this curve rich in Y .

Consequently we have to give the opposite direction to the arrows in fig. 1. Comm. IV.

Of course the isotonic Y -curves have quite another proceeding than the isotonic W -curves, drawn in the figure; we have to imagine the

points m n and o , which we shall call now m_1 n_1 and o_1 , to be situated on the side YX . Then point o_1 is situated the closest to Y , point m_1 the farthest from Y . Drawing this curve we must bear in mind the rule, already previously deduced:

an isotonic curve and a saturation-curve are situated in the vicinity of their point of intersection either both within the conjugation-angle or both within the supplement-angle; if one of those curves touches the one leg of the angle, then the other curve touches the other leg.

In point c of fig. 1 Comm. IV the conjugation-angle is HcY ; the saturation-curve is situated out of this angle, consequently within the supplement-angle; the isotonic Y -curve going through point c must, therefore, be situated also within this angle. If we imagine to be drawn from Y to curve $wcdv$ a tangent, which touches this curve in point r (not drawn) then HrY is the conjugation-angle. As the saturation-curve touches the leg rY , the isotonic curve must touch, therefore, the leg rH .

In the osmotic system:

$$L_b \xleftarrow{\quad} L_d \quad \text{fig. 1 Comm. IV} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

L_b has a greater O.Y.A. than L_d ; consequently the substance Y diffuses in the direction of the arrow in (15). Therefore liquid L_b shall separate solid H and pass into another liquid of the saturation-curve, f. i. into L_c . Then liquid L_d passes into an unsaturated liquid L'_d , which is represented by the point of intersection of the line Yd with the isotonic Y -curve $n'cn_1$ going through point c . Consequently system (15) passes into the osmotic equilibrium:

$$E = H + L_c \mid L'_d \quad \text{fig. 1 Comm. IV} \quad . \quad . \quad . \quad (16)$$

The complex of the liquids L_b and L_d of (15) is represented by a point s on the line bd , not-drawn in the figure. As the quantities of the substances in the total system do not change by the diffusion, the complex of system (16) must be represented also by this point s . The complex $H + L_c$ is represented by a point on the line Hc , which we shall call c' ; liquid L'_d is situated in the point of intersection d' (not-drawn) of line Yd and the isotonic Y -curve going through c . Consequently the line $c'd'$ must go through the point s .

In the osmotic system:

$$L_b \xleftarrow{\quad} L_f \quad \text{fig. 1 Comm. IV} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

the substance Y diffuses from L_f towards L_b , as L_b has a greater O.Y.A. than L_f . Both liquids now pass with separation of the hydrate H into a liquid of curve $wcdv$ situated between b and f . If the complex of the two liquids in (17) is situated f. i. on the line Hd , then (17) passes into:

$$E = H + L_d \mid H + L_d \quad \text{fig. 1 Comm. IV} \quad . \quad . \quad . \quad (18)$$

The directly visible result of the diffusion in system (17) is, therefore, that the hydrate H is separated on both sides of the membrane; in system (15) this hydrate is separated at one side of the membrane only.

All we have deduced above, if H is hydrate of Y , viz. a compound of Y and W , is true also when Y forms a binary compound with the component X ; then the point H is situated on the side YX of this figure.

If Y forms with water and X a ternary compound D , then we can represent the saturation-curve of D by curve $w b v d w$ of fig. 2 Communication IV; the dotted curves in this figure are the isotonic W -curves. The line WD intersects the saturation-curve in the points w and v ; they divide this curve into two branches; we have called w the finishing-point of those branches rich in water and v the point poor in water. Previously we have deduced:

the $O.W.A.$ of a liquid of this saturation-curve is greater, the further it is remoted from the finishing-point rich in water.

Consequently the $O.W.A.$ increases along both branches in the direction of the arrows.

We now imagine in this figure to be drawn the line YD , which intersects the saturation-curve in two points; these points of intersection divide this curve into two branches. We call the point of intersection, which is situated the closest to Y the finishing-point of those branches, rich in Y , the other the point poor in Y . We now find the rule:

the $O.Y.A.$ of a liquid of the saturation-curve is greater, the further it is remoted from the finishing-point rich in Y .

We may consider fig. 2 of this communication as special case of fig. 2 in Comm. IV; here point D is situated on the side WX and is, therefore, a hydrate of the substance X . The line YD divides the saturation-curve $a d g$ into the two branches $a d$ and $g d$; point d is the finishing-point rich in Y . Consequently the $O.Y.A.$ must increase from d towards a and from d towards g ; therefore, in the direction of the arrows. The dotted curves are isotonic Y -curves; consequently b and f have the same $O.Y.A.$, they are isotonic, therefore, with respect to the substance Y ; the same is true for the

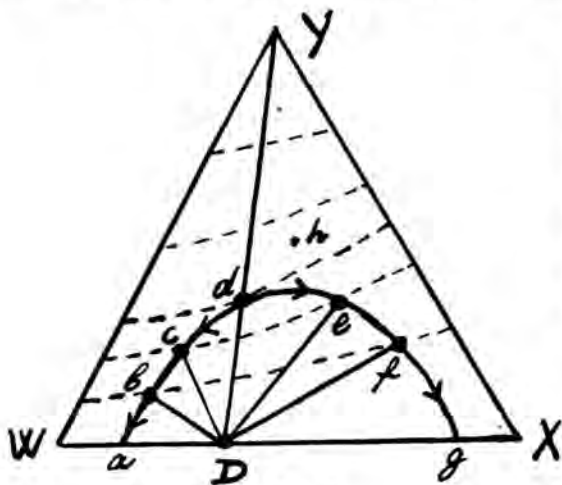


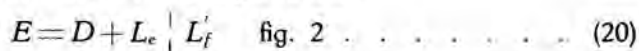
Fig. 2.

liquids c and e . The isotonic Y -curve, going through point d , touches the saturation-curve in this point d . The conjugation-angle in point c is DcY ; the saturation-curve and the isotonic Y -curve are situated in the vicinity of c within this conjugation-angle; this is also the case in the points b , e and f . If the saturation-curve has such a form, that we may draw from Y a line, which touches this curve in a point r , then the isotonic Y -curve, going through r , must touch the line rD .

In the osmotic system:



L_f has a greater O.Y.A. than L_h ; consequently, as is indicated in (19) by the arrow, the substance Y diffuses from L_h towards L_f . It now depends on the ratio of the two liquids in (19), which osmotic equilibrium will be formed at last; f. i. the equilibrium:



may arise; then L'_f is the liquid, represented by the point of intersection of the line Yf with the isotonic Y -curve, going through point e . Therefore, a result of the diffusion of the substance Y , visible at the moment, is, that a hydrate of the substance X is separated at one side of the membrane; at first sight the substance X might seem to be diffusing, instead of the substance Y .

As special case of fig. 2 we may assume that point D coincides with W or X . If D coincides with X , then of curve adg only the branch ad remains, point d of which is situated now on the side XY ; the O.Y.A. then also increases in the direction of the arrows, viz. from d towards a . Then, however, the isotonic Y -curve going through point d , touches no more the saturation-curve in d . If D coincides with W then of adg only remains the branch dg , point d of which is situated now on the side WY , dg now represents the solutions, which are in equilibrium with ice. Then the O.Y.A. of those solutions, saturated with ice, increases also in the direction of the arrows, viz. from d towards g .

We may easily summarise the rules deduced in this and previous communications for the change of the osmotic attraction of the liquids of a saturation-curve. We take the saturation-curve of an arbitrary substance V (component or compound); we call N the diffusing substance. The line NV intersects the saturation-curve of V in one or two points; in both cases one of the points of intersection is situated between V and N ; we call this the „point rich in N “ of the saturation-curve. We now can say:

the O.N.A. (osmotic N -attraction) of a liquid of a saturation-curve is greater, the more this liquid is situated further from the point of this curve, rich in N .

In the special case, that the solid substance, with which the liquids

of the saturation-curve are in equilibrium, is the diffusing substance itself, the line NV does not exist and consequently there is no point on the saturation-curve rich in N . Then the former rule passes into:

all liquids of the saturation-curve of a substance N have the same $O.N.A.$

If we apply this rule to the saturation-curve wv of the substance Y in the figs. 1, 2 and 3 of Communication III, then we find:

the $O.W.A.$ increases along curve wv from w towards v ,

" $O.X.A.$ " " " " " v " w ,

" $O.Y.A.$ is the same for all liquids of curve wv .

For the saturation-curve $wcdv$ of the hydrate H in fig. 1 of Communication IV follows:

the $O.W.A.$ increases along curve wv from w towards v ,

" $O.Y.A.$ " " " " " v " w ,

" $O.X.A.$ " " " " " s " w and from s towards v , if s is the point of intersection of this curve with the line HX .

For the saturation-curve adg of the hydrate D in fig. 2 of this communication we find:

the $O.W.A.$ increases along this curve from a towards g .

" $O.X.A.$ " " " " " g " a .

" $O.Y.A.$ " " " " " d " a and from d towards g .

In the figs. 1—4 of Communication V the arrows indicate the direction in which the $O.W.A.$ increases along the different saturation-curves; of course this is otherwise for the $O.X.A.$ and $O.Y.A.$ of those liquids.

We find for fig. 1 of Communication V:

the $O.Y.A.$ is constant along curve ac and increases on curve cb from c towards b .

If we imagine viz. curve bc to be prolonged up to a point s on the side XY , then s is the point of this curve rich in Y ; the $O.Y.A.$, therefore, must increase along this curve from s towards b , consequently also from c towards b .

For fig. 2 of Communication V we find:

the $O.Y.A.$ decreases from a towards d , rests constant d to c and increases c to b .

For figs. 3 and 4 of Communication V follows:

the $O.Y.A.$ is constant from a to c and increases along the curves cd and db from c to b .

We now may draw easily in those diagrams schematically the isotonic Y -curves; in the vicinity of the side WX their shape comes near to straight lines; in the vicinity of the saturation-curve of Y they get corresponding forms as this saturation-curve.

(To be continued.)

Physiology. — "*On the Segmentation of Skeletal Muscles in the Frog. (Rana esculenta)*". By Dr. S. DE BOER. (Communicated by Dr. C. U. ARIËNS KAPPERS).

(Communicated at the meeting of October 31, 1925).

The question whether the fibres of skeletal muscles receive innervation from one or from different segments is a matter which has of late years engaged the attention of several investigators. On the basis of his histological researches AGDUHR ¹⁾ came to the conclusion that in one and the same fibre of a skeletal muscle endplates of KÜHNE can be found, which are connected with nerve fibres arising from different segments. BERITOFF ²⁾, and also CATTELL and STILES ³⁾ arrived at the same conclusion after their physiological experiments, SAMOJLOFF ⁴⁾, however, basing on the results of his experiments, was induced to think that every separate muscle fibre is innervated only from one anterior root. In a previous publication I gave an extensive summary of the literature on this subject ⁵⁾, so that the above brief indications may suffice here.

The present writer studied this problem first in the M. gastrocnemius of the frog. I injected subcutaneously some drops of a veratrin solution into frogs and after the muscles had been poisoned I stimulated rhythmically one of the two innervating spinal nerves, until the veratrin curve had disappeared and twitches arose. After this an induction shock, administered to the other root, produced invariably a complete veratrin curve. If then this second root was stimulated rhythmically, until after every stimulus a twitch arose, the veratrin effect recovered itself on stimulation of the first root. That the endplates in the muscle are not the cause of the disappearance of the veratrin-effect after rhythmical stimulation of the nerve, was proved by the fact that *direct* stimulation of the muscle also produced twitches. It became evident from these experiments that the two spinal nerves innervate different parts of the M. gastrocnemius. A second series of experiments yielded the same result. I fatigued the M. gastrocnemius by applying rhythmical induction-shocks to the one root. Subsequent stimulation of the other root produced curves without signs of fatigue. (This was known before and CATTELL,

¹⁾ AGDUHR. Anat. Anz. 49. p. 1. 1916; 52. p. 273. 1919.

²⁾ BERITOFF. Ztschr. f. Biol. 78. p. 231. 1923; Pflüger's Arch. 205. pp. 455 and 458. 1924.

³⁾ CATTELL and STILES. Amer. Journ. Physiol. 69. p. 645. 1924.

⁴⁾ SAMOJLOFF. Pflüger's Arch. 204. p. 691. 1924.

⁵⁾ S. DE BOER. The double innervation of the M. gastrocnemius. The Journ. of Physiol. Vol. 60 p. 215. 1925 and Verslag van de vergadering van de Amsterdamsche Neurologen Vereeniging op Donderdag 1 Oct. 1925.

and STILES supposed the explanation to be that on rhythmical stimulation the conductability of KÜHNE's endplates decreases. According to these investigators most muscle fibres contained KÜHNE's endplates, which were connected with the nerve fibres of the 8th and the 9th spinal segments). When after this the second root was again stimulated rhythmically until fatigue reappeared, the effect of the stimulation of the first root had meanwhile been considerably restored. It is seen then that during the rhythmical stimulation of the one root the fatigue recovers itself that had been previously provoked after rhythmical stimulation of the other root.

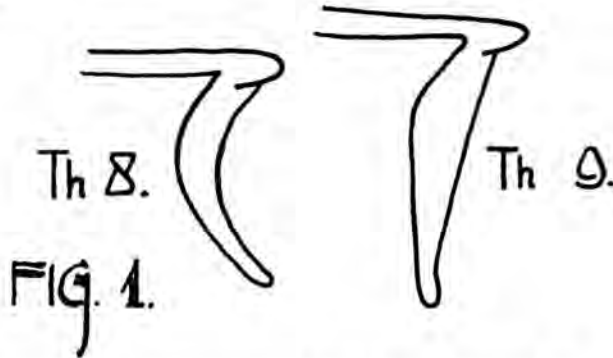
These two series of experiments have established distinctly, that in the gastrocnemius of the frog two parts of the muscle are lying side by side, each of them being innervated by one spinal nerve. However, some room was still left for the possibility that some of the muscle-fibres might be innervated from both segments. To make sure about this I registered the monophasic action-currents. To this end I first stimulated the two spinal nerves separately and after this the N. ischiadicus. It thereby appeared that after the stimulation of the N. ischiadicus the action-current curve was always equal to the sum of the two action-current curves obtained by stimulating the two spinal nerves separately ¹⁾. This proved that none of the muscle fibres of the M. gastrocnemius receives a double innervation. Now it can be imagined that muscle fibres, innervated by the 8th and the 9th spinal nerves are intertwined in the muscle or that the gastrocnemius consists of two groups lying side by side, so that the muscle fibres of the one portion are not intertwined with those of the other portion.

This question I have set at rest. I severed the three or two spinal nerves which innervate the M. gastrocnemius, close to the spinal column; then I prepared out the N. ischiadicus together with the M. gastrocnemius and I suspended the muscle freely on the femur. If then the 8th spinal nerve was faradized, the muscle bent towards the ventral side ²⁾; if, however, the 9th spinal nerve was faradized, the muscle contracted rather in a vertical direction or it curved dorsad. Fig. 1 illustrates this result. In some cases (once in about 15 frogs) stimulation of the 7th spinal nerve also produced a contraction of the M. gastrocnemius. These cases always showed after stimulation of the 7th spinal nerve a curving of the gastrocnemius towards the ventral side. After stimulation of the 8th spinal nerve the curvature was much less pronounced, or the direction was more vertical; after a stimulus had been applied to the 9th spinal nerve the muscle pointed dorsad, or it contracted rather in a

¹⁾ Communicated on the 4th Tagung der Deutschen Pharmacol. Ges. Rostock von 13—15 August 1925, The Americ. Journ. of Physiol. Vol. 75, 1925 and Ned. Tijdsch. v. Geneesk. 14 Nov. 1925.

²⁾ By the ventral side of the muscle is meant the upper surface of the muscle, the frog lying on its back; the under-surface is then the dorsal side.

vertical direction. Once in the course of my experiments a contraction of the M. gastrocnemius occurred after stimulation of the 10th spinal nerve. In this case the muscle pointed dorsad during the stimulation of the 10th spinal nerve; after stimulating the 9th spinal nerve it was directed vertically and after stimulation of the 8th spinal nerve it curved ventral. (See fig. 5).



These experiments demonstrated that the fibres of the M. gastrocnemius, which are innervated by different spinal nerves, do not fall together but are arranged in groups. In order to ascertain this I slit the M. gastrocnemius lengthwise starting from the Achillestendon, and attached each part to a lever. Fig. 2 illustrates the result of this experiment. At

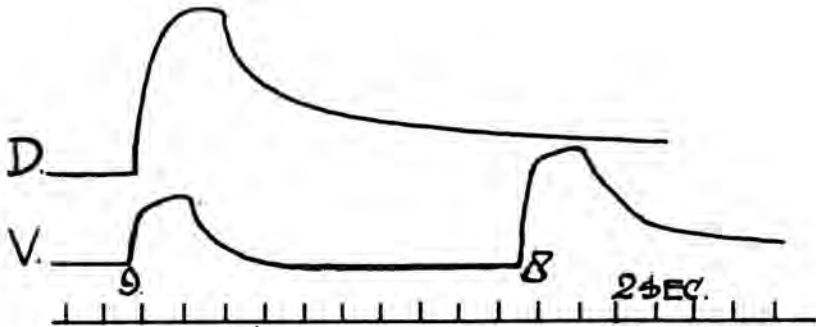


FIG 2.

8 a faradic current was applied to the 8th spinal nerve, after which the ventral part contracted, while the dorsal part did not. At 9 the 9th spinal nerve was stimulated with the consequence that the dorsal part exhibits a marked contraction and the ventral part also contracts, but less than after the stimulation administered to the 8th spinal nerve. So in this muscle the dorsal part contained fibres that were innervated only by the 9th spinal nerve. They have been isolated for the major part in the dorsal portion of the muscle, while all the muscle fibres innervated by

the 8th spinal nerve are located in the ventral portion, in which there is also a small number of the muscle fibres innervated by the 9th spinal nerve. This experiment will be all the more successful the nearer the slit is made to the dorsal side so that the ventral portion is larger than the dorsal. If, on the contrary the slit is applied nearer to the ventral side of the muscle, so that the dorsal part is larger than the ventral, the muscle fibres innervated by the 8th spinal nerve can be partially isolated. This is instanced in Fig. 3. At 9 the 9th spinal nerve received

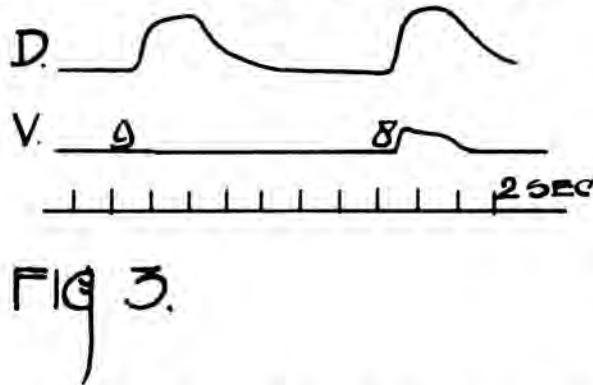


FIG 3.

a stimulation and contraction of the dorsal part ensued; at 8 the 8th spinal nerve was stimulated, which resulted in a contraction of both portions. It follows then that in this way we can isolate at will a part of the 8th or the 9th spinal muscular segment. I always found the 8th muscular segment on the ventral-, and the 9th on the dorsal side of the muscle¹⁾.

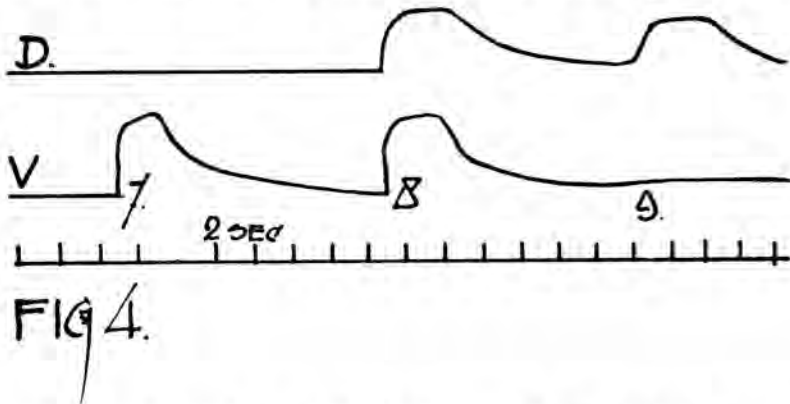
These experiments, then, show conclusively that the muscle fibres of the M. gastrocnemius, innervated by the two spinal nerves are not intertwined, as they revealed to us a ventral group of muscle fibres innervated by the 8th spinal nerve, and a dorsal group that receives innervation from the 9th spinal nerve.

The experiments in which also the 7th spinal nerve innervates the M. gastrocnemius, are also of interest, as is instanced in Fig. 4. The slit was applied from the Archillestendon upwards through about the middle of the muscle. At 7 the 7th spinal nerve was faradized. A contraction of the ventral part ensued, while the dorsal part remained inactive. At 8 the 8th spinal nerve was stimulated. Now both parts of the muscle contract. At 9 the 9th spinal nerve was faradized and now arises a contraction of the dorsal part, whereas the ventral portion remains inactive. It will be seen, then, that in this preparation the muscle fibres innervated by the 7th spinal nerve are all lying in the ventral part, and those that are innervated by the 9th spinal nerve in the dorsal portion.

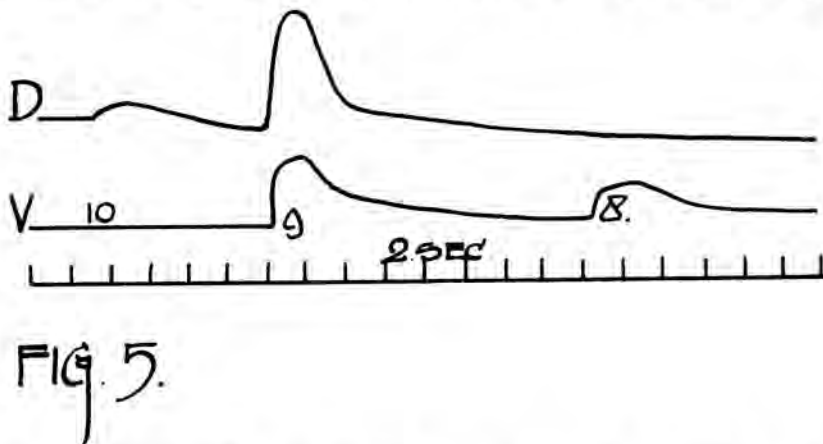
Both parts contain muscle fibres innervated by the 8th spinal nerve.

¹⁾ When speaking of spinal segments of the muscle I mean that portion of it which is located in the M. gastrocnemius. Other portions of the same myotome are lying in other muscles.

So we see that the 7th spinal muscular segment has taken the place of the 8th. The result derived from these curves stands quite in harmony



with what I observed at the freely suspended muscle in those cases in which Th 7, 8 and 9 innervates part of the M. gastrocnemius. Here, indeed, we saw the same morphological changes of the M. gastrocnemius after stimulation of Th 7, viz. a curvature towards the ventral side, that I observed after stimulation of the 8th spinal nerve only in those cases, where the 7th spinal nerve does not participate in the innervation of the M. gastrocnemius. In one experiment I found that the 8th, the 9th and the 10th spinal nerves innervate the M. gastrocnemius. The curves are given in Fig. 5. They show that on stimulating the



8th spinal nerve only the ventral part contracts, on stimulating the 9th spinal nerve both parts, and only the dorsal part after stimulation of the 10th spinal nerve. One question still requires further consideration. We know from segmental anatomy and above all from the work of BOLK¹⁾ and SHERRINGTON¹⁾ that the dermatomes on an extremity

¹⁾ See complete literature by G. VAN RIJNBEEK. Versuch einer Segmentalanatomie. *Ergebn. d. Physiol.* Bd. 18. S. 353. 1908.

are liable to shift in a caudal or cranial direction, according as the extremity has developed itself at the cranial or the caudal side. By a new method I have determined¹⁾ all the dermatomes of an extremity of one and the same animal (cat), and thereby could establish the shifting of all the dermatomes. The extremity is then, as SHERRINGTON calls it, "prefixed" or "postfixed". Now the present investigation has brought to light that also the myotomes can shift in a cranial or a caudal direction. The 7th spinal segment can be substituted for the 8th and conversely the 10th can replace the 9th. This shifting may amount to half a segment, or a quarter of it, or less. In all cases, in which the 7th or the 10th spinal nerve innervates the M. gastrocnemius I found in the frog only unilateral shifting. It is clear, therefore, that shifting is not of necessity bilateral. Accordingly the position of the 8th spinal segment in the M. gastrocnemius, is not always the same and may display variations. It follows that the curving may be different after the stimulation of the 8th spinal nerve, and consequently it is clear that the myotome-parts in a muscle always present the same sequence, and can shift without disturbing this arrangement. Up to the present this had not yet been established. Once more I wish to emphasize the fact that we have to do here with fragments of myotomes. Other parts of it are lying in the other muscles.

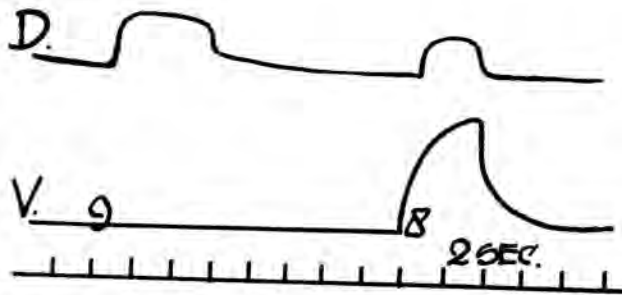


FIG. 6.

The above-mentioned experiments with longitudinal incisions in the M. gastrocnemius were also carried out with the M. Tibialis anticus longus. I cut the greater part of this muscle loose from its environment, and made a longitudinal incision down the middle between the one terminal tendon and the other. Thus the muscle was split up into a ventral-, and a dorsal part. The M. Tibialis anticus longus is innervated by the 8th and the 9th spinal nerves or by the 7th, the 8th, and the 9th. An instance of the first case is given in Fig. 6. Here we see that the stimulation of the 9th induces a contraction of the dorsal part, whereas the ventral part remains inactive. On stimulating Th 8 the dorsal part contracts

¹⁾ S. DE BOER. These Proceedings 18, p. 1133 and 19, p. 321.

slightly whereas the ventral part contracts considerably. Just as in the case of the *M. gastrocnemius* also here the ventral part of the muscle is innervated by Th 8, and the dorsal part by Th 9.

However, here also Th 7 can partake of the innervation, as appears from Fig. 7. On stimulating Th 7 there arose a contraction of the

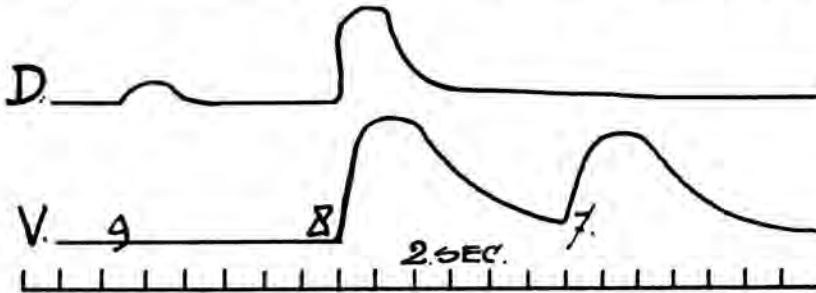


FIG. 7.

ventral part and on stimulating Th 8 a marked contraction of the ventral and the dorsal part ensued, whereas stimulation of Th 9 yielded a small contraction of the dorsal part. It will be seen, then, that also in the *M. tibialis anticus longus* the myotome fragments can shift without disturbing the serial arrangement, so that Th 7 takes the place of Th 8. Hence these relations appear to be similar to those established by us for the *M. gastrocnemius*.

Also in this muscle there are no muscle fibres which receive a double innervation. I demonstrated this by means of the string galvanometer and found that the monophasic action-current curve, obtained after stimulation of Th 8 added to the one produced by stimulating Th 9, was equal to the action-current curve obtained by stimulating the *N. ischiadicus*. Just as in the present experiments with the *gastrocnemius*, I used also here only muscle preparations that were innervated exclusively by Th 8 and Th 9.

Next I continued my experiments with the *M. rectus femoris* and the *M. gracilis major*. In the muscle I made longitudinal incisions after I had cut loose the lower portion from its environment, and thus I split up the muscles into a medial and a lateral part. Next I stimulated the 8th and the 9th spinal nerves and registered the contractions of the medial and the lateral part on a smoked drum. It hereby appeared that the medial part of these muscles is innervated by the 8th spinal nerve and the lateral part by the 9th. In both muscles it will be necessary to ascertain by means of the string galvanometer whether in these muscles part of the muscle receives innervation from both spinal nerves.

By the methods worked out by me heretofore I purpose to prosecute my experiments also with other muscles, while at the same time I shall endeavour to collect data also from other animals.

The above results do not entitle me to draw conclusions for other muscles, as it may very well be possible that fibres of muscles with an intenser function possess a plurisegmental innervation. In a previous investigation I could establish, that the skin areas with a more intensive function are innervated from more segments than cutaneous areas with a less intense function ¹⁾. Thus I could establish that the "overlap" of the dermatomes is more marked on the ventral side than on the dorsal side of the body. This tallies with the stronger function of the skin on the ventral side and with the smaller sensory circles of WEBER in situ on the ventral than on the dorsal side. In previous publications ¹⁾ these relations were dwelt upon at length. Therefore we have also to consider the possibility that muscles with a more intensive function may possess fibres with a plurisegmental innervation. In this direction I shall proceed with my investigations.

When we stimulate one of the two innervating anterior roots of the freely suspended gastrocnemius, it will depend on the position of the segmental parts of the muscle concerned how much the muscle inclines towards the ventral side or whether it will point in a dorsal or in a vertical direction. If the 8th muscular segment is located along the ventral border, then a typical and pronounced curving will appear ventrad after stimulation of the 8th spinal nerve. If, on the contrary, this muscular segment extends dorsad, the curving will be less pronounced after stimulation of the 8th spinal nerve. The frequent morphological change in the various gastrocnemii implies that the position of the muscular segment is not stationary but vacillating.

The fact that the ventral or medial side of the muscles (gastrocnemius, tibialis anticus longus, rectus femoris, M. gracilis maior) receive innervation from more cranial parts of the central nervous system than the dorsal side, is perfectly in keeping with the experience of Prof. BOLK ²⁾. This investigator found for the upper leg and the lower leg that "the medial muscles in these groups originate from the more proximal (higher) segments, and the lateral muscles from the more dorsal (lower) ones".

My own investigation showed that this pronouncement applies not only to the entire muscle but also to parts of it.

¹⁾ See S. DE BOER, These Proceedings 18, 1915, p. 1133 and 19, 1916, p. 321, Ned. Tijdschr. v. Geneesk. Jaargang 1916, II and Psychiatrische en Neurol. Bladen 1918. (Feestbundel WINKLER).

²⁾ L. BOLK, De Segmentale Innervatie van romp en ledematen bij den mensch, Haarlem, F. Bohn 1910.

Zoology. — "*On the Thyroid Glands and on the Phylogeny of the Perennibranchiate and Derotremous Salamanders*". By Prof. J. VERSLUYS.

(Communicated at the meeting of June 27, 1925).

In the latest decennia it has become more and more evident that hormones are highly instrumental to the growth of the animal body, and to the development of several of its chief qualities. But then it is most likely that some of the modifications the animals underwent during their phylogenesis, were associated with changes in the production of the hormones. The factors that brought about the evolution of animals need not have affected the structure of the organs in a direct way only; this may have occurred also indirectly through their influence upon the organs that form the hormones and upon the production of hormones. So the rate of development, which may be of great importance for the acclimatization and consequently for the propagation of a species, is at least sometimes under the control of the hormone-forming organs. Hereby a new point of view was brought forward for the study of evolution. It is of special importance that the production of hormones depends on the climate and probably also on the food; changes of climate or food can through the agency of hormones modify the structure and the psychical properties of an animal. When in course of time the modifications increase, they can be either deleterious, immaterial, or useful to the animal; consequently they can be conducive to the propagation or the extinction of the species. Perhaps in this way, an explanation can be given of the occurrence of some useless properties or of such properties as are even noxious on account of their exorbitancy (DENDY 1911).

Not a few investigators have already pointed out the probable significance of hormones for evolution, e.g. CUNNINGHAM (1908, 1921), BOURNE (1911), DENDY (1911, 1923), TANDLER (1913), MAC BRIDE (1914, 1917), NOPCSA (1917, 1923), KEITH (1919), HART (1920), BOLK (1921A, 1921B, 1922) and GRAHAM KERR (1924). For Man this problem derives additional interest from BOLK's conception that the modified hormone-production played an important part in the descent of Man from Primates, and from KEITH's theory that the differentiation of Man into racial types is associated above all with a different production of hormones. It will, therefore, be undoubtedly of great importance to test these conceptions of the part played by hormones in phylogeny.

The first question we have to answer is whether any modifications in the hormone-forming organs can be found that are correlated with

evolution. As far as I am aware, there is only one example of it on record, viz. that given by NOPCSA (1917). This scientist pointed to the fact that among the fossil *Dinosaurs* there exists a parallelism between an excessively enlarged groove for the hypophysis in the base of the skull (which implies an abnormally large hypophysis) and the gigantism of many of these animals, some of which are the largest of all land-animals. He compares this gigantism with the well-known pathological overgrowth in Man, designated by the name of acromegalia. This disease is very probably a direct consequence of an affection of the hypophysis, which is thereby enlarged and imparts an unusual amount of hormone to the body. It is notorious that the hormone of the hypophysis stimulates the growth. Hence NOPCSA correlates the gigantism of the *Dinosaurs* with an anomalous hypertrophy of their hypophysis.

However the assumption of such a correlation between evolution and hormone-producing organs requires additional evidence, the more so as NOPCSA's example concerns fossil-forms, of which we cannot examine the hormone-producing organ itself; we know only the groove in which it laid, and which it need not have filled up entirely. Now I believe to have found an additional case in the thyroid of the *Urodela*. Its hormone is largely instrumental in the metamorphosis of these animals, as was first demonstrated by GUDERNATSCH (1912A, 1912B, only for *Frogs*) and corroborated by a number of researchers (e.g. by HERINGA, 1922, 1924 and notably for *Salamanders* by JENSEN, 1916, HART, 1917, WINTREBERT, 1908, UHLENHUTH, 1921, 1922, HUXLEY and HOGGEN, 1922, and SWINGLE, 1923, 1924).

The administration of thyroid hormone calls forth the metamorphosis even in very young larvae, whereas withholding it through extirpation of the thyroid body prevents the metamorphosis. Now, in a number of *Urodeles*, in the *perennibranchiate* and the *derotremous Salamanders*, the metamorphosis is either completely suppressed or does not attain completion, so that the development of the animals comes to a standstill in metamorphosis: they are *neotenuous*. It appears that in all these forms the thyroid deviates more or less from the normal¹⁾. Some reports in the literature point in this direction. So SCHMIDT, GODDARD and VAN DER HOEVEN (1862, fig. 3, see page 32) give a picture of a surprisingly large thyroid of the *Giant Salamander* *Megalobatrachus maximus*; the authors add the following remark: "These glands are an assemblage of blind folliculi, measuring 1—2 mm., which are filled with a colloid mass. On the whole these glands reminded us of diseased glandulae thyreoideae in Man with incipient colloid degeneration"²⁾ BOLAU (1899) found in a specimen of the *Giant Salamander*, of the length of 132 cm., very large thyroids 6 cm. in length and 1½ cm. in breadth. It is also of interest that

¹⁾ For the structure of the normal thyroid gland in non-neotenuous *Salamanders* see BOLAU 1899, LIVINI 1902, THOMPSON 1911; and for *Rana* ADLER 1916.

²⁾ Translated from the dutch.

VON EBNER (1877) has described a neotenuous specimen of *Triton cristatus* 13 cm. long, of which the thyroids were excessively enlarged, measuring on either side: length 5, breadth 5, thickness $2\frac{1}{2}$ mm., while the normal dimensions of the thyroid in this animal, in individuals of the same bodylength, are about long $1\frac{1}{2}$ to 2, broad $\frac{3}{4}$ to 1, thick $\frac{1}{2}$ mm. We see then that the thyroids of VON EBNER's larva are about 70 times the normal size. In every respect this animal possessed the structure of a larva with external gills, but it was sexually mature, and of the size of a full-grown animal. This gives reason to assume that there is in this case a correlation of neotony with the hypertrophied thyroids (VON EBNER, of course, did not think of this). Neotenuous specimens of normal *Salamander*-species, especially *Tritons* are not rare, but EBNER's case is the only one in which some information is given on the thyroid. Presumably it is not so anomalous in other neotenuous *Tritons*, otherwise this would have been noticed before (see MAREES VAN SWINDEREN 1925).

Opposed to these reports that point to enlarged thyroids in neotenuous *Salamander*-forms are some others mentioning very small dimensions of these glands. So for instance the thyroid of the *perennibranchiate Salamander Proteus* is described by LEYDIG in 1863 as an extremely small, unpaired, median organ, made up of 15 to only 3 follicles of 0.12—0.15 mm. diameter (however, he has not found the paired thyroid, also present). And concerning the *perennibranchiate form Typhlomolge Rathbuni* miss EMERSON reports that she could not find a thyroid in a series of sections. A detailed investigation has proved that here, indeed, the thyroids are very rudimentary and are even lacking in some individuals. A normally functioning thyroid is not present here (UHLENHUTH, 1923; SWINGLE, 1922).

The present writer examined a number of specimens of *perennibranchiate* and *derotremous Salamanders* for the size and the structure of their thyroid glands, and compared with them the thyroids of a number of normal *Salamanders* and of a few *Axolotls*, i.e. neotenuous individuals of *Amblystoma mexicanum*. We had some difficulty in procuring the necessary material, and the conservation also fell short. Only one individual of *Siren* was at my disposal. *Typhlomolge* I was not in a position to examine, but this is entirely made up for by UHLENHUTH's paper (1923). However, the results of my inquiry seemed sufficiently complete to justify their publication. Already in 1923 a short preliminary communication on my researches was published.

In the first place I examined the size of the thyroids in relation to the body-volume. In a number of specimens of various forms I measured the length, the breadth and the thickness of the thyroid which was most often paired, occasionally with accessory thyroids; by multiplying these numbers and adding up the separate values of the two glands I obtained a number expressing the amount of thyroid-tissue present. This number I divided by the volume of the animal; the quotient constituted the index by which

forms could be intercompared, that furnished a standard to judge of the relative size of the thyroid glands.

It goes without saying that this index varies rather much individually for normal *Salamanders*, with nutritive conditions, with outward circumstances; the amount of colloid¹⁾ present in the thyroid is also of great importance. In my limited material I could not establish a great influence of the age of the animals. In order to get some idea of the normal relation of the size of the thyroids to that of the body in typical *Salamanders*, that is a normal index, I added up the indices of 3 specimens of *Triton cristatus*, 2 of *Triton taeniatus* and 4 of *Salamandra maculosa*, and divided the sum by the number of specimens, 9. The normal index thus obtained is 0.00016921²⁾.

In this connection it should be remembered that the nature of the colloid present in the follicles influences the contraction of the thyroid when conserved in alcohol. Generally the thyroid contains a colloid so consistent as to contract little in alcohol, and to fill up the follicles almost entirely; but sometimes the thyroids in the preparations contain very little colloid, presumably because the colloid was less consistent and has contracted considerably in alcohol. Such is the case with the specimens D and C of *Megalobatrachus*, with *Amblystoma* B and with *Siren*, and here the thyroid has probably contracted more in alcohol than could possibly be the case with a normal consistence of the colloid. In life the thyroids of these specimens were probably larger than is expressed by the indices.

The text-figures A and B represent the thyroids of some of the forms examined; figure B, in which all the heads have been reduced to the same length, gives a good idea of the marked differences in the size of the thyroids.

For a number of neotenuous forms and for some specimens of *Amblystoma* I found the indices given in the table page 833.

When surveying this table we see that in some of the neotenuous forms the thyroids are enlarged, in others more or less reduced, and that these differences do not occur in a disorderly way: a hypertrophy of the thyroid is found in all specimens of *Derometremata* examined and in *Siren*; a reduction is observed in all the other *Perennibranchiates*. This is very evident in *Proteus* and according to UHLENHUTH also in *Typhlomolge*. In these two forms the thyroids are not only very

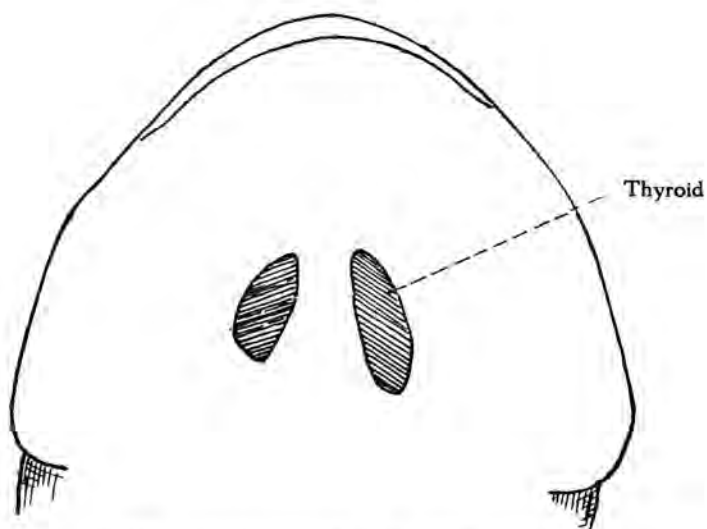
¹⁾ On the difference in the size of the thyroids in *Rana temporaria* from various regions, see ADLER, 1916.

²⁾ The indices were for *Triton cristatus*: spec. A, long 125 mm., 0.0003947; spec. C, long 128 mm., 0.000109; spec. B, long 148 mm., 0.0001688; for *Triton taeniatus*: spec. B, long 86 mm., 0.0001732; spec. D, long 85 mm., 0.0002142; for *Salamandra maculosa*: spec. B, long 166 mm., 0.00017; spec. A, long 168 mm., 0.0001213; spec. C, long 161 mm., 0.0000931; spec. D, long 141 mm., 0.0000786. Specimen A of *Triton cristatus* exceeds the normal.

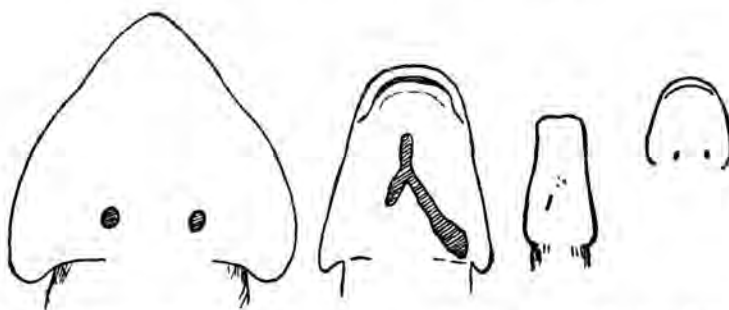
Indices of the Thyroid Glands in some neotenuous Urodela and in an
Amblystoma tigrinum, adult.

Species	Length mm	Body volume cm ³	Index	Size of the Thyroids
<i>Necturus</i> spec. C	168	21	0.000107	about $\frac{2}{3}$ normal
„ spec. A	255	83	0.000189	normal
„ spec. B	408	552	0.000065	$\frac{2}{5}$ normal
<i>Proteus</i> spec. A	150	5	0.000025	$\frac{1}{6}$ normal
„ spec. B	215	15	0.000028	$\frac{1}{6}$ normal
„ spec. C	240	20	0.000012	$\frac{1}{14}$ normal
<i>Siren</i> spec. A	514	297	0.000469	$\pm 3 \times$ normal
<i>Megalobatrachus</i> maximus spec. A	175	28	0.000342	$2 \times$ normal
„ spec. B	380	260	0.000785	nearly $5 \times$ normal
„ spec. D	600	2880	0.000433	rather more than $2\frac{1}{2} \times$ normal
„ spec. C	790	4400	0.000231	nearly $1\frac{1}{2} \times$ normal
<i>Cryptobranchus</i> alleghaniensis spec. B	250	65	0.000343	rather more than $2 \times$ normal
<i>Amphiuma</i> spec. B	550	162	0.000355	„ „ „ $2 \times$ normal
„ spec. A	710	380	0.000326	„ „ „ $2 \times$ normal
<i>Amblystoma</i> larve (<i>Axolotl</i>) spec. D	186	50	0.00121	„ „ „ $7 \times$ normal
„ spec. C	234	63	0.00054	$3 \times$ normal
<i>Amblystoma</i> tigrinum spec. A	230	40	0.000343	$2 \times$ normal

small, but they also display an aberration in their development. Whereas the normal *Urodela* have a paired thyroid (see fig. A, 5), a third, more forward, median, unpaired thyroid is present in *Typhlomolge* as described by UHLENHUTH. Most often one of the three thyroids is lacking, sometimes no thyroid could be detected at all. In *Proteus* I found a similar condition, only the reduction is less marked, and I could always find thyroids, though in two specimens one of the paired thyroids was absent (fig. A 4), once on the left, and once on the right. I find the follicle-epithelium in *Proteus* distinctly flattened, which is suggestive of a feeble function. In *Necturus* the reduction of the thyroid is much less pronounced, but the follicles are very large, their mean diameter being twice that in the normal adult *Salamanders* (I compared *Salamandra maculosa* and *Onychodactylus japonicus*), so their volume is 8 times larger. It follows, then, that the surface of the follicle epithelium in *Necturus* must be proportionately smaller than in normal *Salaman-*



1. *Megalobatrachus maximus* (spec. D).



2. *Necturus maculatus*
(spec. B).



3. *Siren*
(spec. A).



4. *Proteus*
(spec. B).



5. *Salamandra maculosa* (spec. D)

Text-figure A.

Thyroids of some *Urodeles* in situ. All figures $\frac{2}{3}$ nat. size.



Text-figure B.

The same figures as in fig. A, but all reduced to the same length.

ders; the considerable amount of colloid in the follicles has caused the thyroid to expand, but its productive surface is smaller than normal (about half). So we find in three forms of the *perennibranchiate Salamanders* a thyroid that is reduced and there is *hypofunction*. The reduction of the thyroid is most pronounced in *Proteus* and *Typhlomolge*, which also display the greatest anomaly, the more pronounced secondary adaptations, in their bodystructure. In *Necturus* the reduction of the thyroids is much less, while their histological structure is still normal, with a slightly flattened cubic epithelium of the follicle wall; this form in its body structure deviates little or not at all from a normal larva of *Urodeles*.

Quite different is the transformation of the thyroids in the *Derotremes* and the *Perennibranchiate Siren* (in so far as we may form an estimate of the relations in the latter form from one individual). The thyroids are not reduced, but enlarged, as a rule two or three times. This is also the case, when only a small part of the follicles in the alcohol-material is filled with colloid, so that the thyroids are contracted more than is the case with a normal consistence of the colloid (see page 832). Indeed, in some of the specimens examined the dimensions of the follicles are larger than in normal *Salamanders*, but at the same time the consequent diminution of the secreting surface is mostly more or less compensated by a folding of the follicle-wall (in a very marked degree in *Amphiuma*, spec. B; see fig. 3, plate) or by the irregular shape of the follicles (as in *Amphiuma* A, fig. 4, plate). In other specimens, i.e. in *Megalobatrachus*, spec. A, 175 mm. long, (which has almost entirely lost the external gills, except a few remains, but which still has an open gill-slit) the follicles are smaller than normally, so that the secernent surface is still more enlarged than would follow from the hypertrophy of the whole thyroid. In *Siren* the follicles appear to be as large as in normal *Salamanders*. It is, however, of special importance that in the *Derotremes* and *Siren* I invariably found the follicle-epithelium highly cylindrical (fig. 8, 9, plate), for this points to *hyperfunction*. The occasional formation of papillae by the epithelium (fig. 9) also points in this direction. The figures given us by the *Derotremes* bear some resemblance to those of the human thyroid in BASEDOW's disease, in struma parenchymatosa, which is also attended with a hyperfunction of the thyroid (see KOCHER 1912, BREITNER 1924); there we often meet with cylindrical epithelium, with papillae-growth and hypertrophied follicles of very irregular shape with folded wall, like the preparation of *Amphiuma* spec. B., represented by fig. 3.

The thyroid of the *Derotremata* and of *Siren* apparently functions vigorously. In this process we must assume the product to be supplied to the body¹⁾; anyhow the follicles only exceptionally contain colloid of

¹⁾ The colloid is probably not identical with the thyroid hormone which, however, is decidedly present in the colloid.

more viscous consistence, which displays the typical breaking up in columns in the preparations of alcohol material (e.g. in a specimen of *Megalobatrachus*, of which Mr. DE FREMERY furnished the material (see plate fig. 5). Most often the follicles in the preparations are for the greater part empty, just as with struma parenchymatosa. This strikes us all the more, when we compare the thyroid of the *Axolotl*. This is pretty much enlarged (see table p. 833), chiefly in consequence of an accumulation of colloid, through which the follicles are considerably distended and their epithelium is completely flattened (fig. 6, 10, plate). Here the colloid is detained in the thyroid and in consequence the function of the epithelium decreases as is evident from the intense flattening. It can be concluded from the non-appearance of the metamorphosis that there is a hypofunction though the thyroids are enlarged, a condition which, if it should become pathological, would be comparable to colloid goitre (VON EBNER's larva with its 70 times enlarged thyroids, shows that goitre is possible also in *Urodeles*.)

It follows from the above observations that the thyroid of the *perennibranchiate* and the *derotremous Salamanders* is developed abnormally and that two types are to be distinguished:

- a. The reduced to rudimentary type with hypofunction of the *perennibranchiate Salamanders* *Necturus*, *Proteus* and *Typhlomolge*.
- b. The enlarged type with hyperfunction of the *derotremous Salamanders* and of the *perennibranchiate Siren*.

With regard to the second type, however, the question may be asked whether the secretion of the thyroid contains sufficient normal hormone, whether there is perhaps a dysfunction. It would seem to me that dysfunction is no less probable than an overproduction of normal hormone. I am led to think so in virtue of the interesting researches by ADLER (1916). In his cultures of larvae of *Rana temporaria* first at a high temperature (30°—32° C.), and then at low temperature (8°—10°) he obtained numerous larvae that did not metamorphose or were late and tardy in doing so. The thyroid of these larvae appeared to be hypertrophied, grew strongly and exhibited in preparations the typical aspect of a *Basedow-thyroid*; the form of the follicles is irregular, many new follicles are formed, the follicle-epithelium is cylindrical; the colloid in the follicles shows less and less affinity to stains, and grows less and less viscous. So it is clear that the thyroid functions vigorously; the non-appearance or the retardation of the metamorphosis cannot be due to a feeble functioning of the thyroid, it must be ascribed to the quality of the product, which is insufficient. As the thyroid of the *derotremous Salamanders* and of *Siren* reveals a similar transformation and the very tardy metamorphosis implies a lack of hormone, there is some reason to assume a dysfunction also here.

Now, in this connection it is of paramount significance that, just as there are two types of transformation of the thyroid, there are also two

types of neoteny among the permanently neotenous forms of the *Urodeles* (VERSLUYS 1909, 1912, 1923) and that these two coincide.

Necturus, *Proteus* and *Typhlomolge* are completely in the developmental stage of an *Urodele*-larva, just before the metamorphosis. They correspond in their structure with *Axolotls* and the not unfrequent neotenous, perennibranchiate specimens of *Triton* and other *Salamanders*. Like these they must have originated suddenly, because the metamorphosis stayed away, yet the animals became sexually mature and could propagate. That this neoteny is hereditary, we know from the *Axolotl* and has been demonstrated by DE FREMERY and VAN SWINDEREN for a neotenous race of *Triton taeniatus* (DE FREMERY 1924; VAN SWINDEREN 1925). The neoteny of *Megalobatrachus*, *Cryptobranchus*, *Amphiuma*, *Siren*, and the related *Pseudobranchus* however is a quite different one; these animals do not make a halt before the metamorphosis; they commence it, indeed, but they do not finish it. It cannot be that the metamorphosis is here quite suppressed; it is only retarded and not completed. This transformation may have been reached very gradually; the metamorphosis was then at first still almost completed¹⁾, subsequently more and more incomplete²⁾, until even the external gills were retained in *Siren*. On the other hand in several respects the structure of *Siren* is not purely larval, but resembles that of a full-grown animal or anyhow of a *Salamander* in its metamorphosis, which is evident from the well-developed lungs, from the auditory ossicle, from the interruption of the larval palatinum-quadrangle bone-junction, from the structure of the olfactory organ with JACOBSON's organ, and from the occurrence of an independent coracoidbone in the shoulder-girdle. In consideration of this combination of larval structure with that of adult *Urodeles* *Siren* cannot be conceived to have originated suddenly through suppression of the metamorphosis, but only through a gradual slowing and retrogression of the metamorphosis which was lengthened out, just as in the derotremous forms. Although *Siren* and *Pseudobranchus* possess external gills like the *perennibranchiate* *Salamanders* *Necturus*, *Proteus* and *Typhlomolge*, the type of their neoteny is not that of these forms, but is completely the same as that of the *Derotremata*. Now it is remarkable that also the transformation of the thyroid in *Siren* resembles that of the *derotremous* *Salamanders* and is unlike that of the other *Perennibranchiates*.

The specimen of *Siren* examined by me has peculiarly shaped thyroids which extend forward to a considerable distance and unite there to an unpaired median part, corresponding to the processus pyramidalis of the human thyroid (fig. A 3).

¹⁾ As still is the case in the *Giant-Salamander*, that does not only shed the external gills, but also shuts its gill-clefts, though it be only after years.

²⁾ *Cryptobranchus* and *Amphiuma* in which the gill-clefts are always open, and the skeletal gill-arches remain larval.

In the typical *perennibranchiate Salamanders* *Necturus*, *Proteus* and *Typhlomolge*, the larval structure is retained completely; so their neoteny is a *complete* one, and the thyroid is reduced to rudimentary, with hypofunction. *Derotremata* and *Siren* retain the larval form only in part; their neoteny is *incomplete*, and the thyroid of these forms is enlarged with hyperfunction, which probably goes hand in hand with a dysfunction. Here we should bear in mind that the various neotenous forms must have originated independently: they are not interrelated except *Siren* and *Pseudobranchius*, and perhaps also *Megalobatrachus* and *Cryptobranchius*. *Three times the complete neoteny arose independently in Necturus, Proteus and Typhlomolge, and in this process the transformation of the thyroid invariably went in the same direction: hypofunction and reduction. The incomplete neoteny also arose at least three times; once in Amphiuma, a second time in Megalobatrachus and Cryptobranchius, and a third time in Siren and Pseudobranchius; in this case there is always enlargement of the thyroid with hyperfunction.* This points to a correlation of the way in which the thyroid is modified and the type of the neoteny.

What conclusion can we now deduce from these observations with respect to the causes of the neoteny of perennibranchiate and derotromous Salamanders?

There is reason to look for the cause of the neoteny in a shortage of hormone, which brings about retardation or total absence of the metamorphosis. In the completely neotenous *Axolotl* the metamorphosis can be elicited by the administration of a larger amount of hormone¹⁾, so that in this form the neoteny can be unreservedly ascribed to a shortage of hormone (see SWINGLE 1924). This also affords a plausible explanation for the neoteny of *Necturus*, *Proteus* and *Typhlomolge* with their reduced thyroids. However, another explanation also suggests itself, viz. that for some reason or other the body no longer reacts with metamorphosis on the thyroid-hormone (UHLENHUTH 1921). SWINGLE (1924) believes that this must be somewhat the case in the *Axolotl*. Neither do *Necturus* and *Proteus*²⁾ react any more on the administration of thyroid hormone (JENSEN, 1916; SWINGLE, 1924). The degeneration of the thyroids then would result from the suppression of the metamorphosis. But just this is very improbable, for if the normal development of the thyroid were really so closely bound up with the metamorphosis, we might also expect in normal *Salamanders* after the metamorphosis an atrophy of the thyroids. The two cases are comparable.

¹⁾ Here the thyroid produces rather much hormone but retains too much of it, instead of supplying the hormone to the body.

²⁾ Since the fourth arterial arch has disappeared here these forms could not metamorphose completely, nevertheless this process might commence for all that (see BOAS, 1881).

Now, since an atrophy of the thyroid after the metamorphosis does not appear in these animals, and since on the other hand the thyroids continue to grow considerably, keeping pace with the growth of the body, we can neither assume that the degeneration of the thyroids in the neotenus Salamander forms results from the neoteny. The relation must be the reverse, viz. the neoteny resulted from the dysfunction of the thyroids, because the body did not receive sufficient hormone. That the two forms of neoteny, the complete and the incomplete form, present either of them a type of transformation of the thyroid of their own also speaks for a far closer correlation than would exist with a passive degeneration of the thyroids as a result of the suppression of the metamorphosis.

For an explanation of the occurrence of the neoteny let our starting point be a shortage of hormone. Then there are still two possibilities to be considered: 1⁰ this shortage may result from an insufficient production of normal hormone, 2⁰ it may also be that the thyroids do not impart an adequate amount of hormone to the body, but retain it and deposit it in the colloid. The latter is probably the case with the *Axolotl* (UHLENHUTH, 1919, 1923; SWINGLE 1922, 1923 A, 1924). There the thyroid resembles that of Man in colloid-goitre (p. 836), which is a consequence of an inhibited emission of secretion to the body (BREITNER 1924). A factor is missing, which makes the thyroids deliver their hormone; this factor may be a nerve stimulus, or an hormone from the anterior lobe of the hypophysis, or it may arise from a deficient circulation, or lack of oxygen (on the latter factor see BREITNER 1924, p. 4, after MANSFELD-MÜLLER). In this way the complete neoteny of *Necturus*, *Proteus* and *Typhlomolge* can readily be interpreted. By some cause or other the thyroids no longer emitted their hormone, hence they lost their significance and ultimately they became smaller and degenerated. Owing to the retention of the hormone all at once a complete neoteny was engendered, as is typical of these animals.

This interpretation does not apply to the *derotremous* forms and *Siren*, as in them hormone is indeed imparted to the body, which is obvious from the fact that metamorphosis commences. Besides this we have already observed that the structure of the thyroid here points to a hyperfunction and quick emission of the secretion to the body. Most likely we have to do here with a dysfunction, so that the thyroids, although functioning vigorously, and emitting their secretion, yet cannot supply the normal quantity of hormone required by the body (p. 836). The phylogeny of these forms may be imagined to be as follows: The increasing dysfunction of the thyroids retarded the metamorphosis, which began ever later and lasted longer; the animals became sexually mature in their metamorphosis and did not accomplish their metamorphosis. This was gradually lengthened out, it was still gone through entirely, or partly for some points of their anatomy, for others only for a small part or not at all. Here accommodation to outward circumstances can have been of great influence. The thyroids

tried to make up for the shortage of hormone by enlarging, but they did not succeed in filling up the deficiency.

Thus the two types of neoteny as well as the associated types of transformation of the thyroids can be explained and correlated. We think that we have to look for the cause of the neoteny, for the origin of the *perennibranchiate* and *derotremous Salamanders* in the thyroid. Either a change in the hormone production or in the supply of hormone to the body was the cause of the origin of these forms, which could develop to quite new types among the *Urodeles*. This transformation was achieved in the open air, and inadequate forms could not survive; only those forms persisted that were suited to their environment or could soon adapt themselves to it. For the ancestors of the *Derotremata* and of *Siren* an evolution from a more terrestrial life to a permanent aquatic existence can in this connection have been of influence, because the metamorphosis lost part of its importance for the animal by this change.

Lastly the question may be raised what might then have been the cause or the causes of the irregular function of the thyroids. All sorts of factors can have come into play here. It may have been want of iodine or an influence of the changes in the vascular system during the metamorphosis. It cannot be said whether this supposition is right or not.

Summary.

1. The neoteny of the *perennibranchiate* and *derotremous Salamanders* goes hand in hand with an abnormal development of their thyroids. As the hormone of the thyroid controls the metamorphosis, a case is given here in which the phylogenesis of entirely new animal forms is associated with a change in an endocrine organ closely related with it.

2. Among *Urodeles* there are two types of neoteny: that of the *perennibranchiate forms* proper *Necturus*, *Proteus* and *Typhlomolge*, which in their structural development persist in the stage of the full-grown *Urodele* larvae, before the metamorphosis, and that of the *derotremous forms* *Megalobatrachus*, *Cryptobranchus*, *Amphiuma* and of *Siren* and *Pseudobranchius*, which begin their metamorphosis, but do not accomplish it. An entirely different transformation of the thyroids coincides with this. In the first type the thyroids are small to rudimentary, and there is apparently a hypofunction of the thyroids. In the second type the thyroids are enlarged, and there is apparently a hyperfunction of the thyroids, probably associated with a dysfunction. Since the two types of neoteny have originated several times independently of each other, and yet the transformation of the thyroids in each type always went in the same direction, a close relation must needs be assumed between the neoteny and the mode of transformation of the thyroids.

3. The cause of the complete neoteny of the *perennibranchiate forms* is probably to be found in the retention of the hormone in the thyroid, which induced a complete suppression of the metamorphosis. The thyroids lost much of their significance, when they could no longer supply their hormone, or for a small part only.

4. The *derotremous forms* and *Siren*, with their incomplete neoteny, do not retain the hormone in the thyroid. Here the cause of the neoteny is to be looked for in a dysfunction which induced a chronic deficiency of normal hormone, and a marked retardation and final arrest of the metamorphosis. The thyroids tried to supply the deficiency of hormone by an augmented production and increased in size.

5. The *perennibranchiate forms* with their complete neoteny abruptly retained their larval stage; this transformation was not an accommodation to their environment, and after the change the animals had to make the most of their condition as permanent inhabitants of the water. The development of the *derotremous forms* and *Siren* has been very gradual, because their ancestors gradually retained a more and more larval stage; so this transformation could take place under the influence of the claims of their surroundings, and could coincide with adaptations.

6. Nothing is known regarding the cause of the irregular function of the thyroids. It might be ascribed to want of iodine or changes in the circulation during the metamorphosis, or want of oxygen. There is no reason to assume that the cause was the same in all cases.

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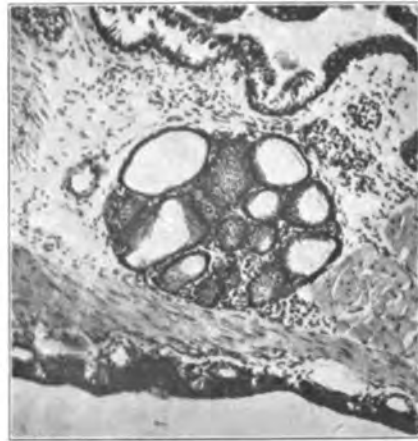


Fig. 1.



Fig. 2.

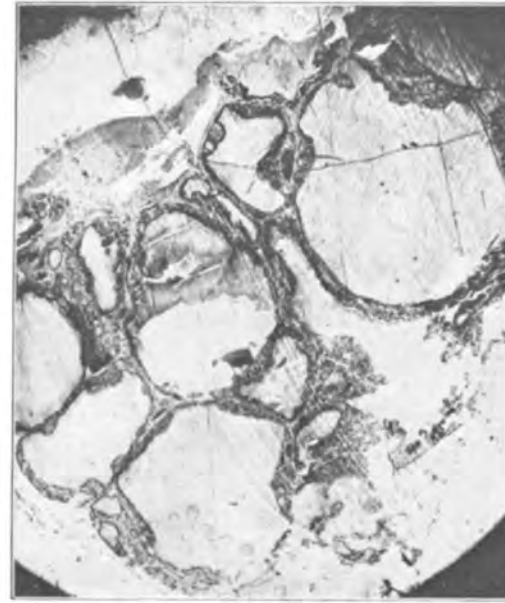


Fig. 5.



Fig. 6.

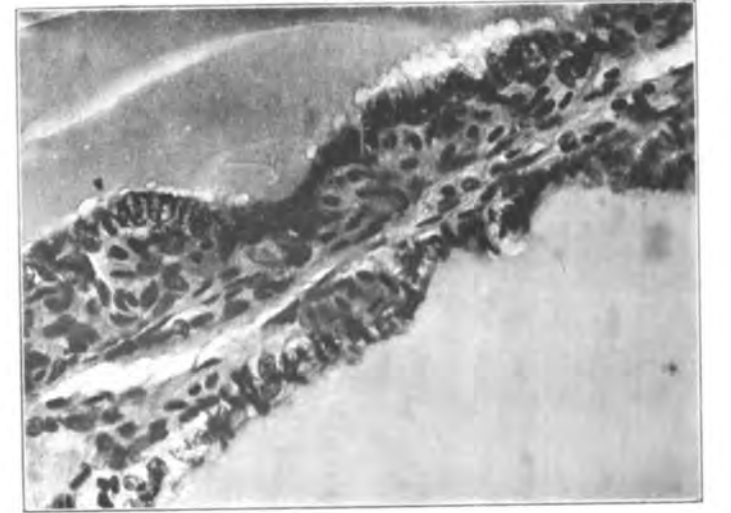


Fig. 9.



Fig. 3.



Fig. 4.

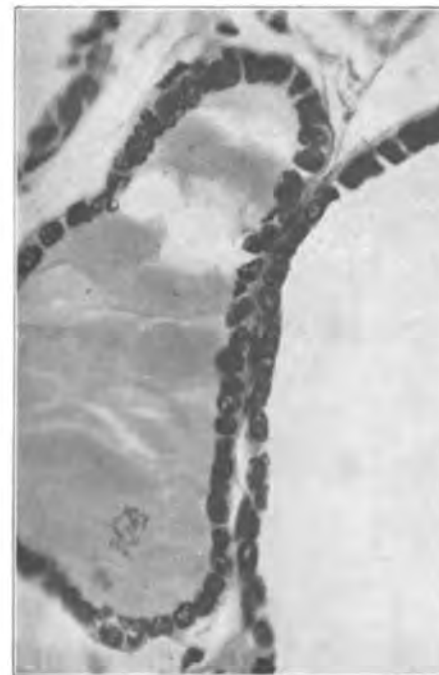


Fig. 7.

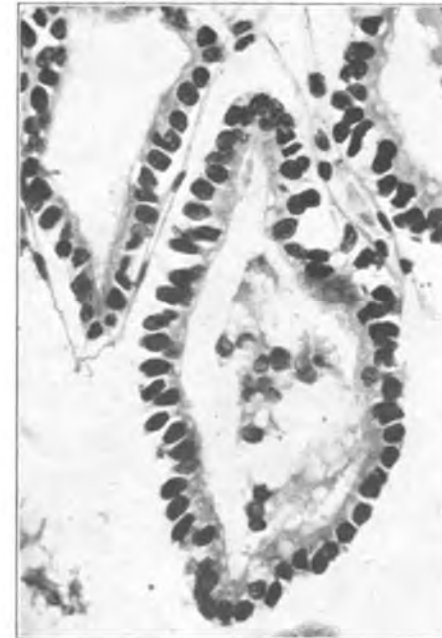


Fig. 8.

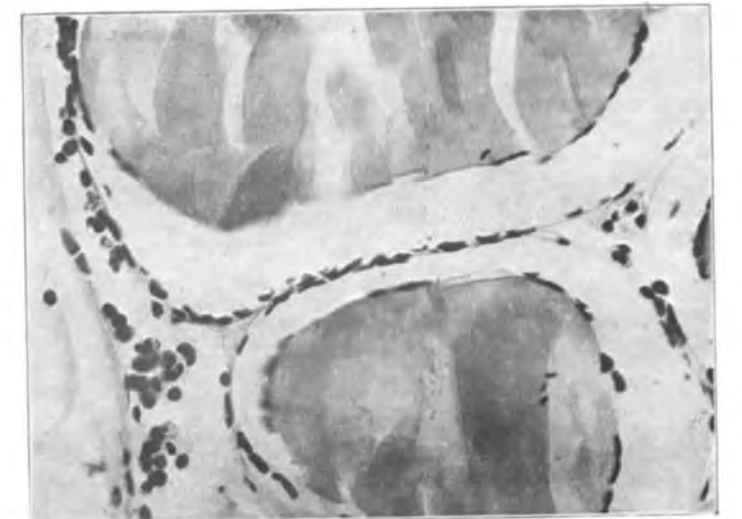


Fig. 10.

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EXPLANATION OF THE PLATE.

Fig. 1. Section through the thyroid of a normal adult *Salamander, Onychodactylus japonicus*; hematoxilin. $\times 40$.

Fig. 2. The same of *Necturus* (spec. B); hematoxilin, eosin. $\times 40$.

Fig. 3. The same of *Amphiuma* (spec. B); hematoxilin, eosin. $\times 40$.

Fig. 4. The same of *Amphiuma* (spec. A); hematoxilin $\times 40$.

Fig. 5. The same of *Megalobatrachus maximus*, of a specimen, examined by Mr. DE FREMERY. Body-length ± 110 cm. The thyroids were about 5 cm. in length, that is very large. Staining with hematoxilin and eosin. $\times 18$.

Fig. 6. Section through the thyroid of *Amblystoma mexicanum* (ex. D), neotinous larva (axolotl). Staining with hematoxilin, eosin. $\times 40$.

Fig. 7. The same of *Necturus* (spec. B); follicle epithelium greatly magnified; hematoxilin, eosin. $\times 190$.

Fig. 8. The same of *Amphiuma* (spec. B); hematoxilin, eosin. $\times 190$.

Fig. 9. The same of *Megalobatrachus maximus* (ex. DE FREMERY). Between the follicles very numerous bloodvessels filled with red blood corpuscles; hematoxilin, eosin. $\times 190$. See fig. 5.

Fig. 10. The same of *Amblystoma mexicanum* (spec. D), Axolotl; hematoxilin, eosin. $\times 190$.

Anatomy. — "*The relative weight of the braincortex in human races and in some animals and the asymmetry of the hemispheres.*"
By Dr. C. U. ARIËNS KAPPERS.

(Communicated at the meeting of September 26, 1925).

Although many investigations have been made on the weight of the cortex, at least in man, there are great controversies in the results. As the methods, by which the investigators have tried to solve this problem, always were indirect ones, this is not surprising.

So, using the figures, given by WAGNER ¹⁾ and CALORI ²⁾ concerning the surface of the brain, DONALDSON ³⁾ (l.c. p. 202—204) calculated this weight by multiplying the surface with the average depth of the human cortex and its specific weight.

On account of his own measurements (l. c. p. 203) he estimated the average depth of the cortex, which, as we know, is locally varying in man (according to BRODMANN ⁴⁾ from 1,8 tot 4,0 m.M.) to be 2,9 m.M. With OBERSTEINER ⁵⁾ he took the S. W. of the human cortex to be 1,034.

DONALDSON, improving the researches of WAGNER by introducing a correction ⁶⁾ for the alcoholic shrinkage of the brainsurface so found the following figures:

Cases	Fresh T. B. W. ⁷⁾	T. W. hem. ⁸⁾	T. W. C. ⁹⁾	Proc. C. hem.
FUCHS	1499 gr.	1312 gr.	743 gr.	56.6 0/0
GAUSS	1492 ..	1306 ..	731 ..	55.9 0/0
Workman KREBS	1273 ..	1114 ..	630 ..	56.5 0/0
Woman 29 years	1185 ..	1037 ..	667 ..	64.3 0/0
Average				58.3 0/0

¹⁾ Massbestimmungen der Oberfläche des grossen Gehirns. Inaugur. Diss. Göttingen 1864.

²⁾ Del cervello nei due tipi brachicefalo e dolicocefalo italiani. Memorie dell'Accademia delle Scienze dell'istituto di Bologna. Serie seconda, Tomo X. 1870 (p. 142—145).

³⁾ The growth of the brain. A study of the nervous system in relation to education. London, Walter Scott ltm, 1895.

⁴⁾ Ueber Rindenmessungen. Centralblatt f. Nervenh. und Psych. 1908 (p. 790) und Lokalisationslehre der Grosshirnrinde. Joh. Ambrosius Barth, Leipzig, 1909.

⁵⁾ The average S.W. found by OBERSTEINER for the fresh cortex of man is properly 1.03305. Conf. OBERSTEINER. Anleitung beim Studium des Baues der nervösen Zentralorgane, 5te Auflage Wien, 1912, pag. 167 and Centr.bl. f. Nerv. h. k. 1894.

The average of the S.W. figures found by DANILEWSKY (already before OBERSTEINER) are also a little less. For the fresh human cortex this investigator found 1.0326. (Die Quantitativen Bestimmungen der grauen und weissen Substanzen im Gehirn; Centralbl. f. d. mediz. Wissensch. N^o. 14, 1880).

⁶⁾ The figures found by WAGNER for the surface of both hemispheres together are: FUCHS 2210 cM², GAUSS 2195 cM², KREBS 1876 cM², and woman 2041 cM².

⁷⁾ T. B. W. = total brain weight to the calamus (without pia).

⁸⁾ T. W. Hem. = total weight of both hemispheres.

⁹⁾ T. W. C. = total weight of the cortex of both hemispheres.

The following table was composed by DONALDSON on account of the surface extension, found by CALORI in 22 brachycephalic and 19 dolichocephalic Italians, measured chiefly in the same way as WAGNER did (see below).

Number of cases	Aver. T. B. W.	Aver. T. W. hem.	Aver. T. W. C.	Aver. perc. C. per hem.
19 Brach. Ital. ♂	1336 gr.	1169 gr.	731 gr.	62.5 %
16 Dolich. .. ♂	1299 ..	1135 ..	690 ..	60.7 %
3 Brach. .. ♀	1148 ..	1005 ..	635 ..	63.2 %
3 Dolich. .. ♀	1110 ..	971 ..	595 ..	61.2 %
Average				61.85 %

From this we see that, on account of the measurements of WAGNER, DONALDSON concludes at an average cortex weight percentage of 58.3, on account of those of CALORI of 61.85 per hemisphere.

It is not without interest to point out, what is meant by weight of hemispheres in such cases. Two methods are used to sever the hemispheres from the remainder of the brain. We understand by hemispheres either all that lies before the corp. quadrigemina ant. or cut them off behind the corpora quadrigemina posteriora (immediately before the pons). The first way is used by BOYD (see below) and then the average weight of the hemispheres is about 87.5% of that of the whole encephalon. The last method (mostly used) is followed by CLAPHAM, BROWNE and others (including myself).

The determination of the surface has been made by WAGNER and CALORI almost in the same manner.

The outer surface of the brain was covered by triangles and parallelograms of goldleaf or tinfoil. These again were spread out, measured and counted. The cortex in the depth of the sulci (which is almost $\frac{2}{3}$ of the whole surface) was determined by measuring the length and the average depth of the sulci and multiplying those figures with two. It is evident that this method contains a source of errors. Moreover the correction of the alcoholic shrinkage causes difficulties. Nevertheless such a correction is necessary, because the volume and the surface shrink considerably in alcohol.

This method, determining the cortical surface in alcohol material, was also applied by JENSEN ¹⁾ on brains of a paralytic, a melancholica and three idiots. He compared his results with those of WAGNER and found that the total cortex surface of his patients varied from 94% to 75.3% from the figures found by WAGNER for GAUSS, the lowest percentage being that of the brain of an idiot and the other percentages, although remaining below those of GAUSS and FUCHS, falling within the group of the woman and the workman examined by WAGNER (l. c. p. 752).

¹⁾ Untersuchungen über die Beziehungen zwischen Grosshirn und Geistesstörungen an sechs Gehirnen geisteskranker Individuen. Arch. f. Psychiatrie 1875 Bnd. V, Heft 3.

His absolute figures are of no avail for my purpose, since he examined pathological material exclusively and his figures have been derived (as the original ones of WAGNER) from alcohol material.

His informations surely would have been of more value, if he himself had also measured the surface of some normal brains; comparisons of two authors being more reliable, since different authors rarely make the same mistakes. It is selfevident that with the relative smaller surface of these brains, also a smaller volume and weight of cortex has been calculated in such cases, as is made probable also by the researches of JÄGER and HENNEBERG on pathological material (l. c. infra).

While the method of all these authors was based on measuring the surface, the average depth and on multiplying these with the S.W. of the cortex, we see that besides the objections mentioned above, this method contains still another source of errors, viz. the question how to find the average cortical depth, which was estimated by DONALDSON to be 2.9, by JENSEN 2.98, and by DANILEWSKY and HENNEBERG 2.5 m.M.

JÄGER¹⁾ has avoided the use of an average depth figure, determining the volume of the cortex directly with the compensation planimeter (already used by ANTON²⁾) in the following way:

JÄGER cut the brain, after it had been put for a short time in 5% formaline, in slices of 1 c.M.

He then first measured the whole circumference of the brain (this being the external border of the cortex) with the planimeter and afterwards the circumference of the white substance (this being the internal limit of the cortex). The latter he subtracted from the first and by this means determined the transverse surface of the cortex of each slice. This figure he multiplied with 1 c.M. thus calculating the volume of the cortex for each slice. For the poles he made corrections.

By multiplying the cortex volume thus found for the total brain with the S.W. 1.034, I determined the weight of the cortex. As, however, in

¹⁾ R. JÄGER. Planimetrische Messungen der Rinden- und Marksubstanz des Groszhirns. Inaugural Dissertation, Halle. 1910.

²⁾ G. ANTON. Gehirnmessungen mittels des Kompensationsplanimeters. Wiener Klinische Rundschau: 1903. See also: Zur Kenntniz der Störungen im Oberflächenwachstum des menschlichen Groszhirns, 1ste Mitteilung, Ibidem, Bnd. IX. 1888.

The planimetric method had been applied already in 1884 by CONTI, who, however, did not determine the whole mass of the cortex, but the relation between the white and the grey substance on three levels, the first *before* the basal ganglia, the second *through*, the third *behind* the basal ganglia, in 4 men and 2 women (Rapport entre la substance grise et blanche du cerveau humain: Internationale Monatschrift für Anatomie und Physiologie Bnd. I, 1884).

Moreover Dr. ANITA TAFT has in 157 cases determined planimetrically the relation between the grey and white substance in the transverse level of the optic chiasm. She attained the interesting result that in children, microcephalics and mongoloid idiots the relation was in favour of the grey substance, in normal cases, manic depressives and praecox patients in favour of the white substance. See Journal of nervous and mental diseases. Vol. 47, 1918.

his article the weight of the hemispheres is mentioned in one case only, the weightpercentage of the cortex of the hemispheres could be calculated in that case only. In a normal, four years old boy with a total brain-weight of 1140 gr. and a weight of both hemispheres together = 997,5 gr. it amounted to 549 gr. or 55 % of the weight of the hemispheres (in an adult normal woman he found 557 gr. cortex).

It appears that these figures of JÄGER are lower than those calculated by DONALDSON from the surface measurements of WAGNER and CALORI.

DONALDSON¹⁾ himself also tried to determine the weight of the cortex, in still another way, viz. by making use of the figures found by DE REGIBUS for the waterpercentage and the S.W. of grey and white substance. If a hemisphere (in casu cortex and white substance without striatum) is weighed and its volume known, we may calculate its average S.W. Knowing that the S.W. of the cortex is 1,034 and that of the white substance 1,041, we may calculate in a given case the relation between the amount of white and grey substance (in casu cortex).

From the figures of DE REGIBUS²⁾, concerning the waterpercentage of grey and white substance (which closely coheres with its S.W.), DONALDSON calculated the quantity of cortex and came to a lower figure than calculated by him from the surface tables of WAGNER and CALORI.

He stated in his way an average of 54.8 % only, which is considerably lower than the 58.3% derived from the surface measurements of WAGNER and the 61.85 % calculated from those of CALORI, and closely resembles JÄGER's (vide supra) result.

Nº. of the brain	Weight 2 hem.	Weight cortex	Perc. cortex per hem.
Nº. 1	1277 gr.	720 gr.	56.3 %
„ 2	1194 „	661 „	55.3 %
„ 3	1152 „	633 „	54.9 %
„ 4	1067 „	562 „	52.6 %
Average			54.8 %

This makes us suppose that the figures found by WAGNER and CALORI for the surface are too high, a supposition that is confirmed by HENNEBERG's³⁾ work, who determined the surface of the brain in a more exact way. I shall mention HENNEBERG's method below, but already

¹⁾ l.c. p. 204.

²⁾ Published in Giacomini: Guida allo studio delle circonvoluzioni cerebrali dell'uomo Torino, 1884.

³⁾ HENNEBERG. Messung der Oberflächenausdehnung der Grosshirnrinde. Journal für Psychologie und Neurologie, Bnd. 17, 1910—11.

will mention at once that, whereas DONALDSON (l.c. p. 205) on account of WAGNER's figures finds a surface of 2352 cm^2 in a brain of 1360 gr. T. B. W. and CALORI in a brain of 1325 gr. a surface of 2439 cm^2 , HENNEBERG only finds a surface of 2052 cm^2 in a brain of similar weight (1320 gr.), consequently 15 % less ¹⁾.

Probably the surface measures of HENNEBERG are more exact than those of WAGNER and CALORI. Whereas these authors divided the brain only in hemispheres or lobes, determining the surface hidden in the sulci only indirectly, HENNEBERG measured this hidden surface also directly, by cutting the cortex (after fixation of the brain in 10 % formaline) in pieces of 1 to 3 cm^3 . In this way all the cortex surfaces could be reached easily and measured directly.

For this purpose he used pieces of silkpaper, which does not swell in water, and then he measured all the pieces together by lifting them under water from the cortex and putting them on milligraphpaper. As objects he used (one case excepted) only the left hemispheres.

In this way he examined three Hannoverians, one Hottentot, one Herero and one Javanese. The cortexweight is calculated by taking the S.W. = 1.034 and the average depth with HENNEBERG ²⁾ and DANILEWSKY (l.c.) = 2.5.

Cases	T. B. W.	Average left hem.	Surface left hem.	Cortex left hem.	% Cortex hem.
German I ♂ 45 j.	— ³⁾	525 gr.	1082 cm^2	279.5	53.4 %
.. II ♂ 22 j.	1510 gr.	655 ..	1240 ..	320.5	48.9 %
.. III ♀ 26 j.	1320 ..	565 ..	1016 ..	262.6	46.5 %
Average					49.6 %
Hottentot ♂	— ³⁾	615 ..	1119 ..	289.0	47.0 %
Herero ♂	1215 ..	530 ..	996 ..	257.5	48.6 %
Javanese ♀	1230 ..	535 ..	1050 ..	271.5	50.7 %

Hence results that HENNEBERG found a still lower average percentage for Europeans (49.6 %) than DONALDSON calculated from the S. W., but also that in his Germans he found variations from 46.5 % to 53.4 %.

¹⁾ TRAMER who determined the surface of the right hemisphere of a normal woman of 35 years came to a figure still 20 % lower than HENNEBERG found for a woman of 26 years. As, however, TRAMER does not mention the T. B. W. of his woman, this figure is uncontrollable. It seems too small even for an average female T. B. W. of 1250 gr. (HENNEBERG's woman had a high brainweight though, this being 1320 gr. which however seems to occur more in Hannover; KRAUSE). See TRAMER: Messung und Entwicklung der Rindenoberfläche des menschlichen Grosshirns. Arbeiten aus dem neurologischen Institute Zürich, Bnd X, 1916.

²⁾ HENNEBERG himself made his calculations estimating the S. W. = 1.03; I made them using a S. W. = 1.034, this being more exact. The average difference is 0.3 % per hemisphere and 0.12 % per T. B. W.

³⁾ In this case the total brainweight is not mentioned by HENNEBERG.

While all these methods of determining the cortexweight are indirect ones and so, probably are more open for errors than a direct method, I made *direct weighings* of the cortex in the following way:

Brains, hardened in formaline¹⁾, were weighed and afterwards halved in the sagittal diameter. Then the cerebellum and the pons were cut off along the corpora quadrigemina posteriora and the hemispheres were weighed. Afterwards these hemispheres were cut by the macrotome of REICHERT, in slices of 2 to 3 m.m. During 3—6 hours these slices were coloured in an aqueous nigrosine solution (1 : 1000), upon which the grey substance marked out almost black against the almost uncoloured white substance.

These slices I put on glass plates and severed the cortex by means of a thin knife. Then I weighed the cortex, after all the pieces (cortex and rest of hemisphere) had evaporated so much that the cortex plus the rest represented again the same weight the hemisphere had before being coloured in the nigrosine solution. This drying is necessary, as by their large surface the pieces absorb a large quantity of water.

In total 6 brains (12 hemispheres) were treated in this way; three Dutch and three Chinese brains from the Dutch East-Indies (formaline material).

My results are expressed not only in percentages of the hemisphere weight, but also in percentages of the T. B. W., the latter giving a more reliable figure for comparison of the left cortex and the right one.

LEFT HEMISPHERES

Cases	T. B. W.	Weight l. hem.	Weight l. cortex	Weight l. rest	% cortex p. hem.	% cortex p. T.B.W.
Dutch. X. ♂ 29 y.	1068 gr.	-474.5 gr.	237 gr.	237.5 gr.	49.99 %	22.2 %
„ Gr. ♂ 42 y.	1375 „	+618 „	+299 „	319 „	48.38 %	+21.74 %
„ Bo. ♂ 18 y.	1360½ „	-621 „	331 „	290 „	53.3 %	24.32 %
Average l.					50.8 %	
Chinese I. N ^o . 11	1014.5 „	-430 „	+218 „	212 „	50.0 %	+21.49 %
„ I. N ^o . 10	1344 „	-576 „	+300 „	276 „	52.1 %	+22.32 %
„ I. N ^o . 12	1425.5 „	-615.5 „	313.5 „	302 „	50.9 %	22.0 %
Average l.					51.0 %	

¹⁾ That as well the weight as the volume increase a little ($\pm 1\%$ FLATAU) in formaline, does alter the relation between cortexweight and hemisphereweight only in a very small proportion. The same avails for the aqueous 1% nigrosine solution. The influence, exercised by the formaline-fixation, in my opinion is even smaller than the greater or smaller quantity of blood in the brain, as the S.W. of the blood is considerable and the vascularisation of grey and white substance differs much.

RIGHT HEMISPHERES

Cases	T. B. W.	Weight r. hem.	Weight r. cortex	Weight r. rest	% cortex p. hem.	% cortex p. T.B.W.
Dutch X. ♂ 29 y.	1068 gr.	+477.5 gr.	+238.5 gr.	239 gr.	49.94 %	+22.33 %
.. Gr. ♂ 42 y.	1375 ..	-613 ..	297 ..	316 ..	48.4 %	21.16 %
.. Bo. ♂ 18 y.	1360 ¹ / ₂ ..	+622 ..	+336 ..	286 ..	54.0 %	+24.6 %
Average r.					50.6 %	
Chinese I. N ^o . 11	1014.5 ..	+437.5 ..	212.5 ..	225 ..	48.61 %	20.94 %
.. I. N ^o . 10	1344 ..	+584 ..	297 ..	287 ..	50.86 %	22.1 %
.. I. N ^o . 12	1425.5 ..	+638 ..	+320 ..	318 ..	50.11 %	+22.45 %
Average r.					49.9 %	
Average for all hemispheres of the Dutch					50.65 %	
.. Chinese					50.45 %	

The halving of the brain being never exact the cortexpercentage per hemisphere is influenced by the inexact halving of the brain, whereas we use the same constant, in expressing the cortexpercentage (right and left) in the total brain weight.

Doing so I found the average cortexpercentage per hemisphere to be 50.65 % in the Dutch, this being almost 1 % more than the figures, found by HENNEBERG in his Hannoverians. This amount (1 %) however falls within the individual variations in the West European races, showing an upperlimit of 54.0 %.

The percentage in the Chinese, mentioned above differs only 0.2 % from the Dutch, which is very little, and falls within the errors inevitable in such examinations. This result is in striking contrast to CLAPHAM's ¹⁾, who, estimating the depth of the braincortex in Chinese coolies of Hongkong (and of Pelewislanders) concluded: "although destitute of any means of accurately measuring the depth of the grey matter of the cerebral convolutions I am convinced that it was appreciably shallower than in the same structure in the average European".

As to an eventual difference between the left and right cortex, my results show that once the right, another time the left cortex was, or seemed to be a little heavier. I value this difference the less, because it depends mostly on absorbed water. If we allow the pieces of cortex

¹⁾ CROCHLEY CLAPHAM. On the brain weights of some Chinese and Pelewislanders. Journal of the Anthropological Society of Great Britain and Ireland. Vol. VII 1878, pag. 92.

half a day to evaporate, the difference between right and left becomes a minimal.

Much has been written on an eventual asymmetry.

BROCA ¹⁾ found in the average the *right* hemisphere of men 1,93 gr. heavier than the left, in women the same hemisphere 0,03 gr. heavier; BOYD ²⁾, however, says: "it is a singular fact confirmed by the examination of nearly 200 cases at St. Marylebone in which the hemispheres were weighed separately that almost invariably the weight of the *left* hemisphere exceeded the weight of the right one by at least the eighth of an ounce", (a very small difference indeed, the eighth of an ounce being 3,7 gr. so the difference in an average brain weight of 1360 gramme would be only 0,27 %; DONALDSON).

Dr. THURNAM (quoted by BROWNE) in the contrary again found the *right* one heavier. According to CRICHTON BROWNE ³⁾ it is a question of age. In 400 lunatics he found the right hemisphere predominating with the exception of women between 40 and 60 and men between 50 and 60, in as much as here the left hemisphere would be a little heavier. He found the greatest differences to exist under 20 years and then always in favour of the right hemisphere, this also being the case with people older than 70 years.

In contrary to the results above mentioned FRANCESCHI ⁴⁾ found in 157 male brains in 49 cases the left hemisphere and in 51 the right one heavier, while in 57 cases they practically were of equal weight.

In 144 female brains he found in 43 cases the left hemisphere, in 46 cases the right one heavier and in 55 cases both hemispheres of equal weight (or varying in decimals of grammes). Also WAGNER (l.c.) and BRAUNE ⁵⁾ sometimes found the left, sometimes the right hemisphere a little heavier.

DONALDSON supposes that, if the brain is always halved in the same position e. g. on the base, the occipital pole directed to the cutter, a righthanded anatomist will allways make the same error.

This personal error, in halving the brain, vanishes in weighing only the cortex, as the cortex of both hemispheres nowhere meets, the cortex of each hemisphere being isolated. So the comparison of the quantity of cortex in the right hemisphere and the left one gives a more trustworthy criterium for an eventual asymmetry, especially if we express both in the same constant, viz. in % of T.B.W. The figures found by myself also prove

¹⁾ Cited by TOPINARD in his *Eléments d'Anthropologie générale* p. 582—583. Paris 1885.

²⁾ BOYD. *Tables of weight of the human body and its internal organs etc.* Philosophical Transactions of the Royal Society of London. Vol. 151, 1861.

³⁾ CRICHTON BROWNE. *The weight of the brain and its component parts in the insane.* Brain Vol. I 1879 p. 516.

⁴⁾ Bollettino della Societa di Scienze mediche di Bologna 1888. Quoted after DONALDSON.

⁵⁾ BRAUNE. *Das Gewichtsverhältnisz der rechten und linken Hirnhälfte beim Menschen.* Arch. f. Anat. und Physiol. 1891.

that none of the hemispheres is constantly superior in cortexpercentage.¹⁾

In three cases (marked in my table by †) the right cortex was a little heavier, in three other cases (marked also by †) the left. HENNEBERG, though examining chiefly left hemispheres, has in one case (his European No. III with a T. B. W. = 1320 gr.) compared the surfaces of both hemispheres and found on the right 1035 c.M², on the left 1026 c.M², the result (multiplied with 2,5 as average depth and 1,034 as S. W.) being only a difference of fully five grammes (0,3 % per T. B. W.) in favour of the right cortex. This figure is within the radius of errors, as is also the average surplus of the right cortex in some of my brains (4,3 gr.) and of the left one in others (3,5 gr.).

My results show at best that the left cortex and the right one never are exactly equal in weight and that once the left and an other time the right one is or seems a little heavier. Nor in animals did I find a constant preponderance (see next page). This accords with the results of FRANCESCHI, WAGNER and BRAUNE, who too, in the hemispheres, found sometimes the left, sometimes the right one a little heavier.

Moreover my results show that halving the brain is a very poor way indeed, to determine any *superiority* of one hemisphere. Whereas of my six brains in one case only, the left hemisphere was heavier, in the other five cases the right one, the cortex determinations show that in three cases the left cortex percentage per T.B.W. was heavier, in the other three the right one. So in two cases (Chinese 11 and 10) in which the left hemisphere seemed to be lighter the cortex was nevertheless heavier.

Here already I should like to remark, that the calculation of cortexpercentage per T. B. W. is of value only for the mutual comparison of the right cortex and left one of one and the same cerebrum, not for the cortexpercentages of different individuals, as in another paper (see the following issue of these proceedings) I shall prove, that the weight of the cerebellum (being an important factor also in the T.B.W.) shows very large personal variations, as well in the Dutch as in the Chinese (from 8 to 12 % of the T. B. W.).

To conclude some remarks on the cortexweight in animals.

Nor here direct weighings have ever been made.

WAGNER measured the surface of the cortex in an Orang, and found it to be 533.5 c.M², and HENNEBERG found in an Ateles (with a T.B.W. = 142,5 gr. and a hemisphere weight = 64.5 gr.) a surface of 172 c.M². As, however, neither the average depth, nor the S.W. of the cortex is known in these animals, we cannot conclude from these figures to a weight percentage.

Supposing the S. W. in WAGNER's case also to be 1,034, and the average depth = 2,47 m.M², the Orang of WAGNER would have a cortexweight almost equal to the cortexweight of my Orang.

¹⁾ This does not eo ipso exclude (areal) local weight asymmetries, although I doubt their constancy. See however also MELLUS. Anat. Record. V. 1911.

²⁾ According to MARBURG the average depth of the cortex, calculated from the frontal, central, temporal and occipital lobus, is even a little bit larger (2,53 m.m) i.e. p. 585.

I weighed the cortex of a Marsupial (*Macropus robustus*), an Edentate (*Choloepus didactylus*), an Ungulate (horse), a Carnivore (dog), two katarhine apes (*Semnopithecus cephalopterus* and *Hylobates syndactylus*) and an Anthropoid (Orang). The figures found for these animals, are shown in the following table.

Examining these figures more closely we observe that, in each of these animals the average cortexpercentage of both hemispheres is as large, or in most cases (*Choloepus*, Dog, *Hylobates* and Orang) even larger than in Man, this being a consequence of the fact (see below) that smaller brains generally have more grey matter than white matter. So we also understand the observation of Miss TAFT, who found in children, microcephalics (and mongoloid idiots) a cortexpercentage, arger than in normals (l.c.).

Next to this statement two more facts are striking in this table.

LEFT HEMISPHERES

Animals	T. B. W.	Weight l. hem.	Weight l. cortex	Weight l. rest	% cortex per hem.	% cortex p. T. B.W.
<i>Macropus rob.</i>	55 gr.	20.5 gr.	10 gr.	10.5 gr.	48.7 %	18.2 %
<i>Choloepus did.</i>	34 ..	13.1 ..	7.1 ..	6 ..	53.8 %	+20.88 %
<i>Canis fam.</i>	78.5 ..	34.1 ..	21.1 ..	13 ..	61.9 %	+26.95 %
<i>Equus cab.</i>	510 ..	187.2 ..	96.2 ..	91 ..	51.3 %	+18.86 %
<i>Semnopith. ceph.</i>	65 ..	27.6 ..	13.1 ..	14.5 ..	47.3 %	20.15 %
<i>Hylobates syn.</i>	105 ..	43.0 ..	25 ..	18.0 ..	58.14 %	23.8 %
<i>Simia satyrus</i>	293 ..	122.7 ..	67.2 ..	55.5 ..	54.77 %	22.87 %

RIGHT HEMISPHERES

Animals	T. B. W.	Weight r. hem.	Weight r. cortex	Weight r. rest	% cortex p. hem.	% cortex p. T. B.W.
<i>Macropus rob.</i>	55 gr.	20.5 gr.	10 gr.	10.5 gr.	48.7 %	18.2 %
<i>Choloepus did.</i>	34 ..	13 ..	7 ..	6 ..	53.8 %	20.58 %
<i>Canis fam.</i>	78.5 ..	33 ..	20.5 ..	10.5 ..	62.1 %	26.18 %
<i>Canis f. collie</i>	77.7 ..	32.35 ..	20.0 ..	12.35 ..	61.9 %	25.74 %
<i>Equus cab.</i>	510 ..	185 ..	96 ..	89 ..	51.9 %	18.82 %
<i>Semnopith. ceph.</i>	65 ..	26.5 ..	13.5 ..	13 ..	51.0 %	+20.77 %
<i>Hylobates syn.</i>	105 ..	44 ..	25.5 ..	18.5 ..	58 %	+24.3 %
<i>Simia satyrus</i>	293 ..	122.5 ..	69.5 ..	53.0 ..	56.73 %	+23.64 %

Firstly the high cortexweight per T. B. W. in *Canis* is astonishing¹⁾, especially in comparison with *Semnopithecus*, which has a smaller brainweight and a higher standing in the phylogenetic series. With both these facts we should rather expect a larger cortexpercentage in *Semnopithecus*, the larger development of the brain in apes causing the pallium to be developed more than the stem.

That a heavier cerebrum ought to have less cortex relatively than a lighter one (at least in the same group or in related animals) is explained by ERNST DE VRIES²⁾ and HOVY³⁾ who showed that, if the brainvolume increases (in related groups), the white matter must increase relatively more than the grey one⁴⁾.

Now dogs and apes are not related but still both are gyrencephalic animals and by the lower standing of the dog as well as by his larger brainvolume we would expect *Canis* to have a lower cortexpercentage than *Semnopithecus*.

This not being the case, but in the contrary *Canis* having a surprisingly high cortexpercentage, consequently that can be explained only by the large development of the mantle and the depth of the sulci in this animal.

It would not surprise me, if the relation between the superficial cortex and the hidden cortex (being in man in the average 1 : 2 and in Orang 1 : 1,56) would be larger in *Canis*.

That the mantle of the brain is exceedingly developed in the first dog, also results from the fact that his hemispheres amount to 86,8% of the T. B. W. (in the collie 83,3%), in my apes the average being 82,9% only.

A second remarkable fact is the high cortexpercentage in *Hylobates*. Although the cortex percentage in the Orang as well as in *Hylobates* is high, in the latter it is still higher than in the former.

We cannot be surprised that in the Orang the cortexpercentage per T.B.W. is higher than in *Semnopithecus*, since in anthropoids the mantle of the cerebrum is more developed than in *Semnopithecus*.

That however *Hylobates* has a higher cortexpercentage than the Orang cannot be explained by its smaller brainvolume alone, since from this standpoint the cortexpercentage in the still smaller brain of *Semnopithecus* ought to be still higher than in *Hylobates*. Which is not so.

That *Hylobates* has a greater percentage than *both* other apes can be only explained by a larger depth of the cortex in *Hylobates* than in the other apes mentioned above.

¹⁾ A second examination of the right hemisphere of a collie confirmed this fact, which besides is also in harmony with the results of DANILEWSKY (l. c.).

²⁾ ERNST DE VRIES. Das Corpus striatum der Säugetiere. Anat. Anzeiger Bnd. 37, 1910.

³⁾ HOVY. On the relation between the quantity of white and grey substance in the central nervous system. These Proceedings 16, p. 311, 1913

⁴⁾ The lower cortexpercentage in *Equus* falls within this group.

This explanation agrees with the measurements of Marburg ¹⁾. This author also emphasizes „dasz die Rindenbreite des Hylobates absolut gröszer ist als die des Orangs, letzere aber gröszer als die der anderen untersuchten Affen.“ (l. c. p. 596).

This is in perfect harmony with my results.

At last still one remark.

Comparing my results with those of DONALDSON ²⁾ for the Norwegian rat, we find (l. c. p. 87) the cortexvolume (XX): being 393,15 m.m., the spec. weight = 1,05 (l.c. p. 76), the cortexweight to be 0,4128 gr. in the rat. The brainweight in this group being 2,054 gr. (l.c. p. 87), the relation of the T. W. C. to the total brainweight = 20,1 % or in one hemisphere 10,05 % per T. W. B.

This is a much smaller percentage than in my animals and in man. We know, however, that in most gyrencephalic animals more cortex is found in the sulci than on the surface, and ought to consider that the rat is lissencephalic. Were apes and man also lissencephalic, i.e. were there no cortex hidden in the sulci, the cortexpercentage of a hemisphere per T. W. B. would be even less than in the rat and amount to 7 % scarcely, whereas it actually is in man and the higher apes more than 22 % per T. B. W.

So also by my figures we may realize the great importance and necessity of fissuration for higher cortical development.

¹⁾ MARBURG. Beiträge zur Kenntniz der Groszhirnrinde der Affen. Arbeiten aus dem Neurolog. Institut in Wien, 1907.

²⁾ DONALDSON. The rat. 2d. ed. Memoirs Wistar Instit. Philadelphia 1924.

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Chemistry. — "*Equilibria in systems, in which phases, separated by a semi-permeable membrane*". XII. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of October 31, 1925).

Systems in which a substance different to water diffuses through the membrane.

In fig. 1 ab represents the saturation-curve of a hydrate H and bc that of the solid substance Y . For the present we let out of consideration the saturation-curve of the solid substance X , represented in the figure by curve de , and, therefore, we imagine this disappeared out of the figure.

If we take the component Y as diffusing substance, then follows, as we have seen in the previous communication, that the O.Y.A. (osmotic Y -attraction) of the liquids of the saturation-curve ab increases in the direction of the arrows, viz. from b towards a . As bc is the saturation-curve of solid Y , all liquids of this curve have the same O.Y.A. The dotted curves represent isotonic Y -curves; in the previous communication we have seen that in the vicinity of curve bc these curves have a similar form as this curve, and that the O.Y.A. of their liquids becomes larger, the farther these curves are situated away from the point Y .

Let us firstly consider the osmotic system



in which, as L_r has a greater O.Y.A. than L_p , the substance Y diffuses in the direction, indicated by the arrow. Consequently L_p moves in the diagram along the line Yp away from the point Y and L_r along the line rY towards the point Y . This diffusion continues till both liquids reach the same isotonic curve f.i. curve Im . Then liquid L_r comes in point s and liquid L_p in point t ; therefore the osmotic system (1) passes into the osmotic equilibrium:

$$E = L_s \mid L_t .$$

If we imagine the complex of the liquids of system (1) to be represented by a point K , then of course the line st must go through this point K .

We now bring into osmotic contact the solid substance Y with a liquid of the field $buXc$, f.i. with the liquid L_i ; then we have the osmotic system



Let us consider now the osmotic system:



in which L is an arbitrary liquid. One can imagine two cases now. If a little Y diffuses from the liquid to the solid hydrate, then is formed at the left side $H + Y$; if, however, a little Y diffuses from the hydrate to the liquid L , then is formed at the left side a little of the solution L_a , which contains water + Y only. Consequently system (6) passes, according to Y diffusing either towards left or right, into one of the systems:



The O.Y.A. of solid $H + Y$ is equal now to that of solid Y , therefore, equal to that of the liquids of curve bc . The O.Y.A. of $H + L_a$ is equal to that of L_a , therefore, equal to that of the liquids of the isotonic curve ak . Consequently we can distinguish two cases, according to the composition of liquid L in (6).

1. The liquid is situated in the field $abck$ (fig. 1).

If we take f.i. the liquid L_p then we have the osmotic system:



If a little Y diffuses from the liquid towards the left, then an osmotic system (7^a) arises. As, however, L_p has a greater O.Y.A. than $H + Y$ (which is equal to that of the liquids of curve bc), Y will diffuse again back to the liquid. Consequently not a system (7^a) will be formed.

If a little Y diffuses from the hydrate towards the liquid, then a system (7^b) arises. L_p has a smaller O.Y.A. than the liquids of the isotonic curve ak , consequently smaller also than liquid L_a . Therefore, this liquid L_a will remove again Y from L_p and will pass by this into solid H . Consequently also not a system (7^b) can be formed.

As system (8) can pass neither into a system (7^a) nor into a system (7^b), it follows, therefore:

the hydrate H can be in osmotic contact with all liquids of the field $abck$, without diffusion occurring.

2. The liquid is situated in the field $ak\ XW$ (fig. 1).

If we take the liquids L_r and L_t then we have the osmotic systems:



If a little Y diffuses from the liquid towards the left, then a system (7^a) arises; as, however, L_r and L_l have a greater O.Y.A. than $H + Y$, Y shall diffuse away back to the liquid. Consequently no system (7^a) will be formed.

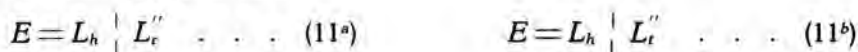
If, however, a little Y diffuses from the hydrate H towards the liquid,

then a equilibrium (7^b) is formed. L_r and L_t , however, have a greater O.Y.A. than the liquids of the isotonic curve ak and, therefore, a greater O.Y.A. than the liquid L_a in (7^b). Consequently L_r and L_t will remove Y from L_a , but L_a will keep its composition by solution of this hydrate, as long as a sufficient quantity of H is present. If a sufficient quantity of solid H is present, then the diffusion continues till the liquids L_r and L_t have reached the isotonic curve ak . The systems (9^a) and (9^b) then pass into the osmotic equilibria:



Herein L_r' and L_t' are the liquids which are represented by the points of intersection of the lines rY and tY with the isotonic curve ak .

If in the systems (9^a) and (9^b) no sufficient quantity of solid H is present, so that it has disappeared already before L_r and L_t have reached the isotonic curve ak , then L_a passes into an unsaturated solution; consequently in fig. 1 it is displaced starting from point a in the direction towards W . The diffusion of the substance Y stops when the liquids come on the same isotonic curve; if this is the case f. i. on curve he , then (9^a) and (9^b) pass into:



in which L_r'' and L_t'' are liquids which are represented by the points of intersection of the lines rY and tY with the isotonic curve he .

We can summarise the previous results in the following way:

If we bring in osmotic contact the solid hydrate H (fig. 1):

- a. with a liquid of the isotonic curve ak then there is osmotic equilibrium;
- b. with a liquid of the field $akcb$ then nothing happens;
- c. with a liquid of the field $akXW$ then the hydrate will flow away totally or partly.

If we assume that also the component X occurs as solid substance, then we can imagine the saturation-curve of X to be represented in fig. 1 by curve de . As follows from our previous communications, the O.Y.A. of the liquids of this curve increases in the direction of the arrows, viz. from e towards d . We now consider the osmotic systems:



in which, therefore, L_d is a binary liquid, which contains the components water + X and is saturated with solid X . We imagine the complex $L_d + X$ to be represented by the point of intersection m_1 of the line Ym and the side WX , which is not drawn. As the O.Y.A. of L_d is greater than that of solid Y and of solid H , the substance Y will diffuse in (12^a) and (12^b) in the direction of the arrow.

The complex $L_d + X$ moves, therefore, by taking in Y , starting from m_1 towards point Y . Consequently liquid L_d firstly traces curve dm and afterwards the line mY . If a sufficient quantity of solid Y and H is present, then (12^a) and (12^b) pass into the osmotic equilibria:

$$E = Y \mid L_z \quad . \quad . \quad . \quad (13^a) \qquad E = H + L_a \mid L_v \quad . \quad . \quad . \quad (13^b)$$

One of the visible results of the diffusion Y is, therefore, the disappearance of the solid substance X . In (13^a) is formed the liquid L_z , which can be in equilibrium with solid Y , in (13^b) the unsaturated solution L_v , which is situated on the isotonic curve ak .

The conversion of (12^a) into (13^a) would take place also, if we take away the membrane; if, however, we take away the membrane in (12^b), then it is clear that (13^b) can not be formed.

In the osmotic system:

$$\text{water} \leftarrow L_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

the substance Y will diffuse from each liquid L_v towards the water. Then the water forms a binary liquid, which moves along the side WY in the direction towards Y . This diffusion continues till both liquids reach the same isotonic curve; if this is f.i. curve no , then (14) passes into the osmotic equilibrium:

$$E = L_n \mid X + L_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The visible result of the diffusion of the substance Y is, therefore, the separation of solid X from a liquid, originally unsaturated; this separation begins, as soon as the liquid L_v has reached the point m of the saturation-curve de .

We now consider the osmotic system:

$$X \mid L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

in which L is an arbitrary liquid. If a little Y diffuses from the liquid towards the left, then is formed there a little of the liquid L_e (fig. 1); then system (16) passes into:

$$X + L_e \mid L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The O.Y.A. of the solid substance X is equal, therefore, to that of the liquid L_e and consequently equal also to the O.Y.A. of the liquids of the isotonic curve eh . Therefore, all liquids of the region $ehWd$ have a greater O.Y.A. and all liquids of the region $ehabc$ have a smaller O.Y.A. than the solid substance X .

Hence follows:

If we bring in osmotic contact the solid substance X (fig. 1):

a. with a liquid of the isotonic curve eh then there is osmotic equilibrium;
 b. with a liquid of the field $ehWd$, then nothing happens; the osmotic system remains unchanged, therefore;

c. with a liquid of the field $ehabc$ then the solid substance X will flow away totally or partly.

The osmotic systems:

$$X \mid \text{water} \quad X \mid L \quad X \mid L_r \quad X \mid L_u \quad X \mid L_t \quad X \mid X + L_m \quad . \quad (18)$$

etc., the liquids of which are situated within the field $ehWd$, remain unchanged, therefore, without diffusion occurring. In the osmotic systems:

$$\left. \begin{array}{lll} X \leftarrow L_a & X \leftarrow H + L_f & X \leftarrow H + Y + L_b \\ X \leftarrow Y + L_q & X \leftarrow L_p & X \leftarrow L_g \end{array} \right\} \quad . \quad (19)$$

etc., the liquids of which are situated within the field $ehabc$, the substance Y diffuses in the direction of the arrows. If a sufficient quantity of solid X is present, then the equilibrium $X + L_e$ is formed at the left side of the membrane; at the other side of the membrane is formed a liquid, which is represented by a point of the isotonic curve eh . If too little solid X is present then is formed at the left side a solution, represented by a point between e and c .

The result of the diffusion is dependent on the ratio of the quantities of the different phases; if we take f.i. the osmotic system, mentioned already in (19):

$$X \leftarrow Y + L_q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This can pass f.i. into one of the osmotic equilibria:

$$L_c \mid Y + L_q \quad X + L_e \mid L'_q \quad L_p \mid L_g \quad . \quad . \quad . \quad (21)$$

in which L'_q is a liquid, represented by the point of intersection of the line Yq with the isotonic curve eh . In the first one of those equilibria the solid substance X has disappeared, therefore; in the second one the solid substance Y and in the last one as well X as Y .

The isotonic curves ak and eh divide the field of the unsaturated solutions into three parts, which behave differently with respect to the solid substances H and X . It follows from our previous considerations:

If we bring in osmotic contact the solid hydrate H or the solid substance X :

a. with a liquid of the field $akcb$, then the hydrate H remains unchanged, but the substance X flows away totally or partly;

b. with a liquid of the field $akeh$, then as well the hydrate H as the substance X flows away;

c. with a liquid of the field $ehWd$, then the hydrate H flows away totally or partly, but the solid substance X remains unchanged.

The three cases, mentioned above, occur only then, however, when the isotonic curve ak , starting in fig. 1 from point a , terminates in a point k between c' and e and, therefore, does not intersect the saturation-curve de . We now imagine the point e anywhere between k and g ; then the isotonic curve starting from a , intersects curve de in a point, which we shall call a_1 . The isotonic curve starting from point e , will also then intersect the saturation-curve ab ; this point of intersection, situated between a and f , is called e_1 . We now find:

If we bring in osmotic contact the solid hydrate H or the solid substance X :

a' . with a liquid of the field $bce e_1$, then the hydrate remains unchanged, but the substance X flows away totally or partly;

b' . with a liquid of the field ee_1aa_1 , then as well the hydrate as the solid substance X remain unchanged;

c' . with a liquid of the field aa_1dW , then the hydrate flows away totally or partly, but the solid substance X remains unchanged.

The field, mentioned above sub b , in which as well the hydrate as the solid substance X flow away, is replaced now by the field mentioned sub b' , in which as well the hydrate as the substance X remain unchanged.

The transition of field b into b' occurs when point e in fig. 1 coincides with point k ; the two isotonic curves ak and he then coincide also. In this special case an osmotic equilibrium:

$$E = H + L_a \mid X + L_e \dots \dots \dots (22)$$

can exist also. This is in accordance with the membrane-phase-rule. (Comm. VII and VIII). If we take constant the pressure of the two separate systems, an osmotic equilibrium has

$$n_1 + n_2 - (r_1 + r_2) + 1 - d$$

freedoms. The number of diffusing substances d is here: one; the number of components on each side of the membrane is two and also the number of phases. Consequently the number of freedoms is:

$$2 + 2 - (2 + 2) + 1 - 1 = 0.$$

Therefore, system (22) is invariant, consequently it exists only at a definite temperature and the composition of the two liquids is completely defined.

As is apparent from the situation of the saturation-curves bc and de in fig. 1 with respect to one another, we have assumed that the temperature, for which fig. 1 is valid, is higher than the eutectic temperature of the binary system XY . If we lower the temperature till below the

eutectic and below the melting-point of ice, then we may obtain a diagram like fig. 2. Herein fg represents the ice-curve viz. the liquids saturated with ice, the O.Y.A. of the liquids of this curve increases in the direction of the arrows viz. from f to g .

We now find for this fig. 2:

the O.Y.A. of solid Y is equal to that of the liquids of the saturation-curve bc ;

the O.Y.A. of solid X is equal to that of solid $X + Y$, consequently also equal to that of the liquids of the saturation-curve bc ;

the O.Y.A. of the solid hydrate H is equal to that of the liquids of the isotonic curve al ;

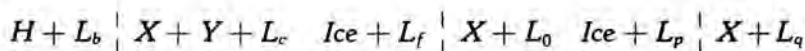
the O.Y.A. of ice is equal to that of the liquids of the isotonic curve fo .

the O.Y.A. of solid Y and of solid X is, therefore, smaller than that of all liquids of the field $abcdgf$.

It is apparent from the position of the isotonic curves in fig. 2 that a.o. the osmotic equilibria:



fig. 2



may occur now, which cannot exist in fig. 1.

We now take the osmotic system:



in which L_s has a greater O.Y.A. than L_r , so that the substance Y in (23) diffuses in the direction of the arrow. Again it now depends on the ratio of the quantities of both the liquids, which will be the result of the diffusion. Two unsaturated liquids viz. can be formed, but (23) can pass also into the osmotic equilibrium:



Herein L'_r is a liquid of the ice-curve, situated between the points f and p ; L'_s is the point of intersection of the line Ys with the isotonic curve, which goes through the liquid L'_r .

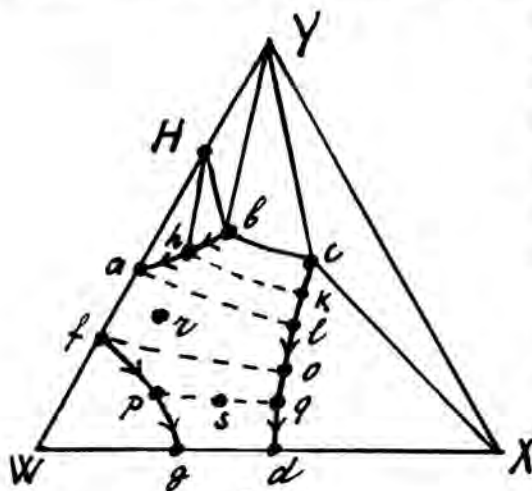
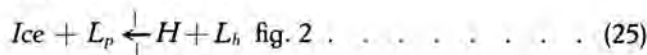
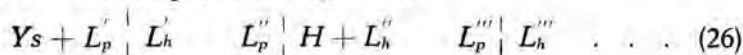


Fig. 2.

In the osmotic system:



L_p has a greater O.Y.A. than L_h ; consequently the substance Y diffuses in the direction of the arrow. According to the composition of the liquids and the ratio of the quantities of the phases, there can arise from (25) a.o. the following osmotic equilibria:



In the first one of those three equilibria L_p' is represented by a point p' of the ice-curve between p and f ; L_h' is represented by a point h' viz. the point of intersection of the line YK , in which K represents the complex $H + L_h$, with the isotonic curve, starting from point p' . In a similar way we find the position of the points, which represent the liquids L_p'' , L_h'' etc.

In the osmotic system:



it is dependent on the composition of the liquid L , whether diffusion of the substance Y will take place or not. The O.Y.A. of the ice, as we have seen above, is equal to that of the liquid L_f , therefore, equal to that of the liquids of the isotonic curve fo .

Consequently if we take in (27) a liquid of the field $focba$, then the ice will melt totally or partly with formation of an unsaturated solution, consisting of water + Y or the solution L_f saturated with ice.

If, however, the liquid L in (27), is situated within the region $fodg$, then no Y diffuses towards the ice and the system rests unchanged, therefore.

If we bring in osmotic contact solid X with a liquid L , then we have the osmotic system:



As long as L is an unsaturated liquid, diffusion of Y can not occur in this system. If viz. a little Y diffuses, then at the left of the membrane the system $X + Y$ occurs, which has the same O.Y.A. as the liquids of saturation-curve bc . As the O.Y.A. of solid X is smaller, therefore, than that of every liquid of the field $abcdgf$ (fig. 2) this diffusion can not occur, therefore, and system (28) remains unchanged.

If L in (28) is a supersaturated liquid with respect to solid Y then, however, it is quite different. If f.i. this is situated in the field bcY , then its O.Y.A. is smaller than that of the solid substance X and consequently (28) is converted into the osmotic equilibrium:



in which L' represents a saturated solution of curve bc .

Summarising some of the previous considerations, we may say:

Ice in osmotic contact with a liquid

of the field $fodg$ remains unchanged;

of the field $focba$ flows away totally or partly.

The hydrate H in osmotic contact with a liquid

of the field $alc b$ remains unchanged;

of the field $aldgf$ flows away totally or partly.

Solid Y in osmotic contact with every liquid of the total unsaturated field flows away totally or partly.

Solid X in osmotic contact with every liquid of the total unsaturated field remains unchanged.

(*To be continued.*)

Physics. — "*The Equilibrium in the Capillary Layer*". By Prof. J. D. VAN DER WAALS Jr.

(Communicated at the meeting of October 31, 1925).

In his theory of the capillary phenomena published in 1893¹⁾ and also still in the "*Lehrbuch der Thermodynamik*" by VAN DER WAALS—KOHNSTAMM, which appeared in 1908, my father has developed a theory of capillarity based on the supposition of a continuous transition from the liquid to the vapour density.

For this purpose he calculated the free energy of a quantity of substance which is in the transition layer between the two phases. With the method followed by him the knowledge of the entropy in the capillary layer was required, and about this he introduced the supposition that it would exclusively depend on temperature and density at the point itself and would be independent of $\frac{dn}{dz}$ or higher derivatives of n (n = number of molecules per ccm. and z = direction normal to the liquid level). In other words: he assigned to every quantity of liquid the entropy which it would possess, if it was amidst a homogeneous phase of its density.

ORNSTEIN²⁾ has pointed out that this supposition cannot be rigidly accurate. He assumed, however, that the radius of the sphere of attraction, within which two molecules still attract each other appreciably, is very great compared with the radius of the molecule. On the ground of this supposition he neglected the influence which the derivatives of the density can have on the entropy.

As, however, the sphere of attraction must not be put much larger than the molecule itself, or at least their radii are of the same order of magnitude, it seems to me that the said influence should be taken into account in a theory of capillarity.

If, however, it is the intention to find the condition of equilibrium of the capillary layer, this may be reached by a shorter way, in which the entropy is not explicitly introduced. We may start from the so-called law of the distribution in space of BOLTZMANN, which teaches that:

$$\frac{N}{\nu_b} e^{\frac{\epsilon}{kT}} = \text{constant in space}$$

(N = number of molecules per molecular quantity, ν_b = the available space in a volume containing a molecular quantity, ϵ the potential energy of a

¹⁾ Cf. among other things J. D. VAN DER WAALS. *Zeitschr. f. Phys. Chem.* **13**, 657, 1894.

²⁾ L. S. ORNSTEIN. *These Proceedings* **11**, 526, 1908.

molecule at the point considered, kT = double the mean kinetic energy per degree of freedom at the given temperature). Or, what comes to the same thing, we may start from GIBBS's principle that the thermodynamic potential μ is constant in space, in which μ may be put equal to $RT \times$ the logarithm of BOLTZMANN's expression ¹⁾.

It is known, that we may put in a homogeneous phase:

$$v_b = \{v - 2b(n)\},$$

in which for $n=0$ $b(n)$ approaches to half the joint volume of the distance spheres, and is smaller for greater value of n . In the capillary layer, however,

$$v_b = \left\{ v - 2b(n) + k_1 \frac{\partial n}{\partial z} + k_2 \frac{\partial^2 n}{\partial z^2} + \dots \right\}$$

must be put, in which k_1 and k_2 represent constants. It is the influence of these constants that has been so far neglected in the theory of capillarity.

If the partial overlapping of the distance spheres should be disregarded (in which case it would also be allowed to put $b(n) = b_\infty = \text{constant}$) these constants could be easily calculated. In the first place it is easy to see that then k_1 is zero, at least if also the grouping of the molecules in consequence of the attraction should be disregarded. In reality k_1 will not be rigorously zero. Here it may be pointed out that in the usual calculation of the energy in the capillary layer (see VAN DER WAALS loc. cit., VAN DER WAALS—KOHNSTAMM, ORNSTEIN loc. cit. and others)

also a term with $\frac{\partial n}{\partial z}$ is omitted, which if the "mutual exclusion of the molecules out of their distance spheres" and the group-formation in consequence of the attraction is fully taken into account, would probably appear not to be rigorously zero either.

In the second place it is easy to calculate what part of a layer of the thickness of dz (dz = small compared with the radius of the distance sphere σ , and a fortiori small compared with the whole thickness of the capillary layer) is occupied by distance spheres of molecules which lie on either side of this layer at a distance $< \sigma$. Neglecting the points mentioned above we find for this fraction:

$$\frac{2b}{v} + \frac{b\sigma^2}{5} \frac{\partial^2 1/v}{\partial z^2}$$

so that:

$$v_b = v \left(1 - \frac{2b(n)}{v} - \frac{b\sigma^2}{5} \frac{\partial^2 1/v}{\partial z^2} \right).$$

With the value of the energy calculated before this gives (see inter alia VAN DER WAALS—KOHNSTAMM p. 229 et seq.):

¹⁾ My father calls the quantity in question (loc. cit.) "total potential" and considers a part of it as "thermodynamic potential". It seems, however, simpler to me not to make the distinction of the energy into "internal or thermodynamic" and "external" (among which latter the capillary energy is reckoned).

$$\frac{2a}{v} - c_2 \frac{\partial^2 1/v}{\partial z^2} + RT \ln \left\{ v - 2b - \frac{v b \sigma^2}{5} \frac{\partial^2 1/v}{\partial z^2} \right\} = \mu = \text{constant in space,}$$

in which

$$c_2 = 2\pi \int_0^\infty u^2 \psi(u) du$$

$\psi(u)$ being defined by:

$$d\psi(u) = -f \Pi(f) df$$

and $\Pi(f)$ representing the potential of the molecular attraction at distance f .

When the b -correction in the equation of state may no more be neglected than the a -correction, and the radius of the sphere of attraction r_a is of the same order of magnitude as σ , the term with $\frac{v b \sigma^2}{5} \frac{\partial^2 1/v}{\partial z^2}$ may no more be neglected than $c_2 \frac{\partial^2 1/v}{\partial z^2}$. This is seen when it is considered that $a = 2\pi \int_0^\infty \psi(u) du$, so that c_2 is of the order of $a r_a^2$.

When the last term of the form under the logarithm sign is small in comparison with the other terms, the following form may be written:

$$\mu = -\frac{2a}{v} + RT \ln \left(v - 2b \right) - \left(c_2 + \frac{v b \sigma^2}{5} \frac{RT}{v - 2b} \right) \frac{\partial^2 1/v}{\partial z^2}. \quad (A)$$

which expression is distinguished from the prevalent one only in this that the coefficient of $\frac{\partial^2 1/v}{\partial z^2}$ is not c_2 , but $c_2 + \frac{v b \sigma^2}{5} \frac{RT}{v - 2b}$. It should, however, be borne in mind that in the other formulae of the theory of capillarity the form in question is not always to be substituted for c_2 in order to take the influence of molecular "exclusion" duly into account. In the calculation of the tangential tensions in the surface layer in consequence of molecular attraction, e.g., as carried out by HULSHOF, no change need be applied, i.e. the formula:

$$p_{\text{tang.}} - p_{\text{norm.}} = \frac{c_2}{2} \left\{ \frac{1}{v} \frac{\partial^2 1/v}{\partial z^2} - \left(\frac{\partial 1/v}{\partial z} \right)^2 \right\}$$

remains unchanged. Only v as function z is now found by solution of (A). It is, therefore, different from what it would be without the term with $\frac{v b \sigma^2}{5} \frac{RT}{v - 2b}$.

In consequence of this another value is found for the capillary constant. Besides, this only holds for that part of the tensions that is determined by attraction. The kinetic pressure, too, will not be quite independent of the derivatives of $1/v$. I have not yet examined how great this amount is, and whether it may be neglected compared with the other terms governing capillarity.

Meteorology. — E. VAN EVERDINGEN: "*The cyclone-like whirlwinds of August 10, 1925.*"

(Communicated at the meeting of October 31, 1925).

1. When in the morning of August 11 the papers in this country, from all quarters in the southern and eastern part of the country, received reports of heavy devastations, reminding in their description of the effect of a hurricane or a cyclone, especially in consequence of the reports saying that Borculo had been "entirely destroyed", the Meteorological Institute was asked for information about the cause of the disaster and publication of its observations. In both respects we were obliged to disappoint the applicants. We could say nothing about the cause but that it ought to be connected with the passage of the line squall of a thunderstorm, which had attracted our attention also at De Bilt by the darkness preceding it, no particularly severe phenomena ensuing however. Hence local observations did not give any clue, nor those at the four principal stations from which we get telegraphic reports at regular intervals — at the moment of the disaster at Borculo, about 7 o'clock p.m., the weather map shows a shallow depression-centre over the northern part of our country, with lowest readings just below 755 mm., and the maximum gradient of pressure in the triangles Flushing—De Bilt—Maastricht and De Bilt—Maastricht—Groningen remains short of 2 mm. per degree for very divergent directions. It is in good harmony with this fact that at none of the principal stations windforce of any extraordinary importance occurred, at some even the gale-limit was by far not attained. For these reasons, however severe the destructions may have been locally, it is not right to talk of a hurricane or a cyclone — with those words we indicate in meteorology phenomena of a much greater size, with a diameter of many hundreds and a length of path of thousands of kilometers. For the local whirlwinds which often, albeit usually in a much more modest form, accompany thunderstorms, the real dutch name "windhoos" (wind-spout) is best adapted. In this case, in view of their exceptional severity and extension, we may talk of cyclone-like whirlwinds.

2. It is probably on account of the very local character of whirlwinds that we are inclined to believe them to be more rare than they really are. In this country, in the period 1888—1913 whirlwinds of more or less importance occurred on the average on 8 days per annum. During the years 1882—1925 the Meteor. Institute got notice of 82 cases, in which at one or more places damage was caused, comparable with what occurred this time on a big scale: trees knocked down or snapped, hay-cocks blown

up and scattered, roofs or even houses damaged. Fig. 1 indicates the localities, where these whirlwinds occurred: much haunted are Sealand and Friesland, remarkably spared the N.-E. part of Groningen and Dutch

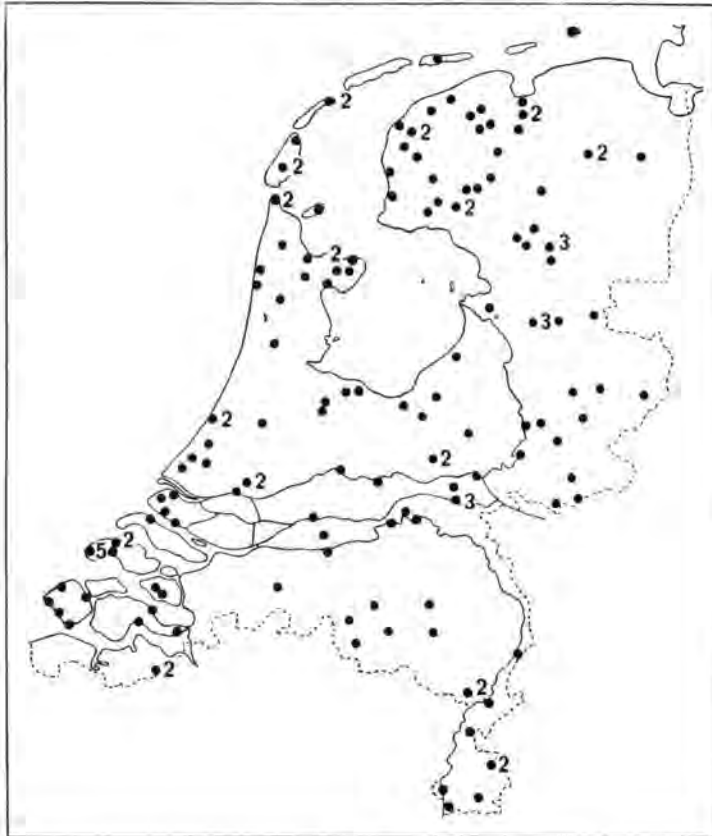


Fig. 1.

Flanders. The total number of cases however is still too small to permit us to draw conclusions, though it seems probable that the proximity of the sea or the influence of heated sands and hills favours the formation of whirlwinds. The distribution of these whirlwinds over the various months was :

Jan.	Febr.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
1	2	2	3	9	11	20	19	9	2	4	—

and bears much resemblance to that which WEGENER has deduced in his remarkable book "Wind und Wasserhosen in Europa" — here however June has sensibly less, July more.

The particularity of the whirlwinds of August 10 does not in the first instance consist in the character of the destructions, which has been formerly equalled at various places. We mention f.i. August 29, 1916

when in Limburg hundreds of trees were smashed ; by chance also August 29, 1919, when near Voorthuizen once more hundreds of trees fell ; July 17, 1920, when a similar case happened in Twente, finally July 11, 1924, when Delft and Alphen on the Rhine were visited. Moreover it is possible that local circumstances have played their part, and hence a comparison is difficult. Extraordinary without doubt was however the extension of the region, where the destruction took place. Immediately after the disaster the Meteorological Institute has asked all its voluntary observers in the southerly, central and easterly part of the country to make a sketch of the extension of the damage in their vicinity, and also the principal papers printed such a request. Many persons have answered to this request with much diligence : moreover we were favoured by the cooperation of Dr. H. K. DE HAAS from Rotterdam, who passed his summer-holidays at Barchem and from there recorded the direction in which trees had fallen at many spots over a large area — we will treat of this afterwards. The writer, together with Dr. C. SCHOUTE, adjunct-Director, and Mr. W. WOLTERS, secretary of the Institute, who likewise passed his holidays at Barchem, visited a large portion of the damaged district in Gelderland and Overijssel by means of a motor car, put kindly at our disposition by the municipality of Borculo. Also Messrs. K. ZWART, retired head-teacher, and J. TH. A. BOTH, functionary of the El. Co. "de Berkel", earned great merit by surveying and charting the direction of fall of trees in the municipality of Ruurlo. Finally we received a map of the whole region visited on two motor car trips in N.-Brabant and Gelderland and Overijssel by Mr. J. G. LEPPER, engineer at Aerdenhout.

The whole of these data enabled us to draw a concise map of the devastated regions. Whereas for some whirlwinds and tornado's, occurred abroad, it has been possible to find out a track, along which within a certain width almost everything is destructed, so much so that f.i. in Scandinavia people speak of an "Asgardsroad" through a wood, in this case one is struck rather by the great lack of regularity and the saltatory character of the destructive action. In the midst of an otherwise uninjured wood we find spots, where all trees have been felled ; along a road of more than 10 km. we find at irregular distances portions, where everything has been devastated by forces across the road, next to large regions almost uninjured — at other places the devastation is limited to a single narrow strip. Therefore it was impossible to map completely the extension of the damage; hence we have only indicated in fig. 2 the devastated regions by a scale of three degrees : narrow horizontal shadings for the regions, where heavy damage was caused to trees, crossed shadings where also buildings were damaged, black where buildings were entirely destructed. A wide horizontal shading indicates damage at few isolated spots.

On investigation it appeared that no reports of damage in Belgium had reached the Meteorological Observatory at Uccle. On the contrary in Germany damage was caused at a rather large number of places. Though

we did not yet receive complete information ¹⁾, we could conclude from reports in the papers that in the N.-E. part the spots devastated are much further apart in the transverse direction than in our country, as may appear

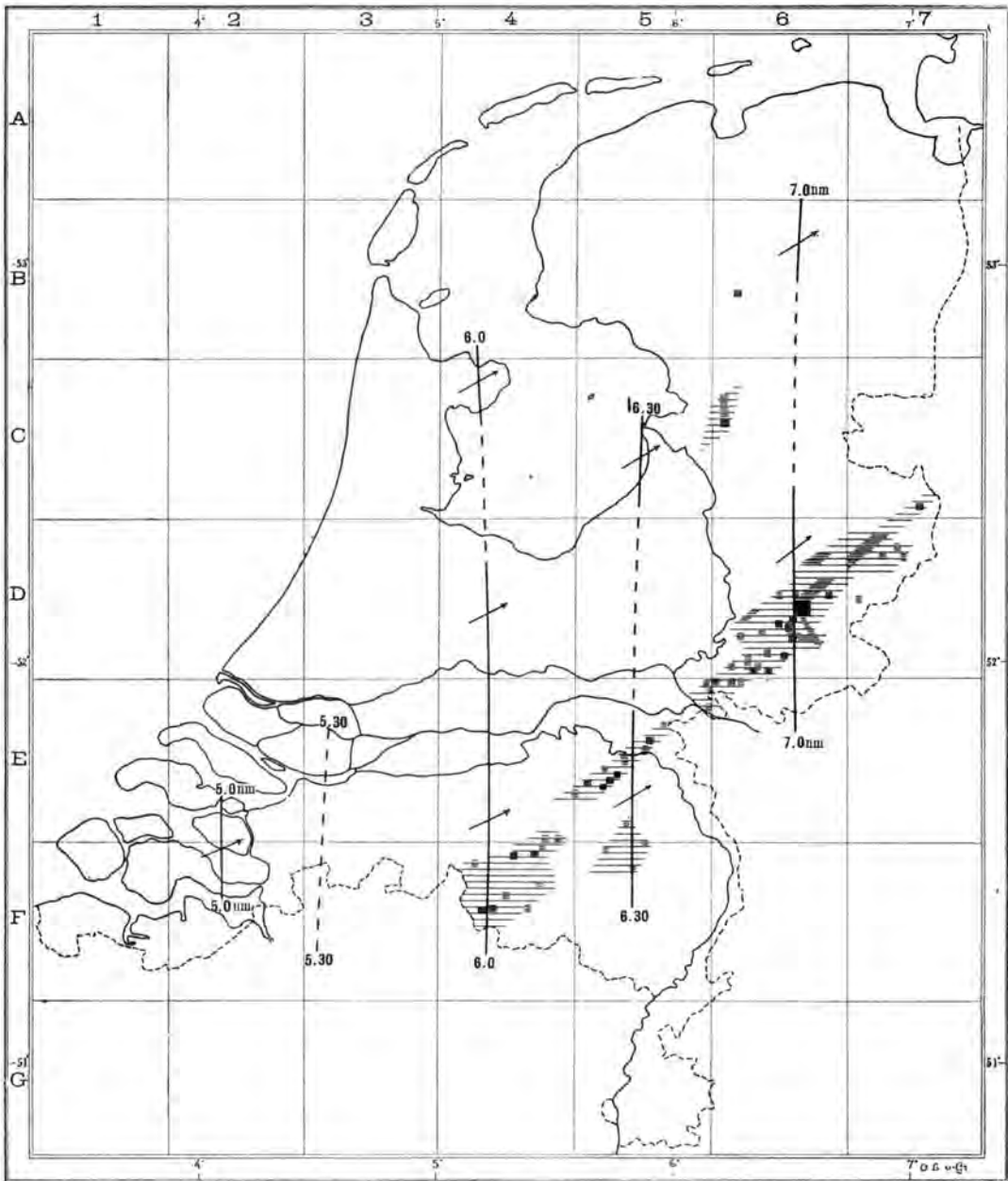


Fig. 2.

¹⁾ While correcting the proofprint we received a map from the „Deutsche Seewarte“ at Hamburg, from which it appears that the squall-lines of the thunderstorm may be followed up to Kiel, and windforce 9—12 of the Beaufort scale was reported largely from three parallel tracks, the prolongation of which to our country contains all the regions devastated there.

from fig. 3. Taking everything together it appears that the length of the track is of the same order as the 4 longest tracks mentioned by WEGENER.

3. It is in the first place the capricious character of the destructions which forces us to ascribe them to whirlwinds. If the effects ought to be

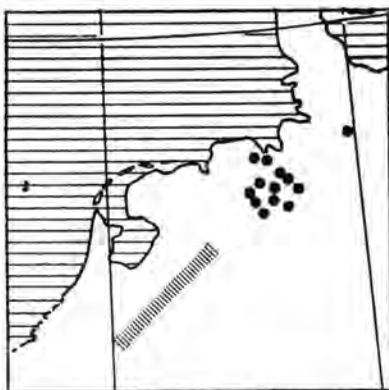


Fig. 3.

ascribed to nothing else but a gale, then the force of a hurricane of such strength would be required, that over a wide area *everything* would have been destroyed. In whirlwinds indeed exceptionally high windforces occur locally and temporarily; even 100 m. p. s. has been mentioned, though nobody can tell with certainty that such velocities have been reached. Indeed, all calculations of the force of the wind from the pressure of the wind, estimated from its destructive effect, yield too high values because it is certain, that other forces of the same

order of magnitude must have been present at the same time. These are the differences in atmospheric pressure, which in the rare cases where a whirlwind came across a barograph have proved to be able to reach 20 to 30 mm. The mean diameter of a whirlwind is something of the order of 100 m. Hence mean pressure gradients of the order of 1 mm of mercury in 5 to 3 meters play a part, locally and near the axis perhaps 10 times bigger. This causes forces of the order of 25 to 40 kg. per m² of an object of 1 m. thickness, hence forces, already equal to the windforces experienced in heavy gales, but differing from these in this respect, that they increase with the thickness of the object on which they are displayed. If such a whirlwind progresses with a big velocity — in this case there is reason to estimate that velocity at 20 to 30 m. p. s. — then there is certainly no time to develop everywhere, an equal distribution of pressure, and we may expect quasi-explosive effects of the not expanded air, which is present inside buildings.

That is why roofconstructions are tilted up, roofcoverings are blown off, windowpanes and even walls are thrown outwards at the side opposite to that, exposed to the strongest wind, even if the walls on that side remained intact, as has been observed in many cases. This also explains the possibility of very different directions of fall of trees at neighbouring places. This, lastly, explains why heavy objects may be carried through the air over rather large distances, borne by a diminution of pressure over and before them, and forced on by air streaming towards the depression and ascending at the same time¹⁾.

¹⁾ I consider this explanation to be more acceptable than WEGENER's supposition, that transport over large distances would take place in a horizontal part of the vortex.

However — even when taking into account these forces, wind pressures of the order of 200 kg. are required to explain several of the masterpieces accomplished by whirlwinds; hence we are obliged to assume wind velocities of more than 50 m. p. s.

We give in the following the few observations, where the funnels of the spouts were actually seen.

Borculo. Dr. J. W. GRONDIJS. "From the Southwest approaches a funnel of a dirty yellow-greenish colour. In a short time the colossus has reached the village. Violent wind, I see the trees in the Bloemerstraat falling with a single blow, direction S.—N., but at the upper end of the street the trees lie N.-W.—S.-E."

Borculo. H. W. HEUVEL. "The clouds arrived revolving like a whirlpool. Somebody tells: At once we saw in the sky something strange. A long straight tube, which rotated quickly at a horrific pace and approached with a terrifying roar."

Nijmegen. R. TEN KATE. "When the squall had approached a good deal and it had grown very dark, I saw at once a large frayed cloud approaching somehow from N.-W. with an amazing velocity in the direction of the squall. This attracted my attention to such a degree, that I inspected the sky more closely and then I saw from a southern direction another cloud approaching in the direction of the squall. Just before the squall had reached the North-Southline over my dwelling, it was reached by the two clouds, whereupon they assumed together a rotary motion and proceeded in the direction of the squall. At the moment this rotation started, the trees began to wave wildly without a distinct direction. The rotation was rather quick (one revolution in about 6 seconds.)"

Zevenaar. Drs. J. G. A. HONIG. "Various persons have seen a dark rotating(?) column moving from S.-W. to S.-E."

Uden. J. TH. FRUNT. "The clouds came together from the directions N.-W. and S. Everyone cried fire. But there was no fire. Then the clouds descended to about 50 m. above the surface, and much sand came with them then towards Uden, there the whole motion of the air was involved in rotation."

These data and the ensuing notice about the estate "Het Espelo" prove beyond doubt that whirlwinds have occurred. The very dark sky and the velocity with which everything proceeded are sufficient reasons, why more numerous descriptions were not received.

4. Details of local destructions are to be found at random in papers and periodicals, and this is not the occasion to treat further of these. Very important however is the result of Dr. H. K. DE HAAS' investigation, which is resumed in fig. 4. For orientation the railways and principal roads in the vicinity of Ruurlo, Lochem and Borculo have been indicated. Every arrow marks the direction of fall of a tree, which stood at the spot, indicated by the *point* of the arrow. Some curved arrows indicate spots, where one

gets very strongly the impression of quickly rotating forces, f.i. because the branches of a group of firs were entirely coiled up. Only those directions

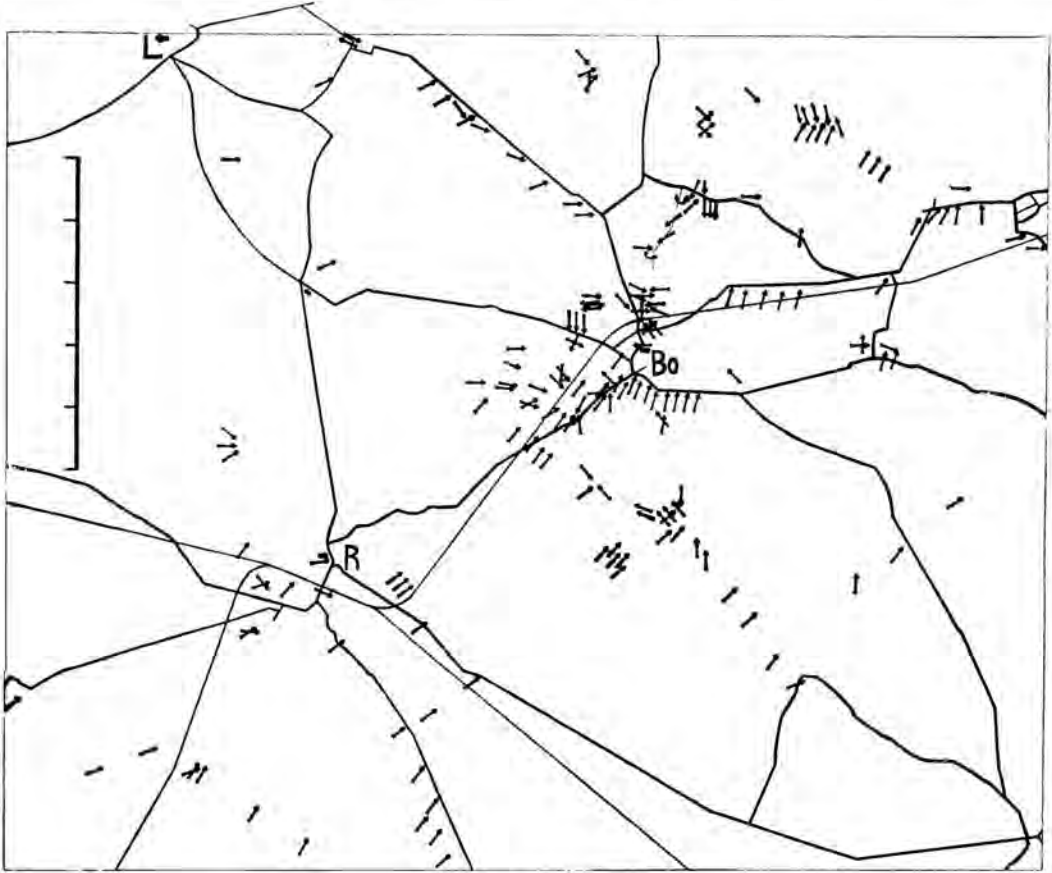


Fig. 4.

of fall have been inserted, where it was certain that the tree lay untouched. As of course in many spots soon clearing had taken place, the number of arrows and their distribution do not give a true picture of the intensity of the whirlwinds; but they do, as far as the direction of the largest forces in any point is concerned. Fig. 5 is a reproduction of the sketch received from Ruurlo. Here the directions of fall diverge still more.

A comparison of these figures with tracks of whirlwinds in WEGENER's collection shows, that this case is among the most complicated. If a single whirlwind proceeds along a straight line, we are able to predict entirely the direction of fall with respect to the track, after making certain suppositions about the velocity of translation and the angle of incidence of the wind with respect to the axis of rotation. It then appears that near the centre all trees must fall in the direction of propagation, whereas on both

sides a region is found, in which the trees are found lying under angles up to 135° with the track — of course subject to the nature of the trees and the minimum windforce sufficient to fell them.



Fig. 5.

Nothing like such a picture here — only small portions along certain roads show some resemblance to it ¹⁾, so as to favour the supposition, that a great number of whirlwinds of relatively small dimensions has been in action, and that sometimes, diverging from the principal direction, these whirlwinds followed the rows of trees along the roads. It is even not impossible, that some whirlwinds followed an adverse track, or showed an adverse direction of rotation. At various places it was possible to conclude to the time-sequence of the successive hurricane blasts, because we can take for granted that the tree lying uppermost had fallen latest. On the evidence of facts like these Dr. DE HAAS thinks he must assume that N.-W. of Borculo several right-hand rotating whirls have occurred.

In the Ruurlo map we are struck especially by the great number of trees, felled from N.-E. in the centre of the Gr. Meene, secondly the great number of isolated spots with numerous felled trees amidst uninjured regions. In these smaller spots the direction of fall does not diverge so much. Everything seems to indicate, that the whirlwinds, descending from the cloudlevel, touched the surface here and there in a saltatory way, and on the occasion of an extremely deep descent over the Gr. Meene developed enough force to fell trees also at the front side. If we assume a general motion in the direction N.-E., we have to distinguish at least 5 whirlwinds in this case only. In these considerations we start from the supposition, confirmed by numerous observations in the case of solitary whirlwinds, that next to the surface the rotation plays only a secondary part in the whirl, the afflux of air being the principal phenomenon. Hence the origin of the rotation, which constitutes the cause of the diminution of pressure, must be looked for in higher strata. In this supposition the progressive motion of the whole mass of air is added to the afflux behind the whirl near the track of the centre, subtracted from it on the front side. If we put the general windvelocity at 20 m. p. s., the felling of trees on the front of the whirl would indicate a velocity of afflux of 40 to 50 m. p. s., if we overlook the pressure-forces, — at the backside then velocities of 60 to 70 m. p. s. must have occurred. We remarked before that the action of pressure differences weakens these conclusions, except in the case of tall trees like firs or poplars, where the pressure effect cannot be very large. But also in other ways estimates are obtained of windforces between 50 and 80 m.p.s.

5. In spite of the very extensive investigations on whirlwinds we cannot say that at the present moment their origin is completely explained. Many facts and experiments however are in favour of the mechanic theory, which assumes that a horizontal vortex is formed when an ascending current forces its way into layers of air, where the velocity strongly increases

¹⁾ On the estate „Het Espelo“ near Enschedé f.i. in a wood a passage has been cut, about 10 m. wide, in which the trees not only have been blown down, but also snapped off. (J. VERKOREN Jr. Director of the Gas- and Waterworks, Enschedé).

upwards. Considering that in thunderstorms firstly strong ascending currents occur, but a thunderstorm of some importance requires also an inversion layer, over which almost always a sudden change in the wind may be expected, this explains at the same time the frequent simultaneous occurrence of thunderstorms and whirlwinds.

Starting from this point of view we have tried in the first place to coordinate the facts, observed at the surface, on the supposition that the whirlwinds occurred everywhere at the moment of the passage of the principal line-squall of the thunderstorm. A great number of reports of the thunderstorm were available for determining the motion of this squall line. Though some possibility of confusion arose from the occurrence of several other thunderstorms, f.i. at de Bilt half an hour before the principal squall, we are of opinion that the squall-lines copied on fig. 2 have a sufficient degree of certainty ¹⁾.

A first item of the research dealt with the air-pressure at the surface. In consequence of our request in the papers for communications of observations and sketches for this day, we got a.o. barograms from Nijmegen, Berg en Dal, Lochem, Goor, and Boekelo, all localities situated pretty near the track of the whirlwinds.

None of these diagrams did however show extraordinary variations of pressure, and this is what we might expect, seeing that the distance remained much greater than the diameter of the biggest whirls. Very important was therefore the receipt of the diagrams of the registering gas-pressure gauges at Nijmegen from the Director of the Gas-works, Mr. G. Philips, as the gauge at Hatert was only few kilometers from the track of the whirlwinds, and did show much bigger variations. In order to reduce the indications of these watermanometers to variations of air pressure we assumed, that a barograph, stationed at Nijmegen on the Oranjesingel, would have registered the same variations of air pressure as a barograph, installed at the Gas-factory, save a difference of few minutes in time. After correction for the difference of level of the observing stations and reduction to pressure in mm. of mercury, the differences of the watermanometer at the factory and at the other points allowed the calculation of the air pressure variations there. We know that all registering cylinders show errors of time, and in this case these were very considerable. Therefore we assumed, that the most marked increase of pressure, shown in the diagram, coincided with the moment of the passage of the whirlwind, so as to allow a calculation of the time-error from the time of passage of the squall-line. The same procedure has been adopted afterwards for the barograms in the vicinity of Borculo.

¹⁾ The very large velocity of this squall, about 72 km. per hour explains the velocity with which, according to eye-witnesses, the destruction approached, and is in harmony with the estimates of the lapse of time in which Borculo was destroyed, which vary from 7 minutes to a quarter of an hour. (Addition during correction: In Germany the velocity increased even to 90 km. per hour).

Fig. 6 shows the barograms for Hatert and Daalsche Dijk near Nijmegen, obtained in this way and compared with the diagram of the float-mercury-barograph at de Bilt. The latter shows a marked thunderstorm-unrest, but nothing particular at the passing of the line-squall at 6.00 — the diagrams for Nijmegen however show very large fluctuations, especially at Hatert.

As evident from fig. 2 the destruction stopped temporarily just beyond Nijmegen, and therefore it was not certain, that the difference in registration at Hatert and Daalsche Dijk was only due to a difference in distance from the track of the whirlwinds. For this reason we abstained from trying to estimate the fall of pressure on the central line by an extrapolation.

Using the observations at principal stations, second order stations and a number of other barograms received, we have then drawn the diagrams in fig. 7 for the distribution of pressure at 2, 4, 5, 6, 6.30 and 7.00 p. m. Only at the moment of the passing of the whirlwinds extraordinary isobars are displayed, but these are very remarkable indeed, as in the neighbourhood of the

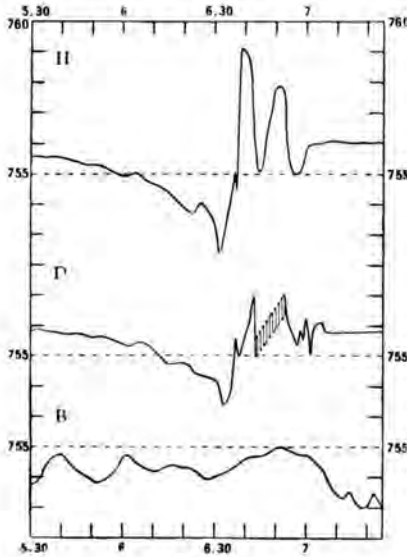


Fig. 6.

track of the whirlwinds, they indicate pressure gradients up to 55 mm. per degree, which, if occurring over larger areas and longer periods, would cause hurricanes of the most destructive kind.

With isobars of a curvature as here occurs however by far the greater part of the gradient is required for change of direction, and moreover it is evident that this pressure distribution did not persist long enough to develop its full windforce. There are no indications of the occurrence of similar gradients farther S.-W., before the whirlwinds appeared. Therefore though we don't exclude the possibility, that in the first place N.-W.ly gales and whirlwinds with a southerly track may be explained by these pressure gradients, we are of opinion, that on the whole these phenomena are to be regarded rather as sequences of than as causes for the formation of the whirlwinds. A large part of the rise in pressure can be ascribed to the replacing of warm by cold air: a temperature difference of 6° C. through a column of air 2000 m. in height gives a rise of pressure of about 4 mm.

6. Fig. 8 shows the distribution of the rainfall in our country according to the reading of the raingauges, at 8.00 a.m. on August 11. It would have been desirable to draw this map exclusively for the rain that fell

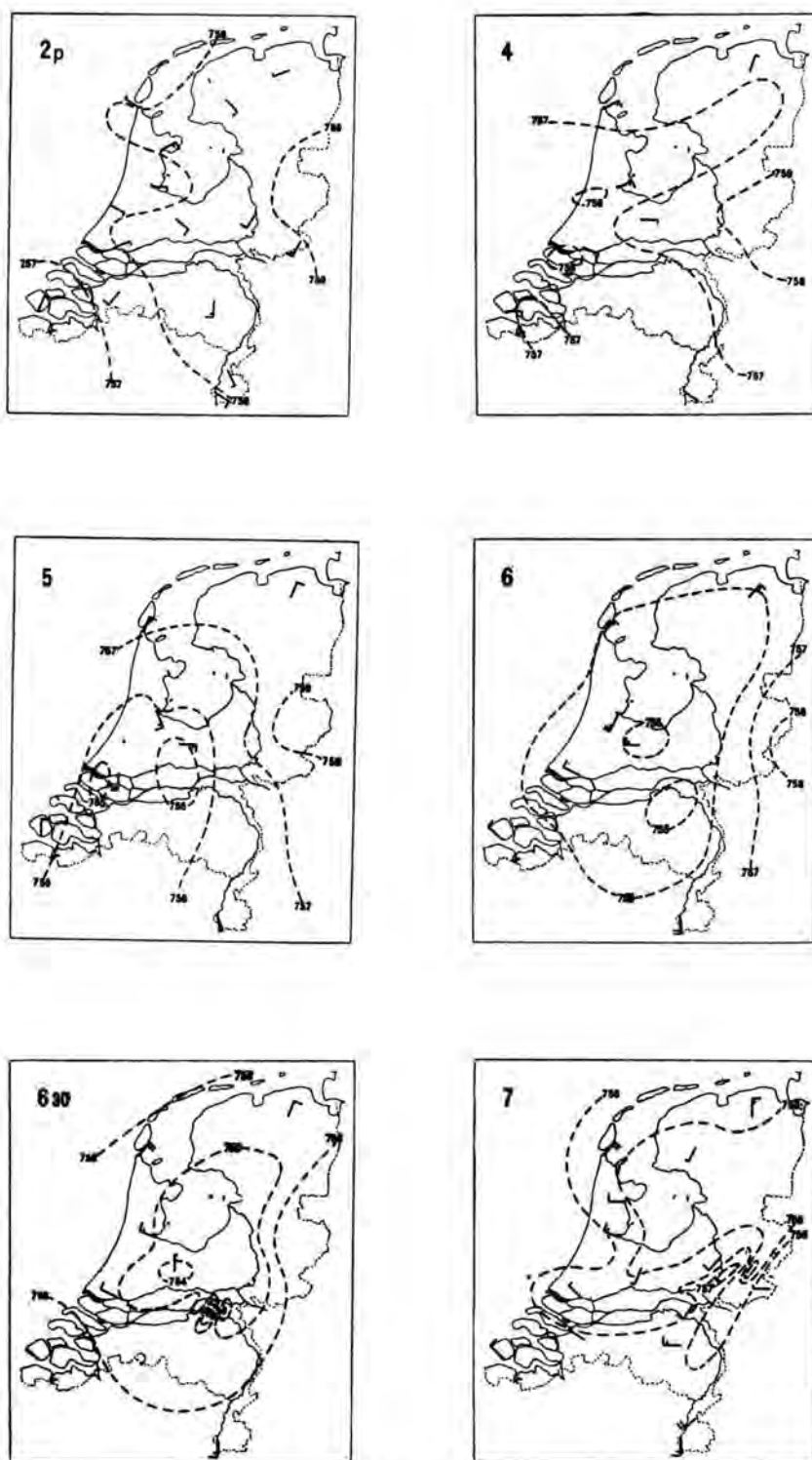


Fig. 7.

with the squall charted in fig. 2. But only a small fraction of the observers has measured separately the rain of this squall, and we only know that at various places this squall has indeed had the largest share in the day's rain. As main result of this investigation we find : 1^o. that the quantity of rain has been very different, varying between 38.5 mm. and nihil ; 2^o. that the region devastated by the whirlwinds has not experienced the heaviest

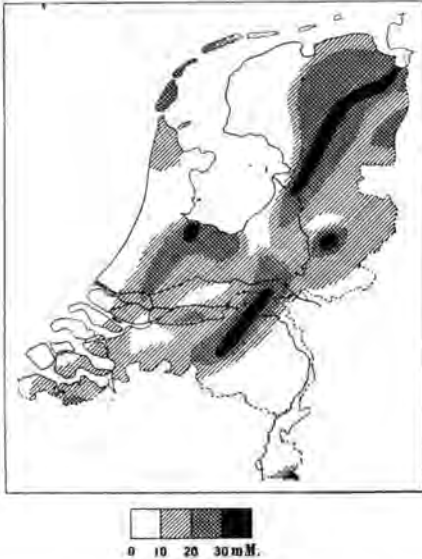


Fig. 8.

then the highest velocity of falling raindrops. Perhaps this is the explanation for the phenomenon, that at many places the squall was preceded by an inkblack sky, from which rain did not yet fall. If such ascending velocities occur simultaneously over a few square kilometers, and if they are fed at the front part of a wedge of incident cold air only by an afflux with a height of a few hundred meters, then we find even in the case of a supply from all sides velocities of more than 20 m. p. s., with an afflux from one side much higher values.

7. The direct cause of the thunderstorm was given by an invasion of cold air from W. under a warm and moist body of air supplied from South. Neither the temperature which occurred even in the eastern part of the country, which remained below 30° C., nor the fall of temperature can be called extraordinary, and doubtless these figures have been surpassed considerably in many heat-thunderstorms. It will appear later on that in the higher strata more important differences were found. Figures 9 and 10 give the course of the isotherms at 2.00 and 7.00 p. m., the arrows indicate roughly the streamlines of the two masses of air. Given the irregular character of the pressure variations and the variable winds caused by these, many more observations would be required to completely determine these lines. Even in this rough form however they suggest the rising

precipitation, but that a region of heavy rain is to be found somewhat to the North and to the left of the track of the whirlwinds in Brabant and Gelderland. From the intensity of the rain the velocity of the ascending currents can be calculated, if we know the vertical extension of the saturated layer and its temperature. If we put the temperature at the surface at 25° C., the weight of the layer of air per m². at 1000 kg., then for a rainfall of 35 mm. in half an hour a vertical velocity of more than 6 m. p. s. is required. Hence it is very probable, that locally and temporarily the ascending velocity surpassed the limit of 8 m. p. s. and so grew larger

currents due in the Achterhoek (Eastern Gelderland) about 7.00 p. m. and the ascending currents on the Veluwe (Western Gelderland), which fed the heavy winds in the back of the squalls.

It is evident from a comparison of fig. 2 and 8, that at different points

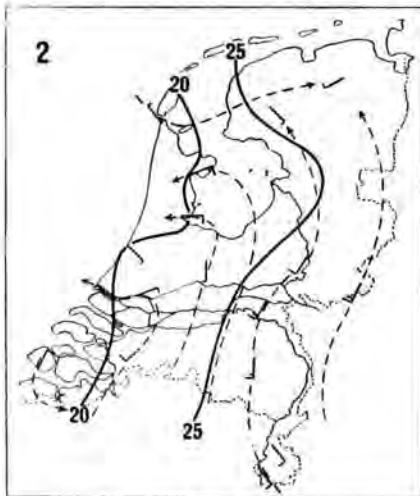


Fig. 9.



Fig. 10.

of a same squall-line very different amounts of rain fell; also fig. 10 suggests various independent squalls, so as to permit doubt, whether the squall-lines connected by a dotted line in the North and the South of the country really belong together. Hence the conditions of flux differed much locally; other differences in the ascending velocities depend on the orographic conditions, whereas preceding thunderstorms may have altered here and there the conditions in the higher strata. Together these are sufficient reasons to explain the large differences in rainfall.

8. In consequence of the constantly increasing application of the investigation of the upper air to the daily forecasts of the weather, we have at our disposal rather complete material of temperatures and velocities of the air in the lower kilometers. By means of aeroplanes the temperature was determined up to a considerable height at Duxford in England, Uccle in Belgium, Helder and Soesterberg in our country, by means of kites or cable balloons at Lindenberg and Friedrichshafen in Germany. Moreover, observations from mountain stations were available in Germany, Switzerland and France. Numerous observations of pilot balloons give the wind directions in the higher strata at various times of the day. Fig. 11 and 12 give a compilation of the morning observations for the levels of 1000 and 2000 m. (1 m.m. = 2.5 m. p. s.)

Remarkable is here especially the large temperature difference at the level of 1000 and 2000 m., between England and Central Europe. With a view to the observation on the Puy de Dome in France, which gives a temperature of 20° at 1500 m., we may assume that this condition existed

likewise in Central France and that the southerly to southwesterly winds at 1000 to 2000 m. carried this warm air to our country. Above 2000 m.

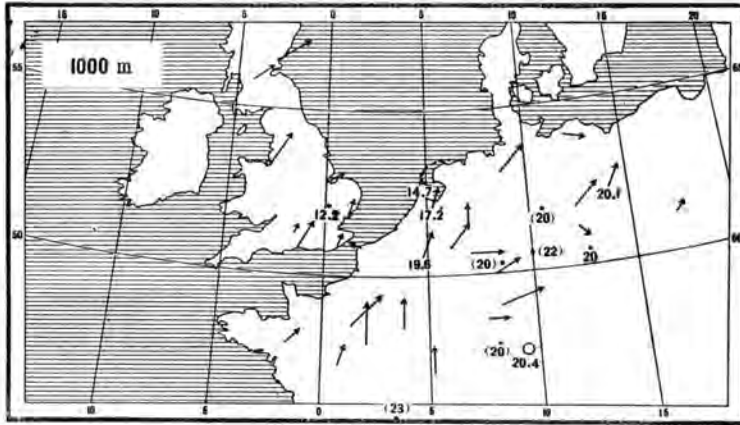


Fig. 11.

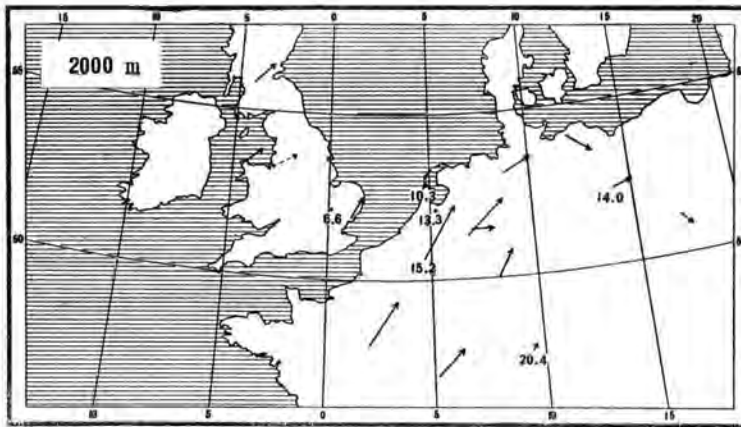


Fig. 12.

the temperature over Friedrichshafen decreased quickly. Whereas in the morning the lapse-rate of temperature over Soesterberg was not very favourable for developing a thunderstorm, conditions grew more and more favourable for such a storm in the afternoon, the more so in the easterly part of the country, where the temperature at the surface was much higher, and surpassed 29° C. If we assume that the conditions experienced in the morning over Friedrichshafen had spread in the afternoon from France to our country, then we find a total lapse of 18° up to 3000 m., in which however at about 2000 m. an inversion must have occurred. These are conditions for heavy thunderstorms as soon as other causes force the lower strata upwards and make them break through the inversion. These other causes are to be found in the much lower temperature and more westerly direction of the air layers in the West, which penetrated like a wedge under the warmer and moist air.

As first demonstrated by MARGULES, the gravitational force accomplishes a considerable amount of work when cold masses of air, which first were found beside warmer masses, spread out under these. With a vertical extension of the layers of 3000 m. and a difference of temperature of 5° C. the whole mass of air may obtain a velocity of 12 m. p. s. The sudden outbreak of stormy winds during a thunderstorm may completely be explained in this way — but velocities of 50 m. p. s. are not easily reached in this manner — for these we want the cooperation of a heavy thunderstorm-squall with a whirlwind.

9. We now come to the observations which in our view contain the key for the explanation of the whirlwinds. The older theories, which f.i. connected the whirlwinds with a rapidly rising current of air, which was said to cause vortices, or which ascribed them to the encounter of two strong wind currents of different directions in the same level, have been found to be failing in most cases. Rapidly rising currents often show no rotation at all. Air currents of very different direction and velocity occur in the same level generally only at distances, very large as compared with the diameter of a whirlwind. On the other hand it is shown daily that very different velocities may occur one over the other and that in that case, especially when inversions limit the turbulence, very sharp discontinuities may be found. Gradually it has become probable, that these continuities of the wind are necessary for the formation of vortices, and that these vortices therefore will rotate in the first instance about a horizontal axis, the higher parts showing the largest velocity in the direction of propagation. According to hydrodynamics, if friction is not considered, a vortex-thread can end only at the boundary of the fluid. WEGENER and KREBS have made the supposition, that waterspouts and whirlwinds constitute the bend-down ends of the horizontal vortices in the higher strata. If both ends are bent towards the earth, the end on the right of the horizontal vortex will show a cyclonic rotation (anti-clockwise), the end on the left an anticyclonic rotation or right-hand rotation. The effect of the earth's rotation on the masses of air streaming towards the vortex will however favour the cyclonic rotation; moreover the other end may bend upwards and terminate at the inversion layer. As a matter of fact observation points to a preponderance of left-handed rotating whirlwinds. Of course the friction near to the surface will cause all kind of complications — f.i. it appears that often a division into a number of whirlwinds occurs.

If this view is correct, the formation of a whirlwind requires a discontinuity of the wind in the vertical and a strongly rising current, in which the discontinuity causes a horizontal vortex. We should expect then, that the yearly range of the whirlwinds bears a certain resemblance to that of the thunderstorms, as the latter ask for a strong rising current, breaking through an inversion. It appears that such is really the case; in this

country, the yearly range of the thunderstorms is, expressed as percentages of the number of days with thunderstorms a year :

Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
2.5	2.5	5.0	8.2	13.2	14.1	15.4	15.1	9.0	8.2	3.9	2.9

that of the whirlwinds :

1.2	2.4	2.4	3.7	11.0	13.4	24.4	23.2	11.0	2.4	4.9	—
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In July and August the whirlwinds are comparatively very numerous.

Also the local differences in frequency of thunderstorms — winter thunderstorms more frequent on the coast, summer thunderstorms on the higher sandy grounds, — are shown in the local distribution of whirlwinds given in fig. 1. If the whirlwind constitutes the vertical prolongation of a horizontal vortex, connected with the rising thundercloud, situated to the left of the whirlwind when looking in the direction of propagation, then the maximum precipitation must fall on the left side of the track of the whirlwind. This is confirmed by our fig. 8. To the right of the track are even places, where no precipitation at all has fallen.

It remains to prove the existence of a considerable discontinuity of the wind. Indeed, in the afternoon of August 10 such a considerable increase of the wind upwards was observed as well at de Bilt as at Uccle, that at first an error was suspected. In calculating the velocities of the various layers of air from the observation of pilot balloons from one station, we have to assume the velocity of ascension to be constant — if the balloon gets a leak, then the velocity of ascension diminishes and too big velocities are calculated. The observation at de Bilt at 1.35 p. m. yielded the following results :

Height	500	1000	1500	2000 m.
Velocity	5	13	20	31 m.p.s.
Direction from 190		200	220	220 ¹⁾

The observation at Uccle was made even later, 4.44—4.54, Amsterdam S. T. hence nearer to the disaster

Height	500	1000	1500	1800	2000 m.
Velocity	16	24	36	41	36 m.p.s.
Direction from 218		222	226	224	223

Lastly it appeared that in the morning in East-England, at Orleans and at Brussels at heights from 2000 to 2400 m. velocities of 20 m. p. s. occurred between masses of air, moving slower as well further W. as further East. Hence there is no doubt, that a very important discontinuity of the wind

¹⁾ In degrees, counted from N. through E.

occurred at a height of 2000 m., leading to velocities of perhaps 40 m. p. s. about the time of the disaster. Such velocities are very rare, especially with a pressure distribution without large gradients at the surface — therefore we may ascribe the serious character of the disaster in the first place to this important discontinuity.

11. The cause of the local occurrence of such high velocities is to be found in the increase of the pressure differences at the level of 2000 m., in consequence of the distribution of temperature, and in the increase of pressure differences at various levels by the secondary depression which passed over our country in the afternoon. The warm masses of air moved from a southerly or south-westerly direction, the cold masses showed a more westerly direction, which accentuated itself especially in the afternoon and penetrated at the surface during the thunderstorm. The difference in barometric pressure between S. England and Friedrichshafen, which in the morning amounted to 7 mm. at 2000 m., to 10 mm. at 5000 m., occurred probably in the afternoon over a distance shorter by one third and was augmented by about 2 mm. by the secondary depression, which must have had its origin at least partly in much higher strata. In this way we arrive almost at doubling the gradient, which hence reached a value of almost 3 mm. per degree, between Brussels and Friedrichshafen even more. This explains sufficiently velocities of such magnitude: the gradient wind at 2000 m. is about 13 m.p.s. per mm. of gradient.

With the general motion of the whole weathersituation towards E. or N.-E., also the region with high wind velocities was transported Eastward. At 11 o'clock the limit just touched the Eastcoast of England (Felixstowe); with the W.-E. components, which during the afternoon were found over England, the displacement until 7 o'clock in the evening would have been about 40, that is about to the central part of our country.

The boundary will probably have had the direction of the warm winds, S.-S.-W. or S.-W., hence in the northern part of our country it was situated further towards East. This is probably the reason, why the thundercloud which caused heavy rain in the northerly part of our country, from Zwolle to Delfzijl, at den Hulst 32.2 mm. in the course of half an hour, has given no rise to the development of heavy whirlwinds, though the destructions in the neighbourhood of Staphorst and Zorgvlied (Smilde), (the isolated spots north of the principal track), show that the limit was nearly reached.

It is evident from the foregoing, that for the formation of so heavy whirlwinds over a large region a rare coincidence of circumstances is required. We need not be amazed therefore, that in order to find in our country a disaster, comparable with that of 1925, we have to go back to the very heavy whirlwinds of August 1, 1674, which made collapse a number of church towers and part of the cathedral at Utrecht.

Résumé : 1. The destructions on August 10, 1925 are to be ascribed to heavy whirlwinds, accompanying a thunderstorm otherwise of no extraordinary intensity, and distinguished from the whirlwinds observed during the last 40 years principally by the extension of their range.

2. Almost all the phenomena observed are in harmony with the view that whirlwinds are the prolongations towards the surface of horizontal vortices in higher strata, a view first pronounced by WEGENER and KREBS.

3. The extraordinary intensity of the whirlwinds is a consequence of the very strong increase of the wind over the level of 2000 m., which in its turn is explained by the very large differences in temperature between W. and Central Europe in the lower kilometers.

with their usual mode of preparation, which may be lowered to 0.13 mg. by a certain process of purification, that DICKENS and DODDS describe the substance as a brown oil, of which in the purest preparation 25 mg. correspond to one rat-unit, whereas STEINACH's mouse-unit weighs 9—13.5 mg. or more. This may be considered pretty well to be the present condition of things.

Therefore we think it progress that we are now able to prepare a substance which brings about very extensive cyclic changes, in a much simpler manner than the rather complicated method of the American and English investigators: moreover, our product has a dry residue of considerably less than 0.1 mg., even less than 0.01 mg. per mouse unit; it is quite free from proteins and is water-soluble. Up to this moment there is no publication containing any proof that the active principle, dissolved in water, is in true solution.

Definition and standardization.

To prevent the repeated use of the term "relatively pure hormone of the estrous cycle" we propose the name "Menformon" for the substance in question, but with the restriction that we understand by it only a substance *which contains at least 10 mouse-units per 1 mg.*

As a mouse-unit (thus included in the definition of "menformon") we define the smallest quantity which is able to produce undeniable cyclic changes of the vaginal epithelium (at least surpassing, at their maximum, the stage described by ALLEN c.s. as "pro-estrus") within 72 hours after the last injection in at least 2 of every three castrated mice, on simultaneous injection.

The injection should be performed with intervals of 4 hours, giving $\frac{1}{3}$ of the total dose at a time; the animals must be castrated at least 25 days before, and they must have been submitted thereafter to a daily control to show that spontaneous cyclic changes are completely absent. In our laboratory the histologic preparations are controlled by two persons independently of each other and without knowledge of what has happened with the animals.

In a few words we shall explain what we mean by "complete absence of cyclic changes". The anatomical investigations by STOCKARD and PAPANICOLAOU¹⁾ furnished a means by which further progress in this field was made possible.

It is well known that the vaginal epithelium in the period of rest of the mucosa consists of 2—4 layers of cells, through which large numbers of leucocytes find their way to the lumen of the vagina. During the estrus the epithelial cells multiply until there are to be seen 14—18 layers of them. The upper layers are cast off as cells and plates without nuclei; the passage of leucocytes is prevented. *This absence of leucocytes* is the most

¹⁾ Am. Jl. Anat. 22, 225, 1917.

important criterion; yet a mere decrease of leucocytes and the massal appearance of epithelial cells which ordinarily are only to be found here and there, constitute an unmistakable change as compared with the negative finding in castrated animals not subjected to the treatment. We consider the action of a substance as *positive* (+) when in the microscopic preparation nearly all leucocytes have disappeared and the epithelial cells predominate, of which last category there must be about as many cells with a nucleus as without one. Frequent occurrence of epithelia *without* nuclei warrants that the pro-estrus has been *passed*, as required in our definition of the mouse-unit. Maximally positive (++) we call the stage in which epithelial cells with nuclei have completely disappeared, and in which moreover most of those without nuclei are cornified.

Up to this moment our experiments have shown that a "maximally positive" (++) reaction (on distributing one mouse-unit over one day) is more often obtained with the original follicular fluid than with the substances prepared from it. These often only give the (++) reaction on repeating the injection the second or third day, even with less than one mouse-unit. This is not merely a question of dosage, for giving 2 or 3 mouse-units in one day needs not produce the same effect. Probably quicker absorption plays a part combined with quicker excretion of the purer preparations, so that only by repeated injections a sufficient concentration during a certain time may be obtained. Thus to obtain a certain effect two factors are concerned: concentration and time.

Important though this problem be, it does not in the least influence the fact that on injecting thrice in the course of one day an unmistakable effect may be obtained, which instead of the continually negative findings in untreated animals doubtlessly shows a change in the sense of the typical estrous cycle, possibly only in a more rapid succession of its stages.

Our diagnoses made in this manner in smears have been confirmed by histologic control of some mice killed for the purpose: when the smear had been labelled (+) their vaginal epithelium showed 10—14 layers.

We require that the animals be castrated at least 25 days before, and that for every experiment at least 3 animals be used, because only the suppression of several cycles seems to make complete castration largely probable; further, because chance can only be excluded when more than one animal, and even at least three, are being used. On using only two animals, different results can compensate each other.

Preparation.

Our first preparations were made from follicular fluid, which, if unchanged, contains in our experience between 600 and 1200 mouse-units per kilogram. ALLEN and DOISY with their method found 2000 rat-units maximally, DICKENS and DODDS c.s. with their extraction-method only 200 rat-units, an amount corresponding to that obtained from ovaria

without follicles. The English investigators therefore decline the particular part ascribed by the Americans to the follicular fluid: we ourselves are inclining toward the American point of view, though we have been able to prepare menformon from whole ovaries and placentae too. Often the follicular fluid, when not quite fresh and sterile, is toxic, so that the animals sometimes die within 1—3 days after the injection. The follicular fluid we sucked from the follicles with a syringe, as far as possible under aseptic precautions.

After observing repeatedly the activity of the unchanged follicular fluid, we tried the purification process of ALLEN and DOISY a few times. This too yielded positive results, though we did not reach the low dry residue as recorded by ALLEN and DOISY in a few cases. Yet we did not spend too much time upon it, because the method is extremely complicated.

We have the impression that, for the first and decisive phase especially, the authors have been strongly influenced by the principles of insulin preparation, and, secondly, by the idea that the active principle would be insoluble in water. This we thought without proof, for though most previous investigators, e.g. FRAENKEL and HERMANN¹⁾ maintained the exclusive lipid-solubility of the ovarian hormones, others, e.g. L. ADLER already in 1912, mentioned the activity of aqueous extracts. Possibly the insolubility in water was only caused by the fact that in the various methods the active principle is extracted together with water-insoluble substances, which prevent the active hormone from dissolving in water.

Thus we aimed at obtaining a water-soluble product.

We thought it one of the most important problems how to free it from proteins. For this purpose, we tried several well-known methods.

After boiling with dilute acid the remaining dry residue was very high, but this experiment confirmed the *thermostability* of the hormone as shown by ALLEN and DOISY. Precipitating with trichloro-acetic acid gave much less dry residue, the solution was perfectly clear, but showed to be very toxic, even after neutralizing. In control experiments with solutions of the sodium salt of trichloro-acetic acid however (of a concentration corresponding to that used in precipitating the proteins) the animals died in much the same manner (perhaps a chlorine intoxication?).

Removing the proteins by the FOLIN-WU-method (as usual in determining the blood-sugar content) proved unsatisfactory.

Better were the results on using colloidal ferric hydroxide.

To one part of follicular liquid 4 parts of physiological saline and about $1\frac{1}{2}$ parts of a 3 % solution of colloidal ferric hydroxide were added, the mixture was then centrifugalized. This yields a turbid yellow fluid which apart from some colloidal $\text{Fe}(\text{OH})_3$ contains the active principle. On evaporation at low temperatures (35°C.) the yellow turbidity precipitates as minute particles, and there results an almost water-clear liquid, faintly

¹⁾ (German) Patentschrift N^o. 309482. Klasse 12.0. Gruppe 26, Ausgegeben 23. 11. 1918.

opalescent and with a dry residue of about 3.3 % : 0.5, 0.75 and 1 cc. of this liquid, injected into castrated mice, constantly gives positive results (0.5 cc. of this liquid corresponded to 0.3 cc. of the original follicular liquid).

The application of this method to larger quantities of follicular fluid, followed by removal of $\text{Fe}(\text{OH})_3$ by means of evaporation and H_2S , showed its usefulness. Such a solution may for instance show a dry residue of 3.35 %, an ash content of 1.06 % and a nitrogen content of 0.47 %.

From such a larger batch we injected, among others, 9 mice, every animal three times ; three mice got 0.5 cc., three others 0.75 cc. and the remaining three 1.0 cc. All except one showed a positive reaction. Repeating the experiment with 0.5 cc. gave strongly positive reactions. Possibly the limit value was even less. But — when prepared by this method one mouse-unit contained about 50 mgr. of dry residue, which compares very unfavourably with the results of the American method and even with those of the English mode of preparation. The only advantage of our method consists in its simplicity.

In view of this unsatisfactory dry residue we further simplified our technic, combining the precipitation of the proteins with the extraction, and then trying to make the hormone pass over into water again. The leading principle must be : to extract the menformon as completely as possible with the least impurities (lipoids included) possible.

To give an example : 10 cc. of follicular fluid and 10 cc. of chloroform are shaken together. The proteins coagulate in part. Then the liquids are separated, the chloroform is evaporated and the residue is taken up in about 5 cc. of distilled water. A perfectly clear watery solution results, having an unweighable content of solid matter. Its activity is rarely more often less than half that of the original follicular liquid, that is to say, if, c.g. 0.6 cc. of follicular liquid contained one mouse-unit, 0.6 cc. of the aqueous solution again contained one mouse-unit.

Though we have already a rather large number of experiments at our disposal we are not yet prepared to say anything definite about the number of mouse-units which may be obtained in this way, nor do we predict anything about the possibility of obtaining by further purification a larger amount of units per cc. than are present in the original follicular liquid, for instance by removing substances with an opposite action (anti-menformon). To settle these questions the number of experiments must be still much greater than it is at present, and, moreover, the limit of accuracy of the method of standardization must be much better known.

Besides chloroform we used carbon sulphide, carbon tetrachloride, benzene, petroleum-ether, tetralin, ligroin, ether, acetone and ethyl acetate. In principle all these yielded identical results, but our experiments are still too few in number. Often the residue from the volatile solvent at first formed an emulsion with the water : in most cases however a simple

filtration made the fluid clear; often the solution was water-clear from the first, and then its content of solids was minimal. Probably this depends, besides on the nature of the solvent, (which must dissolve menformon with as little water-soluble impurities as possible) on the freshness of the follicular liquid, and further on the completeness of the precipitation of the proteins, which then take the other colloidal constituents with them. Finally the completeness with which the volatile solvent is removed plays a part, eventually also the temperature at which this has been done. (We worked at atmospheric pressure, in vacuo and in an air current at about 35°).

All these factors, and many more, are still to be investigated much more completely.

Besides shaking out the follicular fluid directly and eventually coagulating the proteins at the same time, we first dried the follicular liquid itself or solutions prepared from it by the $\text{Fe}(\text{OH})_3$ -method mentioned above, then we extracted the dry residue with chloroform, which in its turn was evaporated, after which the residue was dissolved in water. This solution too yielded identical results, with minimal amounts of solids. This leaves no doubt that *menformon* is *water-soluble*.

Our method may be briefly called the "water-method". When starting from larger quantities, e.g. 1 Litre, of follicular liquid, we found it useful to prevent the forming of emulsions when shaking out with the volatile solvent: this may be done by completing the coagulation of the proteins by adding salt or acids, by centrifugalizing etc.

Solubility, dialysis.

Whether the clear solution obtained by extracting the residue from the volatile solvents with water is a true solution or only a colloidal suspension, we tried to decide by means of dialysis. In previous experiments on purification of our preparations made by means of colloidal ferric hydroxide we found that the activity is lost by dialysis against running water through parchment or collodion membranes. On dialysis of preparations made by the "watermethod" and containing in 10—20 ccm. about 40—80 mouse-units we found in the exarysate (15 and 25 cc. respectively) a rather considerable amount of mouse-units, but less than (about one-fifth of) the calculated amount. But the dialysate too had become weaker than should be the case if the menformon had spread evenly over both exarysate and dialysate. The membrane must thus have retained part of the menformon. This hypothesis was confirmed by the result of efforts to extract it from the membranes again.

Chemical Properties.

The difficulty with which at the present moment larger amounts of the purest "menformon" are available makes it impossible to say much

about its composition. Results with impure preparations are only valuable if they are negative. If, for instance, the impure preparation does not contain phosphorus, the pure product will certainly have none, etc.

Dry residue.

Because, on evaporating unto dryness in the usual manner at 100—110°, amounts of, say 2 cc. of an aqueous solution, containing 20 or more mouse-units, often leave only unweighable quantities of solids, we thought of the possibility of sublimation, and for that reason we dried at temperatures not over 50°. But with these precautions too the residue of 10 cc. (= 160 mouse-units) was not more, and no sublimate was demonstrable with certainty on a watchglass kept above it.

On evaporating 5 ccm. (= 18 mouse-units) in an exsiccator at 37° and at 15°, there was left less than 0.1 mg., probably even less than 0.01 mg. of residue (roughly estimated on comparison with known amounts of other substances). The unweighable residue from other preparations, present, for instance, as rings on a watchglass, did not show any change on further drying at 98°.

In those cases where hardly any residue was obtained (e.g. from 10 cc., containing at least 33 mouse-units) dissolving it again in 10 cc. of water yielded an active (though perhaps somewhat weakened) preparation. From a chemical point of view we thought this preparation somewhat suspect, but it should be borne in mind that also 0.01 mg. of adrenaline and even less are active in adult men.

Slightly impurer preparations (0.06 mg. per mouse-unit), obtained in an exsiccator at 37° (2.2 mg. from 10 cc.) showed a few crystals. Up to this moment we have been unable to identify these. In view of our experience that much purer preparations exist, we think it improbable that *these* crystals have anything to do with menformon itself.

Reactions on proteins, NH₂- or OH-groups; N-, P-, S- and cholesterol-content ¹⁾.

Relatively impure preparations with 0.04 % of dry residue (7—10 M.U. per ccm.) did not show the least *protein*-reaction (Heller's ring-, sulfo-salicylic-, ninhydrin-, biuret-reaction). 2 cc. of a similar preparation yielded no *nitrogen* on determination with the micro-Kjeldahl-method; diazo-benzene sulfonic acid gave a negative reaction on phenol- or aromatic NH₂-groups.

An impure specimen with 3—4 M.U. per cc. and a dry residue of 0.076 % (i.e. about 0.22 mg. per M.U.) yielded 6.6 mg. from 30 cc. on drying at 50°. One-third of this quantity was analysed and showed a nitrogen-content of 2.4 %.

¹⁾ Experiments by Miss E. DINGEMANSE, Ch. D.

It was impossible to demonstrate the presence of *phosphorus* in 2.2 mg., whereas 3.5 mg. of casein with about 0.027 mg. of phosphorus yields a positive reaction.

The nitrogen-content could point to a lecithin-like constitution, but the absence of phosphorus excludes this. Probably the nitrogen too is due to the presence of an impurity.

About the *sulphur*-content we cannot yet say anything: the impure product does not contain demonstrable amounts, but in the same quantity of protein it is quite as impossible to show its presence.

Cholesterol: 2.2 mg. of the impure product, dissolved in chloroform, give a negative cholesterol reaction on addition of acetic anhydride and sulfuric acid, whereas 0.1 mg. of cholesterol gives an unmistakable red or violet colouration. SALKOWSKI's reaction yielded the same negative result. The cholesterol content of the impure substance, if at all present, is thus certainly below 5 %. Addition of 0.3 % of *trikresol*, or of a 0.9 % solution of *sodium chloride* do not alter the aspect of a solution of menformon, nor its potency.

Keeping qualities: After being kept for 3 weeks in an incubator at 37° the solution did not show any change of potency.

We are of opinion, that in menformon we found a new substance, of which we hope to be able to publish something more positive in the near future. This makes it necessary for us to have larger quantities at our disposal which is a matter of considerable trouble considering the difficulty in obtaining the original material.

Physiological action and pharmacological assay.

Repeated injections into *mice* of one or more mouse-units (up to this moment we gave about 4—8 M.U. every day) seem to have no action, apart from the specific effect.

In *rabbits* subcutaneous or intravenous injection of 8—80 M.U. (= 1 to 10 cc), at one time or within 10 minutes, is supported without any ill effects, even when repeated within a few days.

In *men* injection of 1 cc. (= 3—45 M.U.) even when repeated, does not produce any general effects, as experiments on ourselves, as well as those taken by clinical men among our friends on female persons have shown. For this purpose we used solutions to which 0.3 % *trikresol* and 0.9 % NaCl had been added, and of which the sterility had been proved.

Blood-pressure and Heart.

Impure preparations (such as contained more solids than is tolerated by our definition of menformon), when injected intravenously into rabbits in urethane anesthesia, produced a steep lowering of their blood-pressure: on repeating the injection they died. The curves recently published by DICKENS and DODDS c.s. showing repeated lowering of blood-pressure

after intravenous injection are obtained with preparations of considerable impurity as compared with menformon. Only somewhat purer preparations, containing about 5 M.U. per mg. and therefore still too impure as to be comparable with our definition of menformon were *completely devoid of any action* upon the blood-pressure of rabbits or of cats decerebrated with novocain, even after injecting three times 1 cc., i.e. all together 6.6 mg. of solids and about 15 M.U.

Three and more M.U. did not show any definite effect on the isolated frog heart, beating at the Straub cannula.

Blood vessels.

On perfusing a LAEWEN—TRENDELENBURG—KOCHMANN preparation (frog or guinea-pig) we were unable to find definite changes of the width of the blood vessels.

Respiration.

An impure preparation showed some effect upon the respiration of rabbits in urethane anesthesia, along with a lowering of their blood-pressure. Pure preparations, however, do not produce the least alteration of the respiration.

Uterus.

Doses of about 17 M.U. often produce an unmistakable *contraction* in the *isolated uterus* of virgin guinea pigs. The amount of solids in this dose was far below 0.1 mg.; smaller doses did not act with certainty.

The *uterus in situ*, as studied by means of the abdominal window (through which several foeti could be clearly seen), did not show any change on intravenous injection of about 45 M.U. Repetition of the experiment 3 days afterwards remained negative too. The young were born the following day, i.e. about 2—3 days before the normal end of pregnancy. Of course this does not necessarily lead to the conclusion that menformon was the cause, for a similar early birth often occurs without any injections.

Blood sugar.

Injection of 15 M.U. was *without any influence* upon the blood sugar content of rabbits.

Growth.

In spring we performed some experiments with unchanged follicular liquid upon tadpoles. An addition of 10 % of the liquid to the growing medium killed the animals whereas a content of 2 % was without any

influence. On the contrary an amount of only 8 M.U. in total is capable of causing within 10 days an enlargement of more than 200 % of the generative organs in young female rats scarcely capable of holding their own in absence of their mother, as compared with the control animals.

Quite similar results were obtained with young guinea pigs. The control animals were injected with a liver extract prepared in quite the same way and in doses quite equal as regards the quantity of raw material (follicular liquid and liver) to which they corresponded. The animals got 7 injections of 0.2 cc. each within a week. The control animal got altogether 0.06 mg. of solids, the others about 23 M.U. with unweighable residue. In this case too the generative organs of the menformon-animals had a weight which by more than 100 % surpassed that of the controls. This holds good for the animals killed immediately after the last injection, as well as for those which were killed a few days afterwards. This last fact, we think, pleads more in favour of a stimulation of the growth of the generative organs than for the induction of temporary estrous changes.

Summary.

A simple method is described (the "water-method") to prepare a substance (from follicular fluid especially) which is able to induce in castrated mice unmistakable changes of the vagina and uterus that are probably identical with those of the spontaneous estrous cycle. This substance is defined as one in which 1 mgr. of solids represent at least 10 of the so called mouse-units = M.U. These mouse-units are defined, and the conditions for standardization are given.

Provisionally chemical analysis shows the substance to be protein-free, probably also free from nitrogen, from cholesterol, from phosphorus and possibly also from sulphur. Besides in volatile solvents it is readily soluble in water. The name *menformon* is proposed.

Pharmacologically menformon in doses up to 45 M.U. showed perfectly non-toxic in men and animals; intravenous injections up to 80 M.U. did not affect blood pressure nor respiration in any way. Doses of 17 M.U. often caused contractions in the isolated virgin uterus. Up to this moment our observations on the uterus in situ (rabbits with abdominal window) did not show any influence. The effect upon the growth of the generative organs in young, normal female rats and guinea-pigs is evident.

The wide-spread belief that the substances which cause changes similar to the spontaneous estrous cycle are not in true solution in water and the observation that they act upon the blood-pressure both probably took their origin in a failure to free them from impurities, from lipoids especially.

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November 1925.

Physics. — "*The analogue of Clapeyron's law in the case of evaporating electrons*". By J. DROSTE. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of October 31, 1925).

This paper contains the approved solution of a question, proposed in 1924 by the Mathematical Society (Wiskundig Genootschap) at Amsterdam as to the validity of an equation, mentioned further on as equation (7) and relating to the equilibrium of a hot metal with the electrons it emits. This equation, first derived by RICHARDSON¹⁾ on a statistical basis, is easily verified in those cases in which the electric potential can be calculated. It was asked whether or not this equation holds good in the case of an arbitrarily shaped evacuated enclosure bounded by bodies of one and the same metal. It will be found that the question has to be answered in the affirmative.

1. We consider a vacuum bounded by bodies of a given hot metal emitting electrons. In the equilibrium state there will be a temperature T , constant throughout the system. By means of wires of the same metal the electric potential of all the bodies is made equal. As these wires make of all the bodies a single one, we may speak simply of the conductor and its surface; it is supposed only that the wires do not resist relative displacements of the bodies.

In the equilibrium state the electronic gas will have a concentration N , which at the surface has the value N_0 , a quantity depending only on T . The pressure in the gas will be $p = kNT$. As the lines of force end normally at the surface the stress along them will give rise to a normal force acting on the surface, amounting to $\frac{1}{2} \left(\frac{\partial \varphi}{\partial n} \right)^2$ per unit area, φ representing the electric potential. So the total pressure will be normal and have the value

$$A = kN_0T - \frac{1}{2} \left(\frac{\partial \varphi}{\partial n} \right)^2 \quad \dots \dots \dots (1)$$

2. Now consider an infinitesimal, infinitesimally slow change in the system with the temperature T changing by δT and the shape of the space R changing by infinitesimal displacements of the bodies.

This may be imagined as due to an infinitesimal increase $\delta \lambda$ in a parameter λ which, with other parameters, determines the relative position of the bodies. An arbitrary point of the surface will consequently get

¹⁾ Vid. O. W. RICHARDSON, The electron theory of matter (1914), pag. 447, eq. (14).

an infinitesimal displacement, the projection of which on the normal at the surface we call δa ; we suppose this normal to be directed from the space R toward the interior of the conductor.

The work done by the system in consequence of these displacements amounts to

$$\int A \delta a d\sigma = \delta \lambda \int A \frac{\delta a}{\delta \lambda} d\sigma,$$

in which the integral has to be taken over the surface of the conductor.

The energy U of the system being a function of T and λ , it follows from the second law of Thermodynamics that

$$\frac{1}{T} \left(\delta U + \delta \lambda \int A \frac{\delta a}{\delta \lambda} d\sigma \right)$$

or, what reduces to the same thing,

$$\frac{U}{T^2} \delta T + \left(\int \frac{A}{T} \frac{\delta a}{\delta \lambda} d\sigma \right) d\lambda,$$

derived from the former expression by subtracting $\delta \left(\frac{U}{T} \right)$, is an exact differential. This leads to the relation

$$\frac{\partial}{\partial \lambda} \left(\frac{U}{T^2} \right) = \frac{\partial}{\partial T} \int \frac{A}{T} \frac{\delta a}{\delta \lambda} d\sigma$$

or

$$\frac{\partial U}{\partial \lambda} = \int \left(T \frac{\partial A}{\partial T} - A \right) \frac{\delta a}{\delta \lambda} d\sigma.$$

We write this equation in the form

$$\delta_x U = \int \left(T \frac{\partial A}{\partial T} - A \right) \delta a d\sigma, \quad \dots \quad (2)$$

where δ_x means an increment corresponding to $\delta \lambda$ (or, what reduces to the same thing, to the displacements δa), T remaining constant. The same symbol will stand for the increment which a quantity depending on the coordinates gets in consequence of $\delta \lambda$, T as well as the coordinates remaining constant.

3. We now proceed to calculate both members of (2). If the evaporation of an electron produces a constant increase ε of energy, the left hand member of (2) will be

$$\delta_x U = \delta_x \int \frac{1}{2} (\text{grad } \varphi)^2 dS + \varepsilon \delta_x \int N dS;$$

both integrals are to be taken over the space R .

Now the displacements δa , taking place at constant temperature, will give rise to another distribution of the electrons and also to another value of φ ; let $N + \delta_x N$ be the new concentration, $\varphi + \delta_x \varphi$ the new

potential. As N_0 depends only on T , δN will be zero at the surface. The change of $\delta_x U$ consists of two parts:

$$\delta_x U = \int \delta_x \left\{ \frac{1}{2} (\text{grad } \varphi)^2 + \epsilon N \right\} dS + \int \left\{ \frac{1}{2} \left(\frac{\partial \varphi}{\partial n} \right)^2 + \epsilon N_0 \right\} \delta a \, d\sigma.$$

In the former part one has to do with the integral, taken over the original space R , of the increment which the quantity $\frac{1}{2} (\text{grad } \varphi)^2 + \epsilon N$ gets in consequence of the displacements δa ; the second integral has to be taken over the surface of R and represents the alteration which U gets by constant φ and N in consequence of the addition and subtraction of small parts to R .

Now substituting in the right hand member of (2) the value of A , taken from (1), we get

$$\int \left(T \frac{\partial A}{\partial T} - A \right) \delta a \, d\sigma = \int \left\{ kT^2 \frac{dN_0}{dT} - \frac{1}{2} T \frac{\partial}{\partial T} \left(\frac{\partial \varphi}{\partial n} \right)^2 + \frac{1}{2} \left(\frac{\partial \varphi}{\partial n} \right)^2 \right\} \delta a \, d\sigma.$$

Equation (2) thus becomes

$$\begin{aligned} \int \left(\delta_x \left\{ \frac{1}{2} (\text{grad } \varphi)^2 + \epsilon N \right\} dS + \int \epsilon N_0 \delta a \, d\sigma \right) &= \\ &= \int \left\{ kT^2 \frac{dN_0}{dT} - \frac{1}{2} T \frac{\partial}{\partial T} \left(\frac{\partial \varphi}{\partial n} \right)^2 \right\} \delta a \, d\sigma, \end{aligned}$$

which may be written in the form

$$\begin{aligned} \int \delta_x \left\{ \frac{1}{2} (\text{grad } \varphi)^2 dS + T \frac{\partial}{\partial T} \int \left(\frac{\partial \varphi}{\partial n} \right)^2 \delta a \, d\sigma \right. &= \\ &= \left(kT^2 \frac{dN_0}{dT} - \epsilon N_0 \right) \int \delta a \, d\sigma - \epsilon \int \delta_x N \, dS. \end{aligned}$$

But the increase of the number of electrons in R , arising from the displacements δa at constant temperature, is

$$\delta_x \int N \, dS = \int \delta_x N \, dS + N_0 \int \delta a \, d\sigma$$

and consequently it is permissible to write $\delta_x \int N \, dS - \int \delta_x N \, dS$ for $N_0 \int \delta a \, d\sigma$ in the right hand member of the equation just found, so that this member becomes

$$kT^2 \frac{d \log N_0}{dT} \left(\delta_x \int N \, dS - \int \delta_x N \, dS \right) - \epsilon \delta_x \int N \, dS$$

and the equation, after transposition of a term from the right side to the left, becomes

$$\begin{aligned} \int \delta_x \left\{ \frac{1}{2} (\text{grad } \varphi)^2 dS + kT^2 \frac{d \log N_0}{dT} \int \delta_x N \, dS + T \frac{\partial}{\partial T} \int \left(\frac{\partial \varphi}{\partial n} \right)^2 \delta a \, d\sigma \right\} &= \\ &= \left(kT^2 \frac{d \log N_0}{dT} - \epsilon \right) \delta_x \int N \, dS \end{aligned} \quad (3)$$

3. It now will be proved that the left hand member of this equation is zero. To this purpose we begin with the equations

$$\Delta \varphi = N e, \quad (4)$$

$$N e \text{ grad } \varphi = \text{grad } p; \quad (5)$$

from these equations the first enables us to calculate φ if N be given, the second expresses the equilibrium condition for the electrons. By replacing p by kNT equation (5) becomes

$$N e \text{ grad } \varphi = kT \text{ grad } N.$$

Now in φ an additive quantity independent of the coordinates does not matter and so we may take

$$\varphi = \frac{kT}{e} \log N \quad (6)$$

so that (4) becomes

$$\Delta \varphi = e e^{\frac{e}{kT} \varphi}, \quad (4a)$$

in which the two meanings of e are not to be confused.

The quantity φ is a function of the coordinates as well as of T and the parameter λ .

Differentiating (4a) with respect to T and λ successively we find

$$\Delta \frac{\partial \varphi}{\partial T} = \left(\frac{\partial \varphi}{\partial T} - \frac{\varphi}{T} \right) \frac{e^2}{kT} e^{\frac{e}{kT} \varphi}, \quad \Delta \frac{\partial \varphi}{\partial \lambda} = \frac{e^2}{kT} e^{\frac{e}{kT} \varphi} \frac{\partial \varphi}{\partial \lambda}.$$

Multiplying the first of these equations by $\frac{\partial \varphi}{\partial \lambda}$, the second by $\frac{\partial \varphi}{\partial T} - \frac{\varphi}{T}$ and subtracting the results we find

$$\frac{\partial \varphi}{\partial \lambda} \Delta \frac{\partial \varphi}{\partial T} = \left(\frac{\partial \varphi}{\partial T} - \frac{\varphi}{T} \right) \Delta \frac{\partial \varphi}{\partial \lambda}.$$

This may be written in the form

$$\begin{aligned} \text{div} \left(\frac{\partial \varphi}{\partial \lambda} \text{grad } \frac{\partial \varphi}{\partial T} \right) - \left(\text{grad } \frac{\partial \varphi}{\partial \lambda} \cdot \text{grad } \frac{\partial \varphi}{\partial T} \right) = \\ = \text{div} \left\{ \left(\frac{\partial \varphi}{\partial T} - \frac{\varphi}{T} \right) \text{grad } \frac{\partial \varphi}{\partial \lambda} \right\} - \left(\text{grad } \left\{ \frac{\partial \varphi}{\partial T} - \frac{\varphi}{T} \right\} \cdot \text{grad } \frac{\partial \varphi}{\partial \lambda} \right) \end{aligned}$$

or

$$\frac{1}{T} \left(\text{grad } \varphi \cdot \text{grad } \frac{\partial \varphi}{\partial \lambda} \right) + \text{div} \left\{ \left(\frac{\partial \varphi}{\partial T} - \frac{\varphi}{T} \right) \text{grad } \frac{\partial \varphi}{\partial \lambda} \right\} - \text{div} \left(\frac{\partial \varphi}{\partial \lambda} \text{grad } \frac{\partial \varphi}{\partial T} \right) = 0.$$

Multiplying this equation by TdS and integrating over R we get

$$\int \frac{\partial}{\partial \lambda} \frac{1}{2} (\text{grad } \varphi)^2 dS + \int \left(T \frac{\partial \varphi}{\partial T} - \varphi \right) \frac{\partial^2 \varphi}{\partial \lambda \partial n} d\sigma - \int T \frac{\partial \varphi}{\partial \lambda} \frac{\partial^2 \varphi}{\partial n \partial T} d\sigma = 0.$$

Now at the surface it follows from (6) that

$$T \frac{\partial \varphi}{\partial T} - \varphi = T \frac{\partial}{\partial T} \left(\frac{kT}{e} \log N \right) - \frac{kT}{e} \log N = \frac{kT^2}{e} \frac{\partial \log N}{\partial T} = \frac{kT^2}{e} \frac{d \log N_0}{dT}$$

and consequently the second term changes into

$$\frac{kT^2}{e} \frac{d \log N_0}{dT} \int \frac{\partial^2 \varphi}{\partial \lambda \partial n} d\sigma$$

or

$$\frac{kT^2}{e} \frac{d \log N_0}{dT} \int \Delta \frac{\partial \varphi}{\partial \lambda} dS.$$

Since $\Delta \frac{\partial \varphi}{\partial \lambda} = \frac{\partial}{\partial \lambda} \Delta \varphi = \frac{\partial}{\partial \lambda} (Ne)$ we may write

$$\int \frac{\partial}{\partial \lambda} \frac{1}{2} (\text{grad } \varphi)^2 dS + kT^2 \frac{d \log N_0}{dT} \int \frac{\partial N}{\partial \lambda} dS - T \int \frac{\partial^2 \varphi}{\partial n \partial T} \frac{\partial \varphi}{\partial \lambda} d\sigma = 0$$

and from this we find by multiplying by $\delta \lambda$

$$\int \delta_\lambda \frac{1}{2} (\text{grad } \varphi)^2 dS + kT^2 \frac{d \log N_0}{dT} \int \delta_\lambda N dS - T \int \frac{\partial^2 \varphi}{\partial n \partial T} \delta_\lambda \varphi d\sigma = 0.$$

Now at the surface

$$\delta_\lambda \varphi = - \frac{\partial \varphi}{\partial n} \delta a,$$

for we see from (6) that if T remains constant φ will not change at a point which moves with the surface. Substituting, the last term becomes

$$T \frac{\partial}{\partial T} \int \frac{1}{2} \left(\frac{\partial \varphi}{\partial n} \right)^2 \delta a d\sigma,$$

and we get an equation which says that the left hand member of (3) is zero. Consequently (3) becomes

$$\left(kT^2 \frac{d \log N_0}{dT} - \varepsilon \right) \delta_\lambda \int N dS = 0.$$

As it is always possible to displace the bodies in such a way that $\delta_\lambda \int N dS$ is not zero, i.e. that in consequence of the displacements electrons do evaporate or condense, we must have

$$kT^2 \frac{d \log N_0}{dT} - \varepsilon = 0$$

or

$$\frac{d \log N_0}{dT} = \frac{\varepsilon}{kT^2} \quad \dots \dots \dots (7)$$

Geophysics. — "*On the relation between wind or current and mean sealevel in the Indian and the Atlantic oceans and the adjacent seas.*" By P. H. GALLÉ. (Communicated by Dr. J. P. VAN DER STOK.)

(Communicated at the meeting of October 31, 1925).

1. *Introduction.*

In a former communication ¹⁾ in the Proceedings of this Academy the relation between the Trades of the North Atlantic and the mean sealevel in the seas of northern Europe has been investigated. Data about mean sealevel increased considerably since that time, this is the reason why this investigation has been taken up again.

2. *Bay of Bengal and Gulf of Aden.*

The yearly range of the mean level is extremely large at Kidderpore, situated 85 nautical miles up the river from the mouth of the Hooghly, which flows into the extreme north of the Bay of Bengal. Monthly departures from normal are :

—65, —72, —59, —43, —28, —5, +53, +106, +114, +57, —12, —46 ;

here and further on all departures are given in c.m..

Atmospheric pressure has some influence on the waterlevel, pressure in Calcutta shows the following yearly range in m.m. :

+5.9, +4.4, +1.8, —0.9, —3.3, —6.0, —6.3, —4.9, —2.4, +1.4, +4.6, +6.1,

and if mean sealevel at the head of the Bay was only dependent upon pressure, its range would be approximately :

—8, —6, —2, +1, +4, +8, +8, +6, +3, —2, —6, —8.

When we accept this range also for Kidderpore, it is evident that besides atmospheric pressure other influences are responsible for the following range in mean riverlevel at that place :

—57, —66, —57, —44, —32, —13, +45, +100, +111, +59, —6, —38.

The two principal phenomena responsible for this yearly range are :

¹⁾ These Proceedings 17, p. 1147.

10. The monsoons in the Bay of Bengal.

20. The enormous rainfall in this part of India.

At Calcutta and Cherrapunji the monthly rainfall in m.m. is consecutively:

7, 26, 29, 39, 142, 280, 313, 322, 264, 98, 16, 8;
19, 55, 280, 819, 1309, 2670, 2780, 1943, 1352, 355, 38, 6.

It is obvious that the height of the level in the Hooghly must rise or fall with the quantity of rain falling in the basin of the river, but the amount of this rise and fall is unknown to us. We tried to find a correction for the precipitation by calculating month for month the ratio between departure of level for primo May and departure of windforce for medio March, etc.; the windforce calculated in the way indicated in the Table on page 907.

The reason why a phasedifference of six weeks was applied will be found further on.

We intended to smooth the discrepancies between the monthly ratios by taking into account the rainfall, but the mutual differences between these ratios were rather large and did not decrease after a correction for the rainfall.

The amount of rainfall in this region however depends in no small degree upon the monsoon; rainfall and monsoon are not inter-independent; if the Southwest-monsoon is not steady or when its force is below the average the transport of moisted air from the Bay to the windside of the Himalaya-mountains is smaller than normal and rainfall shows a deficit.

The correlation between the energy of the wind in the Bay of Bengal and rainfall in Calcutta and Cherrapunji is consecutively:

$$\begin{array}{ll} r = +0.934 & f = \pm 0.024 \\ = +0.944 & = \pm 0.021 \end{array}$$

Wind is the prime factor and when we consider in our further calculations only the energy of the wind, precipitation is automatically taken into account.

Secondly we pointed to the monsoons as generators of fluctuations in the level.

From November to March the Northeastmonsoon, from May to September the Southwestmonsoon is blowing over the Bay, April and October are transitionmonths.

In connection with the trend of the coastline at the head of the Bay and near the mouth of the Hooghly, wind from the North is off-shore, a wind from the South an on-shore wind.

Monthly direction and force of the wind was computed for the area 10° — 20° N./ 80° — 90° E., the projections of these resultants on the direction North-South give what we call the acting or working components and their squares the monthly energy. An on-shore component is positive, an off-shore negative.

In the following table the different data are given, the force of the wind is given here and further on in Beaufort-units.

Month	Wind		Working component	Energy	Departures from normal	
	Direction	Force			Energy	Level
January	N 42°0	2.7	—2.01	—4.04	—5.27	— 57
February	39	1.3	—1.01	—1.02	—2.25	— 66
March	20	0.3	—0.28	—0.08	—1.31	— 57
April	293	1.2	—0.47	—0.22	—1.45	— 44
May	240	2.5	+1.25	+1.56	+0.33	— 32
June	233	4.3	+2.59	+6.71	+5.48	— 13
July	231	4.2	+2.64	+6.97	+5.74	+ 45
August	234	3.9	+2.29	+5.24	+4.01	+100
Sept.	233	3.0	+1.81	+3.24	+2.01	+111
October	173	0.9	+0.89	+0.79	—0.44	+ 59
Nov.	57	1.5	—0.82	—0.67	—1.90	— 6
Dec.	50	3.0	—1.93	—3.72	—4.95	— 38

It is a known fact that between monsoons and the driftcurrents they cause, a phasedifference exists of about one month.

The current in the Bay of Bengal being seasonally on- and off-shore and being responsible — at least for the greater part — for the range in meanlevel at Kidderpore, it is evident that this phasedifference must be taken into account.

For this reason the correlationfactor was calculated not only between the simultaneous departures from normal of the energy of the wind and the riverlevel, but also between the first mentioned departures in January, February, etc. and departures in the level in February, March ; March, April etc.

The result is given here :

Simultaneously	$r = +0.618$	$f = \pm 0.121$
Phasediff. one month	$= +0.914$	$= \pm 0.031$
„ two „	$= +0.920$	$= \pm 0.031$
„ three „	$= +0.616$	$= \pm 0.121$

This seems to prove that fluctuations and changes in the windsystem in

the northern part of the Bay are followed after about six weeks by fluctuations in riverlevel at Kidderpore.

In the Gulf of Aden the yearly range of mean sealevel is fairly large, before and after correction for atmospheric pressure the following data show the monthly range of mean sealevel for rainless Aden :

+ 5.6,	+ 7.0,	+ 8.1,	+ 9.9,	+10.4,	+3.1,
— 6.4,	—13.8,	—12.6,	— 9.6,	— 3.9,	+2.2;
+10.7,	+11.2,	+10.2,	+10.3,	+ 9.0,	—2.5,
—13.2,	—20.0,	—15.7,	— 7.9,	+ 0.1,	+7.5.

and this fluctuation is in our opinion caused by the monsoons in the Arabian Sea at the mouth of the Gulf.

The wind was computed for the area 10° — 20° N./ 45° — 60° E. ; the monthly vectors were projected on the direction N. 70° E. for the calculation of the working components etc.

The result is given in the next table, a working component in westerly direction is positive, in easterly direction negative :

Month	Wind		Working component	Energy	Departures from normal	
	Direction	Force			Energy	Level
January	N. $67^{\circ}0$	2.8	+ 2.76	+ 7.62	+ 6.91	+ 10.7
February	75	2.6	+ 2.60	+ 6.76	+ 6.01	+ 11.2
March	84	2.2	+ 2.18	+ 4.75	+ 4.04	+ 10.2
April	78	1.3	+ 1.30	+ 1.69	+ 0.98	+ 10.3
May	182	0.9	— 0.23	— 0.05	— 0.76	+ 9.0
June	221	3.2	— 2.59	— 6.71	— 7.42	— 2.5
July	221	4.0	— 3.23	—10.41	—11.42	— 13.2
August	220	3.4	— 2.71	— 7.34	— 8.05	— 20.0
Septemb.	203	2.0	— 1.17	— 1.37	— 2.08	— 15.7
October	80	0.9	+ 0.89	+ 0.79	+ 0.08	— 7.9
Novemb.	59	2.3	+ 2.19	+ 4.80	+ 4.09	+ 0.1
Decemb.	64	2.9	+ 2.82	+ 7.95	+ 7.24	+ 7.5

The reason why in the case of Kidderpore the wind of January was considered in connection with the level of February, etc. is also valid for Aden.

Simultaneously	$r = +0.760$	$f = \pm 0.083$
Phasediff. one month	$= +0.957$	$= \pm 0.017$
„ two „	$= +0.875$	$= \pm 0.058$
„ three „	$= +0.543$	$= \pm 0.134$

Fluctuations and changes in the windsystem of the Arabian Sea are followed by changes in mean sealevel at Aden after about five weeks.

A very fair agreement exists between the results for Kidderpore with its abundant rainfall, and rainless Aden.

The level-data for Kidderpore result from the period 1881—1893, those for Aden from 1879—1893, a lapse of time long enough for the tropics; the wind-data have been computed over the period 1854—1910.

Although a large correlationfactor alone does not prove the existence of a causal relation between the considered phenomena, in this case wind and mean sealevel, daily experience that on-shore and off-shore winds raise and lower the waterlevel forces us to make the conclusion that in the case of Kidderpore and Aden a causal relation exists.

North Atlantic Ocean.

In the Atlantic conditions are not so simple as in the Indian Ocean, they are on the contrary rather complicated.

The great variations in general weatherconditions over Western-Europe and over the northern part of the Atlantic depend for the greater part upon the permanent sub-tropical anticyclone, the tropical belt of low pressure and the semi-permanent Iceland-depression.

Variations in atmospheric pressure in the above-mentioned areas are followed by increased or decreased velocity of the Equatorial current, of the North Atlantic Stream and of its ramifications that flow into the North Sea, the Baltic and the Polar Basin. BREITFUSZ was the first to point to the fact that a period exists in the quantity of Atlantic water flowing into the Polar Basin, with a maximum in winter and spring, a minimum in summer and autumn.

BREITFUSZ's opinion is: „that this flow and ebb is not in the first place dependent upon local circumstances, but that they originate in the Gulfstream and in the many circumstances affecting this stream on its way, thousands of miles long, from its cradle under the equator through the Caribbean Sea, the Atlantic to the Polar Basin”.

Its „cradle under the equator” is the North-Equatorial current, a driftcurrent caused by the Northeast-trade. A Northeast-trade stronger than normal points to a sub-tropical anticyclone better developed than under average conditions and, as shown by HANN, a surplus of pressure in this region generally corresponds with a negative departure of pressure in the Iceland-region.

But under these conditions the Southwesterly air-transport between 40° and 50° northern latitude is stronger than normal and raises the speed and stability of the North Atlantic Stream.

Hitherto, in connection with European waterlevel, only more distant factors were discussed, but as well as for Kidderpore and Aden more local influences near the European coast exist, more or less responsible for fluctuations in mean sealevel.

However, these influences are originally dependent upon the above-named centres of action, and finally we come to the conclusion: Northeast-trade or Equatorial current *prime cause*, fluctuations in mean sealevel around the whole ocean *result*, but not directly connected.

It was tacidly accepted that for our purpose we might consider the driftcurrent instead of the wind, raising this current.

The correlationfactor between wind and current in 15° — 25° N./ 25° — 40° W. is $r = +0.69$ $f = \pm 0.13$; and if in the case of Aden the current in the Arabian Sea was taken into account, the following correlationfactors would have been the result:

Simultaneously	$r = +0.629$	$f = \pm 0.118$
Phasediff. one month	$= +0.906$	$= \pm 0.035$
„ two	$= +0.880$	$= \pm 0.044$
„ three	$= +0.606$	$= \pm 0.123$

Fluctuations in current and mean sealevel follow each other after a fortnight.

Instead of the wind, the current may be taken into account and for our further investigation in the Atlantic Ocean this will be done.

Departures from mean sealevel along the coasts of the Atlantic and adjacent seas are given in Table I; Table II contains the cosine-formulae, the epoch is January 15th, and generally the amplitude of the yearly range is larger than that of the semi-yearly.

The phase of the yearly range increases from 191° at Washington and 204° at Baltimore—Portland, to 245° at Horta, 300° at the entrance of the Channel, over 300° in the Northern part of the North Sea, to 320° at Kabelvaag and Vardö.

In the North Sea and Baltic we meet with the reverse:

The phase decreases from 281° at Katwijk, to 272° at Esbjerg, 262° in the Skager-rak, 229° from Kiel—Swinemünde and increases again along the Swedish and German coast, Stolpmünde—Pillau from 263° to 272° , to 292° at Utö and Lypertö along the Finnish coast.

The discontinuity in the regular course of this phase is probably caused by the big quantities of fresh water, originating from melting ice and snow in spring and early summer and from rain in summer and autumn, that flow into the Baltic, a typical mediterranean sea.

TABLE I.
YEARLY RANGE OF MEAN SEALEVEL IN CM.

Station	Period	Jan.	Feb.	Mrh.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Washington Old Point Comfort	— —	— 7.6	—10.9	—10.1	— 3.3	5.7	11.1	10.6	6.2	2.1	0.3	— 0.5	— 3.1
Baltimore . .	1903—1923	—12	—13	— 8	— 1	4	9	7	10	10	6	— 3	— 9
Atlantic City	1912—1920	— 7	— 9	— 8	— 1	2	4	3	6	6	7	1	— 3
Fort Hamilton	1893—1920	— 8	—11	— 6	1	2	5	5	6	6	6	0	— 6
Portland . . .	1912—1922	— 3	— 4	— 5	— 1	0	2	2	2	2	2	2	— 1
Horta	1905—1923	0.0	— 0.7	— 2.6	— 2.4	— 1.9	0.3	1.3	2.5	1.8	1.4	0.4	0.5
Brest	— —	2.9	— 2.5	— 6.1	— 6.0	— 4.4	— 2.5	— 2.1	— 1.1	1.1	5.2	8.0	7.5
Newlyn	1915—1925	1.1	0.7	— 0.7	— 4.2	— 3.2	— 5.8	— 2.7	— 0.9	0.9	5.2	5.7	3.8
Katwijk . . . Harlingen . . }	1884—1920	1.7	— 3.6	— 6.1	— 8.3	— 9.1	— 4.8	0.4	4.4	3.3	7.2	5.8	8.9
Felixtowe . .	1917—1925	0.6	— 4.0	— 4.0	— 3.4	— 7.0	— 1.2	0.2	2.3	4.2	6.2	2.9	3.8
Dumbar . . .	1913—1925	4.5	0.7	— 5.1	— 8.6	— 7.4	— 5.3	— 1.5	0.3	2.3	5.3	7.1	7.8
Dundee . . .	1867—1912	6.7	0.9	— 5.4	— 9.1	—10.9	— 8.5	— 6.4	— 0.9	— 0.6	7.6	10.6	13.7
Aberdeen . .	1862—1913	5.2	0.6	— 3.7	— 7.9	— 8.8	— 6.7	— 3.4	— 0.6	1.2	6.7	6.7	11.0
Bremerhaven .	1898—1924	3.2	— 2.3	— 9.0	— 7.3	— 9.2	— 0.6	3.7	7.2	3.8	0.3	5.2	5.2
Esbjerg . . .	1889—1902	3.0	— 7.2	— 4.3	—13.6	—12.2	— 8.5	0.7	6.2	8.6	12.8	2.9	12.0
Hirshals . . .	1892—1911	1.6	— 0.7	—10.4	—10.0	—10.8	— 4.1	4.9	8.4	4.0	6.1	5.1	5.8
Frederikshavn	1893—1911	2.7	— 1.6	— 9.4	— 9.6	—10.2	— 3.7	4.3	7.2	4.2	4.9	6.4	5.6
Aarhus . . .	1888—1911	1.9	— 2.4	— 6.7	— 7.8	— 8.0	— 3.6	2.5	5.0	4.3	5.6	5.3	3.8
Fredricia . .	1889—1911	— 0.1	— 1.9	— 5.5	— 6.2	— 5.7	— 2.9	2.1	4.1	5.1	5.0	3.3	2.7
Hornbaek . .	1898—1911	3.2	— 1.9	—11.1	— 9.3	— 8.9	— 2.4	7.0	9.8	5.8	2.4	3.8	1.6
Kopenhagen .	1889—1911	0.5	— 1.1	— 7.5	— 9.1	— 8.4	— 2.8	5.7	8.5	7.1	3.7	2.0	1.7
Korsör . . .	1897—1911	— 0.7	— 0.1	— 6.1	— 7.0	— 5.4	— 3.0	3.8	6.5	6.2	2.8	1.6	2.2
Slipshavn . .	1896—1911	0.4	— 0.6	— 6.2	— 6.7	— 6.3	— 3.1	4.1	6.3	5.5	2.5	3.0	1.0
Gjedser . . .	1898—1911	— 4.3	2.0	— 4.1	— 7.2	— 3.9	— 2.2	5.0	7.8	8.4	1.1	— 3.6	1.0
Varberg . . .	1887—1900	— 2.6	— 6.3	— 7.8	—11.8	— 8.4	— 3.7	5.5	8.2	8.6	9.3	4.0	5.1
Ystad	1887—1900	— 4.9	1.2	— 5.5	— 8.4	— 8.2	— 3.3	4.1	5.4	6.4	7.1	1.4	4.4
Karlskrona .	1887—1900	— 5.4	2.1	— 6.6	— 9.8	—11.0	— 4.0	4.5	6.5	7.2	9.5	1.6	5.4
Landsort . .	1887—1900	— 2.1	1.3	— 8.5	—12.9	—13.0	— 6.0	5.2	8.5	8.8	8.9	2.6	7.4

TABLE I. (Continued).

YEARLY RANGE OF MEAN SEALEVEL IN C.M.

Station	Period	Jan.	Feb.	Mrh.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Grönskär . .	1888—1900	— 1.4	1.9	— 8.7	—13.5	—13.8	— 7.1	5.0	8.4	10.1	9.2	4.0	6.7
Björn . . .	1891—1900	— 2.0	1.8	— 6.5	—11.9	—13.0	— 9.0	4.0	5.0	10.8	6.9	3.9	10.1
Droghällan .	1898—1900	4.8	1.6	— 9.2	—14.3	—15.7	—10.4	2.0	2.6	7.5	7.8	8.0	15.0
Ratan . . .	1891—1900	— 1.7	— 0.5	— 7.3	—12.6	—14.8	—10.7	3.4	4.5	11.6	8.6	8.7	11.2
Kiel	1895—1909	— 3.1	— 0.1	— 3.6	— 3.4	— 3.5	— 0.2	4.7	4.3	5.7	1.0	— 3.1	0.9
Travemünde .	1882—1924	— 3.7	— 1.1	— 3.9	— 4.0	— 2.4	1.1	4.8	5.7	6.0	1.5	— 3.5	— 0.3
Mariënleuchte	1882—1924	— 3.2	— 1.1	— 5.1	— 5.3	— 4.3	0.5	5.6	7.2	5.7	2.3	— 2.8	0.4
Wismar . . .	1882—1924	— 4.1	— 2.2	— 3.2	— 4.7	— 3.2	2.4	6.9	6.5	6.2	1.1	— 4.0	— 1.3
Warnemünde	1882—1924	— 3.1	— 1.5	— 5.5	— 5.8	— 4.7	1.2	6.9	7.4	6.7	1.8	— 2.7	— 0.8
Arkona . . .	1882—1924	— 0.5	0.2	— 5.7	— 8.0	— 7.9	— 2.5	4.1	7.3	6.4	3.2	— 0.2	3.5
Swinemünde .	1882—1924	— 2.5	— 0.1	— 6.2	— 6.6	— 6.2	0.0	6.6	8.8	6.6	0.1	— 3.5	3.0
Stolpmünde .	1911—1924	3.2	— 2.9	—10.2	— 9.4	—11.2	0.1	5.8	9.6	8.8	1.6	— 1.1	5.8
Pillau . . .	1898—1924	3.3	0.8	— 9.9	—11.4	—10.9	— 2.5	7.1	12.2	8.8	— 0.8	— 1.0	4.1
Memel . . .	1898—1918	4.8	2.1	— 9.6	— 4.8	—13.2	— 7.5	2.2	9.4	8.1	— 1.9	0.5	9.4
Christiania .	1886—1890 1904—1918	4.8	— 3.5	—11.4	— 9.9	— 8.1	— 1.2	5.3	9.0	3.2	2.5	4.8	4.6
Oscarsburg .	1872—1881	— 6.0	—16.9	—15.0	—13.6	— 8.4	— 5.6	12.0	11.0	17.6	10.9	7.4	6.3
Arendal . . .	1886—1889	— 0.2	—10.9	— 9.2	—11.3	— 6.3	— 1.5	4.7	7.6	5.6	6.7	6.9	7.9
Stavanger . .	1881—1885 1899—1905 1911—1918	3.3	0.9	— 6.1	— 8.5	— 7.1	— 7.9	— 5.0	2.7	1.8	6.8	10.3	8.4
Bergen . . .	1883—1889 1911—1918	7.8	— 0.1	— 7.7	—13.2	—11.7	— 8.4	— 3.9	1.3	4.0	6.5	12.9	12.7
Trondheim .	1872—1878 1880—1881	18.6	2.0	— 9.1	—16.4	—10.6	— 2.9	— 5.4	—11.5	— 3.7	9.1	18.2	11.3
Kabelvaag . .	1880—1883	22.3	10.1	— 5.5	—15.0	—10.5	—10.5	— 3.2	— 0.2	— 7.5	— 0.5	10.8	8.6
Narvik . . .	1905—1915	11.5	7.6	— 5.3	— 8.1	—13.6	— 9.7	— 6.6	— 6.0	0.3	5.6	11.9	12.3
Vardö . . .	1880—1883	18.2	10.0	— 5.5	—17.8	—14.1	— 8.4	— 0.6	4.7	— 4.0	0.2	9.9	7.9

In chapter 4, North Sea and Baltic data for quantities of this fresh water and precipitation are given.

The course of the phase of the semi-yearly range is in the beginning rather uncertain, at the entrance of the Channel the phase is about 240°.

TABLE II. Formulae Yearly Range. Epoch 15 January.

1	Washington, Old Point Comfort	$+ 9.3 \cos (nt-191^\circ) + 4.1 \cos (2nt-161^\circ)$
2	Baltimore, Atlantic City, Fort Hamilton and Portland. . . .	$+ 7.4 \cos (nt-204^\circ) + 2.0 \cos (2nt-208^\circ)$
3	Horta	$+ 2.3 \cos (nt-245^\circ) + 0.9 \cos (2nt- 7^\circ)$
4	Brest.	$+ 6.2 \cos (nt-294^\circ) + 2.6 \cos (2nt-284^\circ)$
5	Newlyn	$+ 4.8 \cos (nt-307^\circ) + 0.7 \cos (2nt-191^\circ)$
6	Katwijk and Harlingen. . . .	$+ 8.0 \cos (nt-281^\circ) + 1.6 \cos (2nt-345^\circ)$
7	Dumbar, Dundee, Aberdeen. .	$+ 8.9 \cos (nt-306^\circ) + 1.7 \cos (2nt-327^\circ)$
8	Bremerhaven, Esbjerg, Hirshals .	$+ 8.8 \cos (nt-272^\circ) + 3.0 \cos (2nt- 16^\circ)$
9	Hirshals, Fredericshavn, Varberg, Arendal, Stavanger, Bergen. .	$+ 9.1 \cos (nt-262^\circ) + 1.9 \cos (2nt- 3^\circ)$
10	Aarhuus, Fredericia, Hornback, Kopenhagen, Korsör, Slípshavn	$+ 6.8 \cos (nt-261^\circ) + 1.7 \cos (2nt- 33^\circ)$
11	Gjedser, Ystad, Karlskrona . . .	$+ 6.4 \cos (nt-258^\circ) + 2.4 \cos (2nt- 60^\circ)$
12	Kiel, Travemünde, Marienleuchte, Wismar, Warnemünde, Arkona, Swinemünde	$+ 4.9 \cos (nt-229^\circ) + 2.9 \cos (2nt- 42^\circ)$
13	Stolpmünde, Pillau, Memel . . .	$+ 7.4 \cos (nt-263^\circ) + 5.8 \cos (2nt- 29^\circ)$
14	Varberg, Ystad, Karlskrona, Land- sort, Grönskär, Björn, Drög- hällan, Ratan	$+ 9.8 \cos (nt-272^\circ) + 3.0 \cos (2nt- 44^\circ)$
15	Utö en Lypertö. 1892—1900 . .	$+ 11.2 \cos (nt-292^\circ) + 3.5 \cos (2nt- 75^\circ)$
16	Stavanger, Bergen, Trondheim. .	$+ 10.8 \cos (nt-304^\circ) + 3.1 \cos (2nt-323^\circ)$
17	Bodö, Kabelvaag, Narvik, Vardö	$+ 12.3 \cos (nt-322^\circ) + 4.7 \cos (2nt-355^\circ)$

along the North Sea coasts and the Norwegian coast between 300° and 382° , in the Kattegat, the Sount and the Belts it fluctuates between 3° and 60° .

For the observations from Horta, Felixtowe, Dumbar and Newlyn, the German and Norwegian Coast we are indebted to the Director of the Meteorological Office at Ponta Delgada, the Officer in Charge of the Levelling Department of the Ordnance Survey Office at Southampton, the Director of the Geodetical Institute at Potsdam and the Director of Norges Geografiske Opmaaling at Kristiania.

The Dutch observations were provided by Algemeenen Dienst van den Rijkswaterstaat, the Hague, for the origin of other observations we point to the appendix "Literature".

In the region 15° — 25° N./ 25° — 40° W., part of "the cradle of the Gulfstream", monthly departures from normal, in miles per 24 hours, in the velocity of the North-Equatorial current run as follows:

-1.3, -1.8, -1.2, -0.9, -0.3, +0.8,
+2.7, +1.3, +1.6, +0.5, -0.1, -1.3;

they are computed over the period 1855—1905.

For various stations the following correlation factors were calculated:

Washington, Old Point,	Simultaneously	$r = +0.829$	$f = \pm 0.062^1)$
Comfort	Ph.Diff. one month	$= +0.551$	$= \pm 0.138$
Baltimore, Atlantic City,	Simult.	$= +0.869$	$= \pm 0.044$
Fort Hamilton, Portland	One month	$= +0.776$	$= \pm 0.076$
Horta	Simult.	$= +0.668$	$= \pm 0.107$
	One month	$= +0.889$	$= \pm 0.041$
	Two ..	$= +0.778$	$= \pm 0.076$
Newlyn (Lands' End)	Two ..	$= +0.649$	$= \pm 0.114$
	Three ..	$= +0.896$	$= \pm 0.038$
	Four ..	$= +0.907$	$= \pm 0.035$
	Five ..	$= +0.601$	$= \pm 0.124$
Brest	Two ..	$= +0.725$	$= \pm 0.093$
	Three ..	$= +0.885$	$= \pm 0.041$
	Four ..	$= +0.801$	$= \pm 0.069$
Aberdeen	Two ..	$= +0.636$	$= \pm 0.114$
	Three ..	$= +0.921$	$= \pm 0.027$
	Four ..	$= +0.896$	$= \pm 0.048$
Dundee	Two ..	$= +0.584$	$= \pm 0.128$
	Three ..	$= +0.896$	$= \pm 0.038$
	Four ..	$= +0.908$	$= \pm 0.035$
	Five ..	$= +0.715$	$= \pm 0.093$
Stavanger	Two ..	$= +0.745$	$= \pm 0.086$
	Three ..	$= +0.907$	$= \pm 0.035$
	Four ..	$= +0.847$	$= \pm 0.055$
Narvik	Three ..	$= +0.809$	$= \pm 0.069$
	Four ..	$= +0.935$	$= \pm 0.024$
	Five ..	$= +0.805$	$= \pm 0.069$

The general result is a big correlation factor and a phasedifference increasing when considering stations at higher latitude and greater longitude.

Though we cannot imagine a direct relation in such a sense, that a fluctuation in the speed of the Equatorial current is followed after 3, 4 or

¹⁾ A systematical error in the calculations is the cause why the correlation factors between the monthly departures of the velocity of the Equatorial Current and those of the water-level are generally a trifle (0.02) too small in the Proceedings in Dutch.

5 months by analogous fluctuations in supply of Atlantic water along the European coast, simply by direct watertransport, a relation exists so far that the causes, modifying the Equatorial current at the south-side of the sub-tropical anticyclone, modify at the same time the southwesterly wind at its north-side as was explained before.

These southwesterly winds transport smaller or bigger quantities than normal of relatively warm water and air to regions situated more to the North and East. The relatively warm water will have a great influence on the general air-circulation in these northerly regions and this process will continue for a considerable time.

In last instance this general aircirculation affects substantially the watertransport along the European coast. We agree with BREITFUSZ that the supply of water from the ocean to the European coasts and into Polar Basin is of a periodical nature.

4. *North Sea and Baltic.*

Leaving out of consideration the northern part of the British North Sea coast, the main peculiarity of these seas is the welldefined secondary minimum in October and November.

This phenomenon is very clearly to be seen along the German and Swedish coast, not so clearly along the Skagerrak, Kattegat, Sount, Belts and the Dutch coast. In the first named region, the relation between the amplitudes of the yearly and semi-yearly range is as 2.2 to 1, in the last named as 4.5 to 1.

We think we may point to the large amount of fresh water from melting snow and ice in spring and from the large precipitation in summer, that flows into the Baltic, when looking for the cause of this strong semi-yearly range in this sea. WITTING gives the following data for the supply of fresh water (K.M.³) and precipitation (m.m.) for the Bothnian Gulf.

	J.	F.	M.	A.	M.	J.	J.	A.	S.	O.	N.	D.
Fresh water	7	5	6	19	49	30	20	24	18	15	10	9
Precipitation	26	22	20	37	37	48	55	94	42	50	34	31

In the North Sea and the Baltic we find also a big correlationfactor between Equatorial current and mean sealevel, but in these narrow seas local influences play a more important part especially in the Baltic, where conditions for water-circulation are rather unfavourable.

The monthly resultant wind on the Dutch coast was computed from observations made from 1882—1910 on board the lightvessels Terschel-

lingerbank and Schouwenbank, the resultants were projected on the direction N 276° E. the squares of these projections gave the energy; an easterly direction is positive.

The data are given in the following table with monthly departures from mean level over the same period for a combination of Katwijk and Harlingen.

Month	Wind		Working compt.	Energy	Departures from normal	
	Direction	Force			Energy	Level
January	N 217° E	1.01	0.65	0.42	+0.02	+1.9
February	224	0.70	0.52	0.27	—0.13	—4.0
March	242	0.50	0.45	0.20	—0.20	—6.5
April	329	0.44	0.21	0.04	—0.36	—8.9
May	324	0.64	0.35	0.12	—0.28	—7.6
June	309	0.70	0.52	0.27	—0.13	—5.4
July	268	0.96	0.96	0.90	+0.50	+0.8
August	249	1.21	1.15	1.32	+0.92	+4.9
September	258	0.65	0.63	0.40	+0.00	+3.2
October	222	0.91	0.64	0.41	+0.01	+9.2
November	206	0.70	0.34	0.12	—0.28	+4.6
December	208	1.19	0.61	0.37	—0.03	+7.4

The correlation factor is:

$$\begin{array}{lll} \text{Simultaneously} & r = +0.472 & f = +0.149 \\ \text{Phasediff. one month} & = +0.398 & = +0.163 \end{array}$$

From observations made at Swambister, Bergen, Skudesnaes, Flushing and Helder, a resultant windforce "the North Sea wind" was computed. Monthly departures from normal of the energy show the following range:

$$\begin{array}{llllll} +0.72, & -0.38, & -0.26, & -2.29, & -0.37, & -0.45, \\ +1.45, & +1.41, & +0.94, & -0.19, & -0.81, & +0.31, \end{array}$$

and the correlationfactor between these departures and those for mean sealevel at Harlingen and Katwijk (1884—1920) is:

$$\begin{array}{lll} \text{Simultaneously} & r = +0.478 & f = \pm 0.149 \\ \text{Phasediff. one month} & = +0.442 & = \pm 0.156 \\ \text{Simultaneously} & r = +0.781 & f = \pm 0.076 \\ \text{Phasediff. one month} & = +0.578 & = \pm 0.128 \end{array}$$

and for the Swedish coast from Varberg till Ratan:

Simultaneously	$r = +0.624$	$f = \pm 0.117$
Phasediff. one month	$= +0.615$	$= \pm 0.121$

The correlationfactor is the biggest when simultaneous departures are considered; in the North Sea the relation is much smaller than in the Baltic. For the correlationfactor between departures in the velocity of the Equatorial current and those in mean sealevel in the North Sea and the Baltic, the result is:

Katwijk and Harlingen:

Phasediff. one month	$= +0.624$	$= \pm 0.114$
.. two ..	$= +0.806$	$= \pm 0.069$
.. three ..	$= +0.880$	$= \pm 0.045$
.. four ..	$= +0.648$	$= \pm 0.131$

Travemünde-Swinemünde:

Simultaneously	$r = +0.771$	$f = \pm 0.080$
Phasediff. one month	$= +0.833$	$= \pm 0.059$
.. two ..	$= +0.600$	$= \pm 0.125$

Varberg-Ratan:

Phasediff. one month	$= +0.740$	$= \pm 0.086$
.. two ..	$= +0.841$	$= \pm 0.055$
.. three ..	$= +0.798$	$= \pm 0.069$

5. Conclusions.

1. Range in mean sealevel in the Indian and Atlantic Ocean and the adjacent seas is for the greater part a result of fluctuations of wind and current in regions, either far away from, or more in the neighbourhood of the place where mean sealevel is considered.

2. The Northeast-Trade or the Equatorial current is not the prime cause of fluctuations in mean sealevel on the European coast, but the regions of high and low pressure, that cause this wind and current, are substantially the generators of these fluctuations.

3. The correlationfactor between monthly departures of the velocity of the current or energy of the wind at a great or fairly great distance and departures in mean sealevel is generally large and varies between $+0.829$ and $+0.957$.

4. The correlationfactor between monthly departures of the local

wind in the North Sea and departures in mean sealevel in the North Sea and the Baltic varies between $+0.472$ and $+0.781$.

5. The phasedifference between monthly departures of the velocity of the Equatorial current and those of mean sealevel in the Atlantic Ocean and European coasts increases gradually :

Northeast part American coast	Simultaneous
Horta	one month
Channel	three months
North Sea	three months
Northern part Norwegian Coast	four months.

A discontinuity in the regular course of this phasedifference exists in the Baltic.

German coast	one month
Swedish coast	two months.

6. LITERATURE.

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In the case of linear correlation the probability formula runs:

$$dW = \frac{h h' \sqrt{1-\gamma^2}}{\pi} e^{-(h^2 u^2 - 2\gamma h h' u u' + h'^2 u'^2)} du \cdot du' \quad . \quad . \quad . \quad (11)$$

being

$$u = x - \bar{\xi} \quad , \quad u' = x' - \bar{\xi}'.$$

We have now the empirical data

$$Y_{kl} = \int_{x_{k-1}}^{x_k} \int_{x'_{l-1}}^{x'_l} D \cdot dx \cdot dx' = \int_{u_{k-1}}^{u_k} \int_{u'_{l-1}}^{u'_l} \frac{h h' \sqrt{1-\gamma^2}}{\pi} e^{-(h^2 u^2 - 2\gamma h h' u u' + h'^2 u'^2)} du \cdot du'$$

being

$$u_k = x_k - \bar{\xi} \quad , \quad u'_l = x'_l - \bar{\xi}'$$

For the extreme limits we must take:

$$\begin{aligned} x_0 &= -\infty, & x_n &= +\infty, & x'_0 &= -\infty, & x'_n &= +\infty, \\ u_0 &= -\infty, & u_n &= +\infty, & u'_0 &= -\infty, & u'_n &= +\infty. \end{aligned}$$

By substituting

$$hu = t \quad , \quad h'u' = t'$$

we arrive direct at the unimodular probability formula:

$$y_{kl} = \int_{t_{k-1}}^{t_k} \int_{t'_{l-1}}^{t'_l} \frac{\sqrt{1-\gamma^2}}{\pi} e^{-(t^2 - 2\gamma t t' + t'^2)} dt \cdot dt'.$$

Putting

$$\sqrt{1-\gamma^2} \cdot t = z \quad , \quad t' - \gamma t = \zeta,$$

we find (cf. the canonic form I)

$$dW = \frac{1}{\sqrt{\pi}} e^{-z^2} dz \cdot \frac{1}{\sqrt{\pi}} e^{-\zeta^2} d\zeta = ds \cdot d\sigma,$$

being written

$$s = \Theta(z) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^z e^{-v^2} dv \quad , \quad \sigma = \Theta(\zeta) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\zeta} e^{-v^2} dv$$

In this case z and s are functions only of t , hence only of x ; on the contrary ζ and σ are functions both of t and t' , hence both of x and x' .

To $x_0 = -\infty$ corresponds $t_0 = -\infty$, $z_0 = -\infty$, $s_0 = 0$;

„ $x_n = +\infty$ „ „ $t_n = +\infty$, $z_n = +\infty$, $s_n = 1$.

To $x'_0 = -\infty$ and x finite corresponds $t'_0 = -\infty$ and t finite, thus $\zeta = -\infty$, $\sigma = 0$.

To $x'_{n'} = +\infty$ and x finite corresponds $t'_{n'} = +\infty$ and t finite, thus $\zeta = +\infty$, $\sigma = 1$.

Introducing the notation

$$\begin{aligned} z(x_k) &= z_k & \zeta(x_k, x'_{l'}) &= \zeta_{kl} \\ s(x_k) &= s_k & \sigma(x_k, x'_{l'}) &= \sigma_{kl} \end{aligned}$$

with

$$\begin{aligned} z_0 &= -\infty & z_n &= +\infty & \zeta_{k0} &= -\infty & \zeta_{kn'} &= +\infty \\ s_0 &= 0 & s_n &= 1 & \sigma_{k0} &= 0 & \sigma_{kn'} &= 1, \end{aligned}$$

we obtain

$$\int_{x=-\infty}^{x_k} \int_{x'=-\infty}^{x'_{l'}} D \cdot dx \cdot dx' = \frac{1}{\sqrt{\pi}} \int_{z=-\infty}^{z_k} e^{-z^2} dz \cdot \frac{1}{\sqrt{\pi}} \int_{\zeta=-\infty}^{\zeta_{k,l}} e^{-\zeta^2} d\zeta = s_k \cdot \sigma_{kl},$$

whence

$$\sum_{i=1}^k \sum_{j=1}^{l'} \int_{x_{i-1}}^{x_i} \int_{x'_{j-1}}^{x'_j} D \cdot dx \cdot dx' = s_k \cdot \sigma_{kl}. \quad (12)$$

We can now get rid of t' (i.e. of x') by integrating over x' (i.e. over t') between the extreme limits $x'_0 = -\infty$ and $x'_{n'} = +\infty$ (resp. $t'_0 = -\infty$ and $t'_{n'} = +\infty$); so we find

$$\int_{x=-\infty}^{x_k} \int_{x'=-\infty}^{+\infty} D \cdot dx \cdot dx' = \sum_{i=1}^k \sum_{j=1}^{n'} \int_{x_{i-1}}^{x_i} \int_{x'_{j-1}}^{x'_j} D \cdot dx \cdot dx' = s_k \cdot \sigma_{kn'} = s_k \times 1 = s_k \quad (13)$$

This integral obviously is equal to the sum of the frequency contents of all the rows $x = \xi_1$, $x = \xi_2, \dots, x = \xi_k$, divided by the total number N . So the value of s_k results from

$$s_k = \frac{\sum_{i=1}^k \sum_{j=1}^{n'} Y_{ij}}{N} \quad (14)$$

On the other hand the integral $\int_{x=-\infty}^{x_k} \int_{x'=-\infty}^{+\infty} D \cdot dx \cdot dx'$ is a function of x_k .

We therefore find to each x_k a value of s_k , i. e. a value of the

function $s(x)$. Furthermore the relation $s = \Theta(z)$ conjugates to each s_k a value of z_k .

Besides the pairs $s_0 = 0, z_0 = -\infty$ and $s_n = 1, z_n = +\infty$, we thus obtained $n-1$ pairs

$$(s_1, z_1) \quad . \quad (s_2, z_2) \quad . \quad . \quad (s_{n-1}, z_{n-1}).$$

If the correlation is really linear, all these $n-1$ values of z must satisfy the linear relation:

$$z = \sqrt{1-\gamma^2} \cdot t = \sqrt{1-\gamma^2} \cdot hu = \sqrt{1-\gamma^2} \cdot h(x-\xi) = ax + b.$$

By interpreting x and z as rectilinear coordinates, the points (x, z) must be found on the straight line $z = ax + b$.

Inversely the collinear disposition of the points (x, z) empirically determinates points to the possibility of linear correlation between x and x' . Properly speaking this only shows that the quantity x , considered by itself, is distributed according to the normal law.

As the function $z(x)$ empirically found (which in this case is linear) is wholly independent of x' , it gives us no indication at all, neither with regard to x' , nor to the connection between x and x' .

To determine the relation between x and x' we must appeal to the function $\sigma(x, x')$.

Integrating $\iint D dx dx' = \iint ds \cdot d\sigma$ over an infinitely narrow strip along $x = x_i$, the breadth of which is Δx_i , the integral being taken over x' from $x'_0 = -\infty$ to x'_1 , we find the value of this integral to be

$$L_{i1} = \Delta x_i \cdot \int_{x'=-\infty}^{x'_1} D(x_i, x') dx' = \Delta x_i \cdot \int_{x'=-\infty}^{x'_1} \left\{ \frac{ds}{dx} \cdot \frac{\partial \sigma}{\partial x'} \right\}_{x=x_i} dx',$$

or, putting

$$\frac{ds(x)}{dx} = \chi(x),$$

to

$$L_{i1} = \chi(x_i) \cdot \Delta x_i \cdot \{ \sigma(x_i, x'_1) - \sigma(x_i, x'_0) \} = \chi(x_i) \cdot \Delta x_i \cdot \sigma_{i1}.$$

Integrating along this same strip over x' from x'_0 to $x'_{n'}$, i.e. from $-\infty$ to $+\infty$, we obtain

$$L_{in'} = \chi(x_i) \cdot \Delta x_i \cdot 1.$$

So the quantity σ_{i1} (i.e. the value of the function $\sigma(x, x')$ at $x = x_i$ and $x' = x'_1$) is found to be the quotient $\frac{L_{i1}}{L_{in'}}$, whence

$$\sigma_{i1} = \frac{\Delta x_i \cdot \int_{-\infty}^{x'_1} D(x_i, x') dx'}{\Delta x_i \cdot \int_{-\infty}^{+\infty} D(x_i, x') dx'}.$$

We may find an approximate value of σ_{il} by taking a strip of finite breadth Δx_i round $x = x_i$.

As we only have at our disposal strips round $x = \xi_k = x_{k-1/2}$ having the breadth c , we are able to determine only approximately the value of $\sigma_{k-1/2, l} = \sigma(\xi_k, x'_l)$ by the formula

$$\sigma_{k-1/2, l} \doteq \frac{c \cdot \int_{-\infty}^{x'_l} D(\xi_k, x') dx'}{c \cdot \int_{-\infty}^{+\infty} D(\xi_k, x') dx'} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (15)$$

where \doteq signifies: approximately equal to.

The numerator of the fraction (15) equals the N^{th} part of the frequency content of the row of ξ_k from the lower limit up to the class-limit x'_l . The denominator is the N^{th} part of the frequency content of the whole row of ξ_k . Hence

$$\sigma_{k-1/2, l} \doteq \frac{\sum_{j=1}^l Y_{kj}}{\sum_{j=1}^{n'} Y_{kj}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (16)$$

In this way we find the value of the function $\sigma(x, x')$ belonging to each pair $(\xi_k, x'_l) = (x_{k-1/2}, x'_l)$.

By means of the relation $\sigma = \Theta(\zeta)$ we assign to each value of σ a value of ζ . Thus we obtain by each combination $(\xi_k, x'_l) = (x'_{k-1/2}, x'_l)$ a value $\zeta_{k-1/2, l}$.

If the correlation is really linear, ζ must appear to satisfy the relation

$$\begin{aligned} \zeta_{k-1/2, l} = t'_l - \gamma t_{k-1/2} &= h' u'_l - \gamma h u_{k-1/2} = h'(x'_l - \bar{\xi}') - \gamma h(\xi_k - \bar{\xi}) = \\ &= h'(x'_l - \bar{\xi}') - \gamma h(x_{k-1/2} - \bar{\xi}) = ax_{k-1/2} + \bar{a}x'_l + \beta. \end{aligned}$$

Inversely, if ζ satisfies the equation $\zeta = ax + \bar{a}x' + \beta$, it furnishes a second indication that the correlation is linear. From the 5 coefficients a, b, \bar{a}, β the 5 quantities $\bar{\xi}, \bar{\xi}', h, h', \gamma$ may be computed.

In the same manner we may analyze the frequency scheme by means of the quantities s' and σ' (resp. z' and ζ'). Then z' and $s' = \Theta(z')$ are functions only of x' ; ζ' and $\sigma' = \Theta(\zeta')$, on the contrary, are functions of both x and x' .

The value of $s'_l = s'(x'_l)$ is to be determined by

$$s_l = \frac{\sum_{i=1}^n \sum_{j=1}^l Y_{ij}}{N} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (14')$$

The numerator is the total frequency content of the columns belonging to $\xi'_1, \xi'_2, \dots, \xi'_l$. So we obtain $n' - 1$ pairs (x', s') ; hence by means of

whence

$$N = S'_{\alpha'} = \sum_{j=1}^{n'} R'_j ;$$

c'. then $s'_l = s'(x'_l)$ results from

$$s'_l = \frac{S'_l}{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19')$$

d'. and z'_l from

$$s'_l = \Theta(z'_l) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{z'_l} e^{-v^2} dv.$$

e'. Add only the frequencies $Y_{1l}, Y_{2l}, \dots, Y_{kl}$ in the column ξ'_l , which correspond to $\xi_1, \xi_2, \dots, \xi_k$; hence

$$P'_{k,l} = \sum_{i=1}^k Y_{il} ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20')$$

f'. then $\sigma'_{k,l-1/2} = \sigma'(x_k, x'_{l-1/2}) = \sigma'(x_k, \xi'_l)$ is derived from

$$\sigma'_{k,l-1/2} = \frac{P'_{k,l}}{R'_l} ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21')$$

g'. and $\zeta'_{k,l-1/2}$ from

$$\sigma'_{k,l-1/2} = \Theta(\zeta'_{k,l-1/2})$$

h'. Finally ζ'_{kl} is determined by interpolation.

At present the functions $z(x), z'(x'), \zeta(x, x')$ and $\zeta'(x, x')$ are determined with more or less accuracy at the angular points of the frequency scheme. We shall now make use of these functions in seeking a set of variables $t(x, x')$ and $t'(x, x')$ linearly correlated.

As it has already been shown, from

$$dW = ds \cdot d\sigma \rightleftharpoons ds' \cdot d\sigma' \rightleftharpoons D(x, x') \cdot dx \cdot dx'$$

we may derive the equations

$$D(x, x') = \frac{\partial(s, \sigma)}{\partial(x, x')} = \frac{\partial(s', \sigma')}{\partial(x, x')}$$

or

$$D(x, x') = \frac{ds}{dx} \cdot \frac{\partial\sigma}{\partial x'} = \frac{ds'}{dx'} \cdot \frac{\partial\sigma'}{\partial x}.$$

On the other hand we have

$$ds = \frac{1}{\sqrt{\pi}} e^{-z^2} dz, \quad d\sigma = \frac{1}{\sqrt{\pi}} e^{-\zeta^2} d\zeta, \quad ds' = \frac{1}{\sqrt{\pi}} e^{-z'^2} dz', \quad d\sigma' = \frac{1}{\sqrt{\pi}} e^{-\zeta'^2} d\zeta',$$

whence

$$dW = \frac{1}{\pi} e^{-(z^2 + \zeta^2)} dz \cdot d\zeta \rightleftharpoons \frac{1}{\pi} e^{-(z'^2 + \zeta'^2)} dz' \cdot d\zeta' \quad . \quad . \quad . \quad (22)$$

We have thus got two sets of linearly correlated variables, viz. (z, ζ) and (z', ζ') , but the coefficient of correlation is zero; properly speaking there is no correlation at all between them. We have solved the problem, it is true, but this solution is by no means satisfactory. In the above discussion about the requirements of a useful solution, we have already explained why we do not remain by the two sets of variables in question.

In future we shall introduce z and z' — in the place of x and x' — as fundamental variables. Then ζ and ζ' become, in general, functions both of z and z' . Thus the two-dimensional differentials $dz \cdot d\zeta$ and $dz' \cdot d\zeta'$ will be transformed in this way:

$$dz \cdot d\zeta \rightleftharpoons dz \cdot \frac{\partial \zeta}{\partial z'} \cdot dz', \quad dz' \cdot d\zeta' \rightleftharpoons dz' \cdot \frac{\partial \zeta'}{\partial z} \cdot dz.$$

So we find for dW :

$$dW = \frac{1}{\pi} e^{-(z^2 + \zeta^2)} \frac{\partial \zeta}{\partial z'} \cdot dz \cdot dz', \quad dz' = \frac{1}{\pi} e^{-(z'^2 + \zeta'^2)} \frac{\partial \zeta'}{\partial z} \cdot dz \cdot dz', \quad \dots \quad (23)$$

whence

$$e^{-(z^2 + \zeta^2)} \frac{\partial \zeta}{\partial z'} = e^{-(z'^2 + \zeta'^2)} \frac{\partial \zeta'}{\partial z} \quad \dots \quad (24)$$

We next put

$$z^2 + \zeta^2 = r^2, \quad z'^2 + \zeta'^2 = r'^2 \quad \dots \quad (25)$$

In order to orient ourselves in the treatment, we shall previously make a simplifying supposition, viz. that at each point (x, x') or (z, z') holds

$$r' = r, \quad \dots \quad (26)$$

whence, on account of (24), we have also at each point

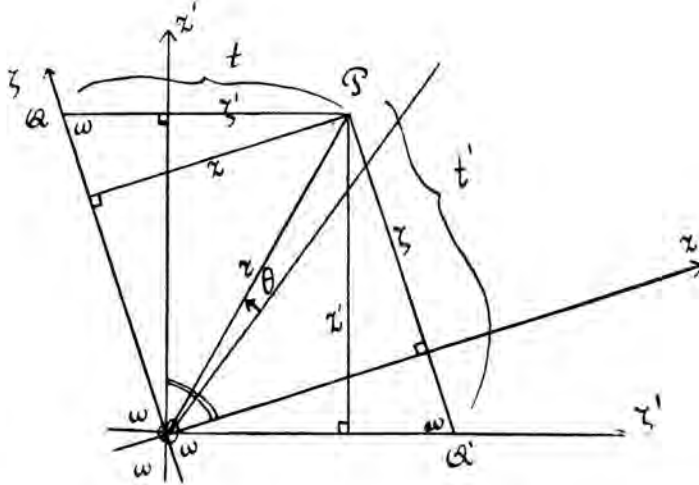
$$\frac{\partial \zeta}{\partial z'} = \frac{\partial \zeta'}{\partial z} \quad \dots \quad (27)$$

The result of computing the values of the functions z, ζ, z', ζ' must make out whether the expressions $r^2 = z^2 + \zeta^2$ and $r'^2 = z'^2 + \zeta'^2$ are equal at each point, or at least nearly equal. We may not expect a complete empirical concordance between r^2 and r'^2 , if even it did exist theoretically, since the computed values of ζ and ζ' are exposed to inevitable inaccuracies. Especially on the borders of the frequency domain we must be prepared for a bad concordance between the theoretical and the empirical values.

We shall next make use of two rectangular systems of coordinates: (z, ζ) and (z', ζ') , having the same origin.

The way in which the functions z, z', ζ, ζ' are introduced, viz. as argument of the Θ -function, points out, that they all are permanently increasing functions, resp. of s, s', σ, σ' . Moreover, by ranging the values of x to ascending magnitude and by adding the successive frequencies,

we obtained the quantities s and σ' (defined by (14) and (16')) as permanently increasing functions of x . Hence z and ζ' are also permanently increasing functions of x , and ζ' , so far as it depends on z , is an in-



creasing function of z , or, in other words: $\frac{\partial \zeta'}{\partial z} > 0$. This result might be also derived from (23). Likewise ζ , so far as it is a function of z' , continually increases with z' , i.e. $\frac{\partial \zeta}{\partial z'} > 0$.

Representing these variables by coordinates, it appears that the z -axis and ζ' -axis on one hand, and the z' -axis and ζ -axis on the other hand, must include an acute angle. We will denote its complement by ω . Hence ω is the angle between the z -axis and the z' -axis.

The equation (26) suggests the introduction of polar coordinates r and θ . The angle θ is to be measured from the bisector of the z - and z' -axis, in the direction from the z -axis to the z' -axis.

We now have

$$\begin{cases} z = r \cos\left(\frac{\omega}{2} + \theta\right) \\ \zeta = r \sin\left(\frac{\omega}{2} + \theta\right) \end{cases} \quad \begin{cases} z' = r \cos\left(\frac{\omega}{2} - \theta\right) \\ \zeta' = r \sin\left(\frac{\omega}{2} - \theta\right) \end{cases} \quad (28)$$

Since, besides the equation $r = r'$, no relation is supposed to exist between z, ζ, z', ζ' , the angle ω introduced may vary from point to point.

The system (z, ζ) being fixed, each point has its own system (z', ζ') , only with the same origin as the system (z, ζ) . So the angle ω may be a function of r and θ . The equation (27), however, which is necessarily attached to (26), implies — as it will be shown — that ω is a function of r only.

In order to express ζ as a function of z and z' , we write

$$z' = z \cos \omega + \zeta \sin \omega,$$

whence

$$\zeta = \frac{z' - z \cos \omega}{\sin \omega}, \quad (33)$$

so that

$$r^2 = z^2 + \zeta^2 = \frac{z^2 \sin^2 \omega + z'^2 - 2zz' \cos \omega + z^2 \cos^2 \omega}{\sin^2 \omega} = \frac{z^2 - 2zz' \cos \omega + z'^2}{\sin^2 \omega}. \quad (34)$$

Now putting

$$t = \frac{z}{\sin \omega}, \quad t' = \frac{z'}{\sin \omega}, \quad \cos \omega = \gamma,$$

we find

$$t^2 - 2\gamma t t' + t'^2 = r^2.$$

From the figure we have obviously $t = PQ$, $t' = PQ'$.

Here we have an expression for the exponent (r^2) having the unimolecular form desired. It is, however, more especially to be preferred, because the quantity t is connected with z (so with x) in the same way as t' is connected with z' (so with x'). Only the angle ω , which (like $\gamma = \cos \omega$) is a function of r , makes t still dependent on z' , and t' also on z , this dependence being however symmetrical.

If, after computing $\operatorname{tg} \omega$ from (32) for different combinations ($z_k, z'_l, \zeta_{kl}, \zeta'_{kl}$) ω appears to be rather constant, there is, on account of the many sources of perturbations, much reason to consider ω really as a constant.

Of the function $\operatorname{tg} \omega$ of this constant the values furnished by (32) are "observed values". From these not wholly concurring observations the most probable value of ω must be determined by adjustment, and from the value of ω thus found, the most reliable value of $\gamma = \cos \omega$ may be derived.

If we have reason indeed to consider ω as a constant, then t is a function only of z , thus of x , and t' a function only of z' , thus of x' . We have then arrived at a linear correlation between a function of the observed quantity x and a function of the observed quantity x' , with a coefficient of correlation equal to the cosine of ω .

The adjustment of $\operatorname{tg} \omega = \frac{B}{A}$ must be effectuated in the following way:

Taking A and B as rectangular coordinates, and putting $\operatorname{tg} \omega = M$, each pair (A, B) is then represented by a point $P(A, B)$. Then M is the direction constant of the line OP , uniting P to the origin O .

Speaking geometrically: we seek the line $B = MA$ passing through the origin, which is best fitted to the given points (A, B) .

The quantities A, B are, as functions of z, z', ζ, ζ' , in the last instance, functions of x and x' . So each pair (A, B) corresponds to a pair (x, x') . Now the pairs (x, x') are not equally probable. These different probabilities of (x, x') will come out at different weights of the pairs (A, B) . The pairs (x, x') , for which the values of A and B are known, refer to the class-limits, to the angular points of the frequency frame. But the chances, or the frequencies Y , proportional to them, are given empirically in the combinations $(\xi_k, \xi'_l) = (x_{k-1/2}, x'_{l-1/2})$. We may now take as the frequency of the pair (x_k, x'_l) the average of the frequencies belonging to the four surrounding class-centres:

$$(\xi_k, \xi'_l) = (x_{k-1/2}, x'_{l-1/2}), \quad (\xi_k, \xi'_{l+1}) = (x_{k-1/2}, x'_{l+1/2}), \quad (\xi_{k+1}, \xi'_l) = \\ = (x_{k+1/2}, x'_{l-1/2}), \quad (\xi_{k+1}, \xi'_{l+1}) = (x_{k+1/2}, x'_{l+1/2}).$$

So we take as the frequency of (x_k, x'_l) :

$$\frac{1}{4} (Y_{kl} + Y_{k, l+1} + Y_{k+1, l} + Y_{k+1, l+1}).$$

Hence the weight of the combination (k, l) , which is proportional to the frequency of (x_k, x'_l) may be equalled to

$$G_{kl} = Y_{kl} + Y_{k, l+1} + Y_{k+1, l} + Y_{k+1, l+1}, \quad \sum \sum G_{kl} = 4N.$$

So we have several points (A_{kl}, B_{kl}) with weights G_{kl} and we want to fit to them the line $B = A.M$ passing through the origin.

This problem does not properly differ essentially from that of linear correlation. Indeed, given N combinations (ξ_k, ξ'_l) with frequencies Y_{kl} , according to the theory of linear correlation, the combination of the arithmetic means $(\bar{\xi}, \bar{\xi}')$ is the most probable one.

$u_k = \xi_k - \bar{\xi}$, $u'_l = \xi'_l - \bar{\xi}'$ being the deviations from the resp. means, the combination (u_k, u'_l) may be represented by a point with rectangular (rectilinear) coordinates u_k, u'_l ; then the points (u_k, u'_l) , which have equal probability, lie on an ellipse

$$h^2 u^2 - 2\gamma h h' u u' + h'^2 u'^2 = \text{constant},$$

where h, h' and γ are constants.

The straight line, best adapted to all the points, appears to be the common major axis of all these ellipses. The angle φ , which the major axis makes with the axis of u , is determined by

$$\text{tg } 2\varphi = \frac{-2\gamma h h'}{h^2 - h'^2}.$$

We have now:

$$\mu = \overline{u^2} = \frac{1}{2h^2(1-\gamma^2)} \quad \mu' = \overline{u'^2} = \frac{1}{2h'^2(1-\gamma^2)} \quad \lambda = \overline{u u'} = \frac{\gamma}{2hh'(1-\gamma^2)}$$

whence

$$\mu : \mu' : \lambda = h'^2 : h^2 : \gamma h h'.$$

So we obtain

$$\operatorname{tg} 2\varphi = \frac{2\lambda}{\mu - \mu'}.$$

Applying this to the present case, we have

$$\mu = \overline{A^2} = \frac{\sum G_{kl} A_{kl}^2}{4N}, \quad \mu' = \overline{B^2} = \frac{\sum G_{kl} B_{kl}^2}{4N}, \quad \lambda = \overline{AB} = \frac{\sum G_{kl} A_{kl} B_{kl}}{4N},$$

whence

$$\operatorname{tg} 2\varphi = \frac{2\overline{AB}}{\overline{A^2} - \overline{B^2}}.$$

Incidentally we shall also compute the mean error of the value of φ , obtained by the above adjustment.

From $\operatorname{tg} 2\varphi = \frac{2\lambda}{\mu - \mu'}$, results

$$\sec^2 2\varphi \cdot \Delta \varphi = \frac{(\mu - \mu') \Delta \lambda - \lambda \Delta \mu + \lambda \Delta \mu'}{(\mu - \mu')^2},$$

so that

$$\sec^4 2\varphi \cdot \overline{\Delta \varphi^2} = \frac{(\mu - \mu')^2 \overline{\Delta \lambda^2} - 2\lambda(\mu - \mu') \overline{\Delta \lambda \cdot \Delta \mu} + 2\lambda(\mu - \mu') \overline{\Delta \lambda \cdot \Delta \mu'} + \lambda^2 \overline{\Delta \mu^2} - 2\lambda^2 \overline{\Delta \mu \cdot \Delta \mu'} + \lambda^2 \overline{\Delta \mu'^2}}{(\mu - \mu')^4}.$$

We now have

$$\overline{\Delta \lambda^2} = \frac{\lambda^2 + \mu\mu'}{N}, \quad \overline{\Delta \lambda \cdot \Delta \mu} = \frac{2\lambda\mu}{N}, \quad \overline{\Delta \lambda \cdot \Delta \mu'} = \frac{2\lambda\mu'}{N},$$

$$\overline{\Delta \mu^2} = \frac{2\mu^2}{N}, \quad \overline{\Delta \mu \cdot \Delta \mu'} = \frac{2\lambda^2}{N}, \quad \overline{\Delta \mu'^2} = \frac{2\mu'^2}{N},$$

therefore

$$\sec^4 2\varphi \cdot \overline{\Delta \varphi^2} = \frac{(\mu\mu' - \lambda^2) \{ (\mu - \mu')^2 + 4\lambda^2 \}}{N(\mu - \mu')^4}$$

or, since

$$\sec^2 2\varphi = 1 + \operatorname{tg}^2 2\varphi = \frac{(\mu - \mu')^2 + 4\lambda^2}{(\mu - \mu')^2},$$

$$\varepsilon_{\varphi}^2 = \overline{\Delta \varphi^2} = \frac{1}{N} \frac{\mu\mu' - \lambda^2}{(\mu - \mu')^2 + 4\lambda^2},$$

so, in the present case:

$$\varepsilon_{\varphi}^2 = \frac{1}{N} \cdot \frac{\overline{A^2} \cdot \overline{B^2} - \overline{AB}^2}{(\overline{A^2} - \overline{B^2})^2 + 4\overline{AB}^2}.$$

The tangent M of the angle φ , included between the major axis and the A -axis, is the most probable value of the fraction $\frac{B}{A}$. So M too is the most probable value of $\operatorname{tg} \omega$, whence φ is the most probable value $\bar{\omega}$ of ω .

Thus we must compute this most probable (mean) value $\bar{\omega}$ of ω from

$$\operatorname{tg} 2 \bar{\omega} = \frac{2 \bar{A} \bar{B}}{\bar{A}^2 - \bar{B}^2} \quad \text{with} \quad \varepsilon_{\bar{\omega}}^2 = \frac{1}{N} \frac{\bar{A}^2 \cdot \bar{B}^2 - \bar{A} \bar{B}^2}{(\bar{A}^2 - \bar{B}^2)^2 + 4 \bar{A} \bar{B}^2} \quad (35)$$

where

$$A = z z' - \zeta \zeta' \quad , \quad B = z \zeta' + z' \zeta.$$

It is now our object to find the mean (i.e. the most probable) value of the coefficient of correlation $\gamma = \cos \omega$. We choose for this

$$\bar{\gamma} = \cos \bar{\omega}, \quad (36)$$

its mean error being

$$\varepsilon_{\bar{\gamma}} = \sin \bar{\omega} \cdot \varepsilon_{\bar{\omega}} \quad (37)$$

So, our first result, based upon the simplest suppositions, runs:

If, for each combination (z_k, z'_l) , the expression $r^2 = z^2 + \zeta^2$ is found to be practically equal to $r'^2 = z'^2 + \zeta'^2$ and if ω is found to be tolerable constant, then, in solving the problem, we may choose for t and t' :

$$t = \frac{z}{\sin \omega} \quad , \quad t' = \frac{z'}{\sin \omega} \quad , \quad \bar{\gamma} = \cos \bar{\omega}$$

where each of the final variables appears to be a function of only one of the primary variables, e.g. t of x , and t' of x' .

If, the relation $r^2 = r'^2$ being satisfied, ω is not a constant, and so depends on $r (= r')$, then in

$$z^2 - 2 \cos \omega \cdot z z' + z'^2 = r^2 \sin^2 \omega$$

ω is variable together with r .

Then the ellipses $r = \text{const.}$ ($\omega = \text{const.}$) are no longer homothetic. We, however, may transform them into a set of homothetic ellipses, in the following way:

We turn the coordinate system (z, z') 45° , so that the axes of the new coordinates u and v coincide with the axes of symmetry. Accordingly putting

$$z = \frac{u-v}{\sqrt{2}} \quad , \quad z' = \frac{u+v}{\sqrt{2}},$$

we obtain

$$\begin{aligned} z^2 - 2 \cos \omega \cdot z z' + z'^2 &= \frac{(u-v)^2 - 2 \cos \omega \cdot (u^2 - v^2) + (u+v)^2}{2} = \\ &= (1 - \cos \omega) u^2 + (1 + \cos \omega) v^2 = r^2 \sin^2 \omega \end{aligned}$$

or

$$\frac{u^2}{1 + \cos \omega} + \frac{v^2}{1 - \cos \omega} = r^2.$$

Now, introducing a constant angle Ω , we put

$$u = U \sqrt{\frac{1 + \cos \omega}{1 + \cos \Omega}}, \quad v = V \sqrt{\frac{1 - \cos \omega}{1 - \cos \Omega}},$$

and so find

$$\frac{U^2}{1 + \cos \Omega} + \frac{V^2}{1 - \cos \Omega} = r^2.$$

By turning back the coordinate axes into their former position, by means of the transformation

$$U = \frac{Z + Z'}{\sqrt{2}}, \quad V = \frac{-Z + Z'}{\sqrt{2}},$$

we obtain the equation

$$Z^2 - 2 \cos \Omega \cdot Z Z' + Z'^2 = r^2 \sin^2 \Omega,$$

after which the substitution

$$Z = T \sin \Omega, \quad Z' = T' \sin \Omega$$

leads to

$$T^2 - 2 \cos \Omega \cdot T T' + T'^2 = r^2.$$

Finally, the variables T and T' depend on z, z' (resp. t, t') according to the following formula:

$$\begin{aligned} T = \frac{Z}{\sin \Omega} = \frac{U - V}{\sin \Omega \cdot \sqrt{2}} &= \frac{\sqrt{\frac{1 + \cos \Omega}{1 + \cos \omega}} \cdot u - \sqrt{\frac{1 - \cos \Omega}{1 - \cos \omega}} \cdot v}{\sin \Omega \cdot \sqrt{2}} = \\ &= \frac{\cos \frac{\Omega}{2}}{\cos \frac{\omega}{2}} (z + z') - \frac{\sin \frac{\Omega}{2}}{\sin \frac{\omega}{2}} (-z + z') \\ &= \frac{2 \sin \Omega}{2 \sin \Omega} \end{aligned}$$

$$\begin{aligned} T' = \frac{Z'}{\sin \Omega} = \frac{U + V}{\sin \Omega \cdot \sqrt{2}} &= \frac{\sqrt{\frac{1 + \cos \Omega}{1 + \cos \omega}} \cdot u + \sqrt{\frac{1 - \cos \Omega}{1 - \cos \omega}} \cdot v}{\sin \Omega \cdot \sqrt{2}} = \\ &= \frac{\cos \frac{\Omega}{2}}{\cos \frac{\omega}{2}} (z + z') + \frac{\sin \frac{\Omega}{2}}{\sin \frac{\omega}{2}} (-z + z') \\ &= \frac{2 \sin \Omega}{2 \sin \Omega} \end{aligned}$$

or

$$\left. \begin{aligned} T &= \frac{\sin \frac{\omega + \Omega}{2} \cdot z + \sin \frac{\omega - \Omega}{2} \cdot z'}{\sin \omega \cdot \sin \Omega} = \frac{\sin \frac{\omega + \Omega}{2} \cdot t + \sin \frac{\omega - \Omega}{2} \cdot t'}{\sin \Omega} \\ T' &= \frac{\sin \frac{\omega - \Omega}{2} \cdot z + \sin \frac{\omega + \Omega}{2} \cdot z'}{\sin \omega \cdot \sin \Omega} = \frac{\sin \frac{\omega - \Omega}{2} \cdot t + \sin \frac{\omega + \Omega}{2} \cdot t'}{\sin \Omega} \end{aligned} \right\} \quad (38)$$

Theoretically we are wholly free in choosing Ω . If, however, we try to relate T as closely as possible to t (and z), and T' to t' (and z'), then we shall dispose of Ω in such a way that the average value of $\omega - \Omega$ is as small as possible. This may be attained by taking for Ω the mean value $\bar{\omega}$ of ω . This mean may be computed:

either empirically in the same way as if ω is practically constant (see (35))

or theoretically, if we have a clear idea about the functional relation existing between ω and r . When, in this case, $\omega = f(r)$, then

$$\bar{\omega} = \int_0^{\infty} f(r) dW = \int_0^{\infty} f(r) r e^{-r^2} dr.$$

Thus we go on with

$$\left. \begin{aligned} T &= \frac{\sin \frac{\omega + \bar{\omega}}{2} \cdot z + \sin \frac{\omega - \bar{\omega}}{2} \cdot z'}{\sin \omega \cdot \sin \bar{\omega}} = \frac{\sin \frac{\omega + \bar{\omega}}{2} \cdot t + \sin \frac{\omega - \bar{\omega}}{2} \cdot t'}{\sin \bar{\omega}} \\ T' &= \frac{\sin \frac{\omega - \bar{\omega}}{2} \cdot z + \sin \frac{\omega + \bar{\omega}}{2} \cdot z'}{\sin \omega \cdot \sin \bar{\omega}} = \frac{\sin \frac{\omega - \bar{\omega}}{2} \cdot t + \sin \frac{\omega + \bar{\omega}}{2} \cdot t'}{\sin \bar{\omega}} \end{aligned} \right\} \quad (39)$$

together with

$$T^2 - 2\gamma TT' + T'^2 = r^2, \quad \gamma = \cos \bar{\omega}.$$

The variables T and T' may now be submitted to the transformation (9):

$$\begin{aligned} t &= \frac{\sin(\tau + \bar{\omega})}{\sin \bar{\omega}} T - \frac{\sin \tau}{\sin \bar{\omega}} T' \\ t' &= \frac{\sin \tau}{\sin \bar{\omega}} T - \frac{\sin(\tau - \bar{\omega})}{\sin \bar{\omega}} T'. \end{aligned}$$

After reduction we obtain

$$\left. \begin{aligned} t &= \frac{\sin\left(\frac{\omega + \bar{\omega}}{2} + \tau\right)}{\sin \bar{\omega}} t + \frac{\sin\left(\frac{\omega - \bar{\omega}}{2} - \tau\right)}{\sin \bar{\omega}} t', \\ t' &= \frac{\sin\left(\frac{\omega - \bar{\omega}}{2} + \tau\right)}{\sin \bar{\omega}} t + \frac{\sin\left(\frac{\omega + \bar{\omega}}{2} - \tau\right)}{\sin \bar{\omega}} t' \end{aligned} \right\} \quad (40)$$

or

$$\left. \begin{aligned} t &= \frac{\sin\left(\frac{\omega + \bar{\omega}}{2} + \tau\right)}{\sin \omega \cdot \sin \bar{\omega}} z + \frac{\sin\left(\frac{\omega - \bar{\omega}}{2} - \tau\right)}{\sin \omega \cdot \sin \bar{\omega}} z', \\ t' &= \frac{\sin\left(\frac{\omega - \bar{\omega}}{2} + \tau\right)}{\sin \omega \cdot \sin \bar{\omega}} z + \frac{\sin\left(\frac{\omega + \bar{\omega}}{2} - \tau\right)}{\sin \omega \cdot \sin \bar{\omega}} z' \end{aligned} \right\} \quad (41)$$

We may still freely dispose of τ . It is not necessary that τ should be a constant; it may be a function of z and z' or only of r .

We shall choose τ in such a way that the expression (41) for t gets rid of the term with z' . For this we evidently must put

$$\tau = \frac{\omega - \bar{\omega}}{2};$$

then we obtain

$$\left. \begin{aligned} t &= \frac{z}{\sin \omega} \\ t' &= \frac{\sin(\omega - \bar{\omega})}{\sin \omega \cdot \sin \bar{\omega}} \cdot z + \frac{1}{\sin \omega} z' \end{aligned} \right\} \quad (42)$$

So doing we have succeeded in making one of the variables (t) into a pure function of z , i. e. of x . But then the other variable is a function both of z and z' (thus also both of x and x').

Similarly it would have been possible, by a suitable choice of t , to make the variable t into a function only of z' (i. e. only of x'), or the variable t' into a function only of z (i. e. only of x), or into a function only of z' (i. e. only of x'). So our second result runs:

If, for each combination (z_k, z'_l) , the expression $r^2 = z^2 + \zeta^2$ is found almost equal to $r'^2 = z'^2 + \zeta'^2$, but if the condition that in each combination (z_k, z'_l) ω has the same value, is not fulfilled, then it is possible to take for one of the final variables (for instance t) a function of only one of the primary variables (for instance x), the other final variable (t') remaining a mixed function of x and x' (see (42)). In this case there exists a functional relation between ω and r .

Further on we shall give some hints for finding out the function $\omega = f(r)$.

(To be continued).

Chemistry. — ERNST COHEN and SABURO MIYAKE: "*The influence of minute traces of Water on Solution Equilibria.*" II

(Communicated at the meeting of October 31, 1925).

Introductory.

In the first paper under the above title ¹⁾ it was shown that the solution equilibrium between salicylic acid and benzene is shifted by the presence of minute traces of water, the solubility of salicylic acid markedly increasing by the addition of water. We also stated that the phenomenon in question can manifest itself in consequence of the presence of occluded water, so that, if the solubility of substances must be determined with accuracy, great care should be taken to work with pure (dried) substances. At the time we pointed out that the minute quantity of occluded water can be accurately determined by solubility determinations. The experiments which are described in this paper, have been made in order to become acquainted with the influence of minute traces of water in other solution equilibria, and moreover — the measurements which refer to this part of the problem will be described first — to prove, more directly than was done in the first paper, that the phenomena which are investigated here, are indeed (true) equilibria.

As the method of procedure was fully explained in the first communication we need not go into details here.

All the solubility determinations have been carried out at 30°.50 C.

1. *The Equilibrium in the System Salicylic acid — Benzene.*

1. We used the salicylic acid (preparation KAHLBAUM "für kalorimetrische Bestimmungen", vide our first communication under A. § 1a), which, according to the method described there (B. § 2. 2) was recrystallized from dry ether (vide first communication under A. § 1. c). The acid had been kept for a long time in vacuo over P_2O_5 , and had been powdered every day until the smell of ether had totally disappeared.

2. The benzene (free from thiophene) had been treated in the way previously described (vide first communication under A. § 1. b.). Whereas in our first investigation we simply poured the liquid out of the flask into the shaking bottles, so that it came in contact with the moist air in the laboratory, we now pressed it from the flask by means of air which had been carefully dried over sulphuric acid and then over P_2O_5 . After having used the apparatus for a month we ascertained that practically the benzene

¹⁾ These Proceedings 28, 702 (1925); Zeitschr. f. physik. Chemie 118, 37, (1925).

had remained unchanged: the solubility of the salicylic acid which had been determined at 1.00; 1.02; 1.01; 1.02 *), was found to be 1.02 at the end of that period (vide first communication § 13).

3. In order to prove that the phenomena, described in the first communication, are indeed equilibria, we set to work as follows: In each of two shaking bottles about one gramme of dry acid and about 40 gms. of dry benzene is weighed; then these bottles are sealed. One of the bottles is immediately put into the thermostat, the temperature of which has been set to the temperature of the experiment ($30^{\circ}.50$ C.). The second bottle, with its contents, is heated in a water bath to such a temperature that the solute has been almost, but not wholly, dissolved. Then this bottle is also placed in the thermostat, and both bottles are shaken for the same length of time, at the temperature of the experiment.

The same manipulations are carried out with two bottles, the contents of which differ from those mentioned above in that they contain moist benzene (of an accurately determined water percentage) instead of dry benzene.

In this way the final condition is reached in both cases (dry and moist benzene), as well from the side of supersaturation as from that of undersaturation.

TABLE I.
Solubility of Salicylic acid in Benzene.
Temperature $30^{\circ}.50$ C.

Number of the experiment	Period of shaking in hours	Thousandths of weight $\frac{0}{0}$ of water	Solubility in weight $\frac{0}{0}$
1	4	0	1.00 1.02*
2	3	0	1.01 1.02*
3	3	66	1.16 1.17*
4	4	71	1.19 1.18*

As we see from Table I we find identical values for the solubilities, within the errors of the experiment, in other words: in the dry system, as well as in the wet, we have indeed true equilibria.

Weight % means gms. of solute in 100 gms. of solution.

2. The Equilibrium in the System Salicylic acid — Chloroform.

4. When the chloroform had been for a long time on P_2O_5 , it was distilled from fresh P_2O_5 , in the way previously described (vide first

*) Means that equilibrium is reached from the side of supersaturation.

communication A. § 1*b.*). The tapping from the flask was done as described in § 2.

When tapping the saturated solutions of salicylic acid we placed the bulb E (Fig. 1 first communication) always in ice water, so as to keep the tension of the vapour over the solution as low as possible.

The following figures prove that the analysis by evaporation of the solvent (vide first communication § 5) gives good results, whether dry chloroform is taken or moist: 0.2631 gms. of dry salicylic acid dissolved in about 17 gms. of dry chloroform gave 0.2629 gms. after the solvent was evaporated. When the residue had been in vacuo over sulphuric acid and salicylic acid for the night, the weight proved to be 0.2629 gms. Further 0.3681 gms. of the acid, which had been dissolved in about 20 gms. of moist chloroform (water-content of the chloroform 0.0354 gms. of water in 100 gms. of chloroform) gave 0.3676 gms. after being treated in the same way.

Table 2 contains the results of the experiments with chloroform.

TABLE 2.
Solubility of salicylic acid in Chloroform.
Temperature 30°.50 C.

Number of the experiment	Period of shaking in hours	Thousandths of weight $\frac{0}{0}$ of water	Solubility in weight $\frac{0}{0}$	
5	3	0	1.55	1.56*
6	5	0	1.56	1.55*
7	3	35.4	1.64	1.63*
8	3	60.8	1.69	1.68*
9	3	108.1	1.72	1.71*
10	3	saturated	1.73	1.72*

For further elucidation of the term "saturated" in this table and the following ones, we wish to observe that the solvent had previously been shaken with excess of water at 30°.50 C. and after separating it from the excess of water was used for the determination of solubility.

3. *The Equilibrium in the System Salicylic acid — Carbon Tetrachloride.*

5. The carbon tetrachloride we used was free from sulphur; when it had been on P_2O_5 for a week, it was distilled from a fresh quantity of P_2O_5 . The method of keeping it and of transferring it to the shaking bottles is described in § 2.

In this case too the analysis of the saturated solutions can be made by evaporation of the solvent, as may be seen from the following figures:

0.0432 gms. of salicylic acid, dissolved in about 15 gms. of CCl_4 , gave, after evaporation of the solvent, 0.0426 gms. of acid. In the second experiment we weighed 0.0321 gms. into the bottle and found back 0.0321 gms.

Table 3 gives a summary of the results.

TABLE 3.
Solubility of Salicylic acid in Carbon tetrachloride.
Temperature $30^\circ.50$ C.

Number of the experiment	Period of shaking in hours	Thousandths of weight % of water	Solubility in weight %	
11	3	0	0.36	0.35*
12	5	0	0.35	0.35*
13	3	8.7	0.35	0.36*
14	3	22.7	0.36	0.36*
15	3	65.9	0.36	0.37*
16	3	saturated	0.36	0.36*

4. *The Equilibrium in the System o-Nitrobenzoic acid — Benzene.*

6. With a view to some experiments on the metastability of this acid as a consequence of enantiotropy or monotropy, we had acquired a rather large quantity. We used preparations supplied by different factories. After having been recrystallized from water they gave identical results. This was seen f.i. when determining their solubility in water.

TABLE 4.
Solubility of o-nitrobenzoic acid in Benzene.
Temperature $30^\circ.50$ C.

Number of the experiment	Period of shaking in hours	Thousandths of weight % of water	Solubility in weight %	
17	3	0	0.35	0.35*
18	3	37.7	0.43	0.43*
19	3	66.3	0.49	0.49*
20	3	89.1	0.49	0.50*
21	3	saturated	0.50	0.50*

Also in this case we found the evaporation method, when determining the solubility, very useful. Thus 0.0327 gms. of acid, dissolved in 15 gms.

of moist benzene (water content 0.2226 gms. of water in 100 gms. of benzene) gave 0.0327 gms. of acid after evaporation of the solvent. When the residue had been for 24 hours in vacuo over P_2O_5 and *o*-nitrobenzoic acid, we found 0.0327 gms. In a second experiment in which 0.0558 gms. had been weighed into the bottle, we found in the same way 0.0559 gms.

Table 4 contains the results of these measurements.

5. *The Equilibrium in the System o-Nitrobenzoic acid — Chloroform.*

7. As the experiments in this case were carried out in exactly the same way as in the system salicylic acid—chloroform, it will suffice to point out that the evaporation process yields accurate results. Thus, after weighing 0.0906 gms. of acid into the bottle, we found 0.0907 gms. after evaporation. In another experiment 0.0414 gms. instead of 0.0418 gms.

TABLE 5.
Solubility of *o*-nitrobenzoic acid in Chloroform.
Temperature 30°.50 C.

Number of the experiment	Period of shaking in hours	Thousandths of weight % of water	Solubility in weight %	
22	3	0	0.45	0.45*
23	5	0	0.45	0.45*
24	3 $\frac{1}{4}$	25.6	0.51	0.52*
25	3	31.2	0.56	0.56*
26	3	saturated	0.55	0.56*
27	3	..	0.56	—

6. *The Equilibrium in the System Anthracene — Benzene.*

8. We have also investigated the influence of minute traces of water on the equilibrium between a non-electrolyte and benzene. We chose anthracene as a non-electrolyte.

A so-called pure preparation (resublimated) gave in the solubility determination in dry benzene (period of shaking 3 hours) the values of 2.05; 2.09. When the period of shaking was five hours we found 2.08; 2.09. When this preparation had been recrystallized from dry benzene we found 2.00; 2.00. To check the result we recrystallized this preparation from dry ether, left the mass thus obtained for some days in vacuo over P_2O_5 , and then determined the solubility again in dry benzene. Now we found 2.00; 2.00. We used this preparation for our final solubility determinations in benzene.

In this investigation we also made use of the evaporation method in

order to analyze the saturated solutions, when the following experiments had proved that, in this case too, accurate results were obtained; 0.1646 gms. of anthracene gave 0.1648 gms. after evaporation of the dry benzene in which they had been dissolved. In a second experiment we dissolved 0.1603 gms. of anthracene in moist benzene; we found 0.1605 gms.

TABLE 6.
Solubility of Anthracene in Benzene.
Temperature 30°.50 C.

Number of the experiment	Period of shaking in hours	Thousandths of weight $\frac{0}{0}$ of water	Solubility in weight $\frac{0}{0}$
28	3	0	2.00 2.00*
29	3	0	2.00 2.00*
30	3	38.9	2.00 2.00*
31	3	88.8	1.98 1.99*
32	3	saturated	1.98 1.98*

9. We shall not dwell upon the older literature about the solubility of the substances we investigated, as it refers to preparations, the purity (dryness) of which had not been closely examined. Therefore it is of no importance for the problem which occupies us here.

Summary.

Minute traces of water have great influence on solution equilibria in the systems salicylic acid — benzene, salicylic acid — chloroform, o-nitrobenzoic acid — benzene, o-nitrobenzoic acid — chloroform. No influence could be ascertained in the systems salicylic acid — carbon tetrachloride, and anthracene — benzene.

We intend to treat further conclusions in a subsequent communication.

VAN 'T HOFF-Laboratory.

Utrecht, September 1925.

Physiology. — G. GRIJNS: "*Diet and reproduction.*"

(Communicated at the meeting of October 31, 1925).

It is since long custom among breeders to feed animals, which are raised for reproductive purposes, along an other scheme as those, that will be used for working or butchering. Especially to much fattening is avoided in the first class. On a direct relation of nutrition and fertility textbooks give little or nothing.

It is only the last few years, since everywhere investigations on vitamins and on the adequacy of different albumens are going on, that this relation has been attended to and publications on this topic are growing more numerous. However they often differ very much, even they are sometimes contradictory.

HART, STEENBOCK and HUMPREY stated¹⁾ that cows on a diet exclusively derived from the oat plant only bore dead young and such as died soon after birth. Addition of casein or A-vitamin did not ameliorate the condition, but calcium did. As oat is poor in calcium compounds, the cause of failure in reproduction was calcium starvation.

McCOLLUM, in collaboration with SIMMONDS and PARSONS²⁾ found, that rats on rations poor in albumen or containing an inadequate albumen reproduce badly and that starvation of A-vitamine leads to infertility.

The same thing recently was demonstrated by SIMMONNET³⁾ who examined in extenso the influence on females and males separately.

Lack of watersoluble B also stops reproduction.

The failure of reproduction in these cases may be attributed to the fact, that, when food-substances that are necessary for building up the young bodies are absent, the young can not thrive and die from starvation. This may occur in the womb already, when either abortion or resorption of the foetus will take place; or during lactation.

MATTILL experimented with CONKLIN⁴⁾ and afterwards with STONE⁵⁾ on the relation between nutrition and reproduction. They stated that rats fed on milk only grew well till about 90 days, there after they grew more slowly than rats on normal rations. Addition of yeast extract promotes growth, but in both cases they were infertile. Starch did not improve

¹⁾ Research Bullet. Agric. Exp. Station Madison 49, 1920.

²⁾ MC. COLLUM, N. SIMMONDS & H. T. PARSONS. Protein values of food. Journ. of Biol. Chem. XLVII, p. 111, & 139, 1921.

³⁾ H. SIMONNET. Influence de la carence en facteur lipo-soluble sur les fonctions de reproduction. Annales de Physiol. et de physicochimie biol. T. I. N^o. 3 p. 332, 1925.

⁴⁾ H. A. MATTILL & R. E. CONKLIN. The nutritive properties of milk. I. Journ. of Biol. Chem. XLIV p. 137, 1920.

⁵⁾ H. A. MATTILL & N. C. STONE. The nutritive properties of milk. II. ibid. LV. p. 443, 1922.

reproduction. Out of 8 male rats, mated with females on normal diet 5 proved sterile. Supplementing milkpowder with brewersyeast gave some litters, but all died within two days.

Several investigators remark that a too high content of albumen damages the rearing of the young.¹⁾

To quite different results ANDEREGG²⁾ arrives. He fed rats on milkpowder supplemented with dextrin, agar 4 % (for bulk) and ferric citrate 0.2 %. On 70 % milkpowder and 26 % dextrin 23 out of 70 young were reared; on 60 % milkpowder with 36 % dextrin and a small amount of saltmixture growth was better than normal and reproduction normal.

8 females on a diet of milkpowder 60, casein 6, citrate of iron 0.2, agar 4 and dextrin 29.8 bore 129 young of which 75 or 59 % were reared. 9 females in whose ration 2.4 dextrin had been substituted by saltmixture bore 235 young of which 202 or 86 % were weaned, what equals normal nutrition.

When skimmed milkpowder was used instead of wholemilkpowder most females were infertile, the others having small litters.

A. also investigated the influence of wheatembryo on reproduction. He fed a mixture of casein 18, butterfat 5, saltmixture 3.7, wheatembryo from 1.5 to 9 and dextrin to make 100. All rats that got less than 6 % wheat embryo were sterile.

16 females on 7 % wheatembryo bore 79 young from which 32 or 29 % were reared. For 6 females on 8 % these figures were 65 and 59 or 91 % and 3 rats on 9 % wheatembryo raised all their 17 young.

ANDEREGG leaves undecided whether supplementing of lacking vitamin B, or of some other factor plays a part here. In my opinion A-vitamin might as well be a limiting factor here.

BARNETT SURE³⁾ found rats on a diet chiefly composed of milkpowder, to which dextrin, saltmixture and water- and fat-soluble vitamins had been added, mostly sterile. Addition of different aminoacids did not improve this, so that the failure of reproduction can not be attributed to inadequate albumen. Fresh lettuce and velvet beans⁴⁾ were able to conserve reproduction. Also when the milkpowder was fed with rice, with corn or with oat the animals bore young.

In a later experience⁵⁾ he supplemented a ration of artificial nutriment,

¹⁾ SMITH. Journ. of Biol. Chem. XXVIII p. 215. 1917. HART & STEENBOCK. J. o. Biol. Chem. XXXIII p. 313. 1918. GLADYS HARTWELL. Bioch. Journ. XV p. 564 and ibid. XVI p. 78. 1922.

²⁾ L. F. ANDEREGG. Diet in relation to reproduction and rearing of the young. J. o. Biol. Chem. LIX p. 587. 1924.

³⁾ BARNETT SURE. Dietary requirements for reproduction I. J. o. Biol. Chem. LVIII p. 681. 1924.

Id. id. II J. o. Biol. Chem. LVIII p. 693.

⁴⁾ *Stizolobium deeringianum*. From Georgia and Southern States.

⁵⁾ BARNETT SURE. Dietary requirements for reproduction. III. J. o. Biol. Chem. LXII p. 371. 1925.

that contained sufficient A-, B-, and C-vitamin with several extracts and oils, withdrawing so much starch, that the caloric value remained constant. He then found, that cotton seed oil (5 %) or olive oil was apt to support fertility; the same did ethereal extracts from wheatembryo, yellow corn and hempseed. Coconut oil, linseed oil and sesam oil proved ineffective. He therefrom concludes to the existence of a reproduction controlling vitamin.

To the same conclusion come EVANS and BURR¹⁾. On a ration of albumen, fat, starch, saltmixture, yeast extract and cod liver oil their rats become infertile in the first or the second generation. In males this leads in a great deal of cases to testicular atrophy. Then it is irreparable. In females ovulation persists, but when fertilised by normal males, between the 12th and 20th day the foetus die and resorption occurs.

From wheatembryo they could extract with ether a substance, that was not destroyed by saponifying with 20 % alcoholic kalihydroxide. After a series of treatments with methylic alcohol, pentane, benzene etc. they arrive at a concentrated liquor, one drop of which a day is able to conserve fertility in rats on the above mentioned diet. They propose to name the active substance Vitamin E. This substance is present in small quantities in the intern organs, a little more in bodyfat and muscles. Animals on E-free diet are exempt of it. It is abundant in wheat especially in the embryo, also in green parts of plants and in a number of seeds and resistant to heating.

Against the experiments of ANDEREGG, who saw good reproduction on wholemilkpowder, they state, that by adding more fat infertility appears, what could be explained for by assuming that at a higher fat intake more vitamin E is wanted.

SURE²⁾ demonstrated the solubility of this fertilising factor in benzene and in acetone.

MATTILL, CARMAN and CLAYTON³⁾ demonstrated that the wheatembryo exhausted with ether is ineffective, they found also, that diminution of the fatcontent of a milkpowder diet raised the number of fertile animals.

MILLES and YATES⁴⁾ fed a mixture of casein 15, salts 2, cod liver oil 1, and yellow corn 80. Rats were reproductive on this diet. But if previously the corn was extracted with water they were infertile. Addition of yeast to the latter succeeded in obtaining young in the first generation, but the second one was sterile.

1) H. M. EVANS & G. O. BURR. The antisterility vitamin fat soluble E. Proc. Nat. Acad. of Science U. S. A. Vol. 11 No. 6 p. 334. 1925.

2) B. SURE. Dietary requirements for reproduction. VI. J. o. Biol. Chem. LXIII. p. 211. 1925.

3) H. A. MATTILL, J. S. CARMAN & M. M. CLAYTON. The effectiveness of the X-substance in preventing sterility in rats on milkration high in fat. J. o. Biol. Chem. LXI. p. 729. 1925.

4) H. G. MILLES & W. W. YATES. The relation of natural foodstuffs and their treatment on growth and reproduction. J. o. Biol. Chem. LXII. p. 259. 1925.

SUPPLEE and DOW¹⁾ investigated the influence of storage of milk-powder on reproduction. They compared relatively fresh powder to such that had been stored for two years. The old powders had been tinned partly without precaution, partly in a CO₂ atmosphere, in a third part an oxygen binding preparation had been used. Casein, saltmixture, agar and dried brewers yeast were added. The rats fed on fresh milk-powder, and those on the stored powder to which an oxygen binding substance had been added, proved fertile, the other lots did not.

A new complication brings the investigations of DANIELS and HUTTON,²⁾ who found, that rats on pure milk diet were mostly infertile, and that the few young born never produced litters. Milkpowder was no better. Addition of ferric citrate gave a little improvement but not much. If 7 grams of soyabeanmeal was added, cooked in 1 L. of milk, reproduction was excellent. Ashes of soyabeanmeal was as well. This in connection with the analysis of the ashes brought them to try mixtures of aluminium-kalium-sulfate, natriumfluoride, natriumsilicate and manganesulfate which gave very good results till in the sixth generation. There after they tried mixtures of 2 or 3 of the 4 compounds combined with milk; the results however are so surprising, that I doubt if not another factor than the salts may have escaped their attention. A diet of milk and aluminium gives fertility, one with milk aluminium and manganese infertility; milk and silicate give reproduction, milk, silicate and fluoride do not; milk, silicate, fluoride and alumina do.

The authors come to the conclusion that lack of some anorganic compounds in milk causes the failure of reproduction.

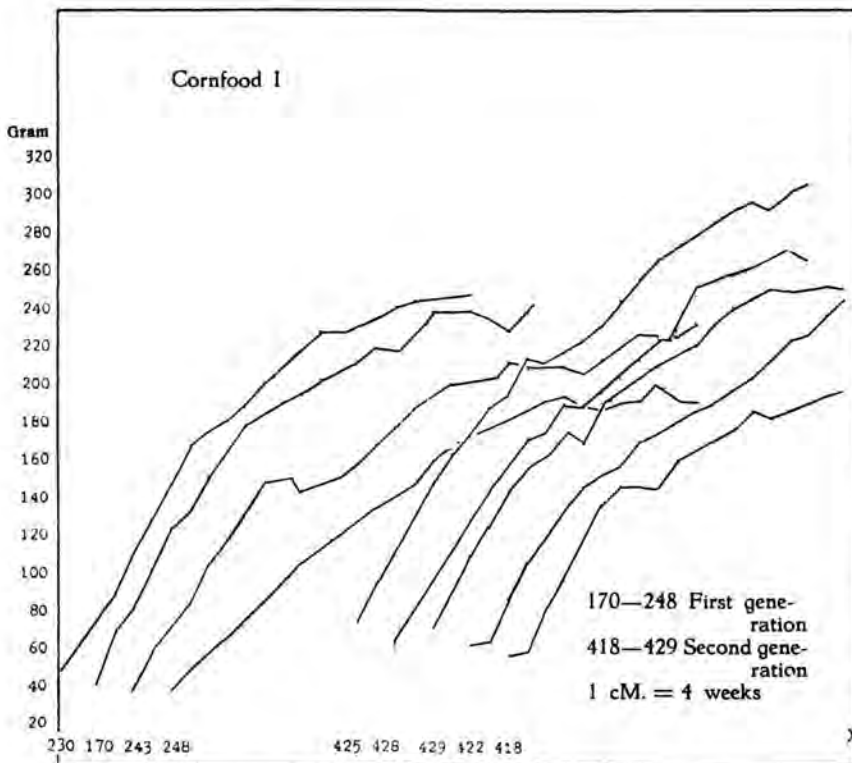
When I consider all the experiments on the relation of milk to reproduction, I come to the conception that milk may contain all the foodstuffs, that are necessary for normal reproduction, but in scarcely sufficient quantity. Now it has been shown, that especially in regard to the accessory foodstuffs the composition of the milk greatly depends on the food of the cow. Moreover the quantity of reserves of foodstuffs the young animals possess in the beginning of the experience varies with the nutrition of their mothers. So it is easily conceivable, how in the case of some experimentators milk proved to be adequate for maintenance of fertility, in that of others not.

Milk has often given rise to discrepancy. HOPKINS and other English workers found 2 cc. milk a day sufficient to complete a diet of artificial food, while American authors wanted 4 to 6 cc. MC. COLLUM was at variance with English investigators on the C-vitamin content of milk. So it will be better to experiment with more uniform compounds.

To prevent confusion it will be necessary too, to discriminate in all our examinations between fertility of males and of females, for it is not likely

¹⁾ G. C. SUPPLEE & O. D. DOW. Reproductive potency of dry milk as affected by oxidation. J. o. Biol. Chem. LXIII. p. 103. 1925.

²⁾ A. L. DANIELS & M. K. HUTTON. Mineral deficiencies of milk as shown by growth and fertility of white rats. J. o. Biol. Chem. LXIII p. 143. 1925.

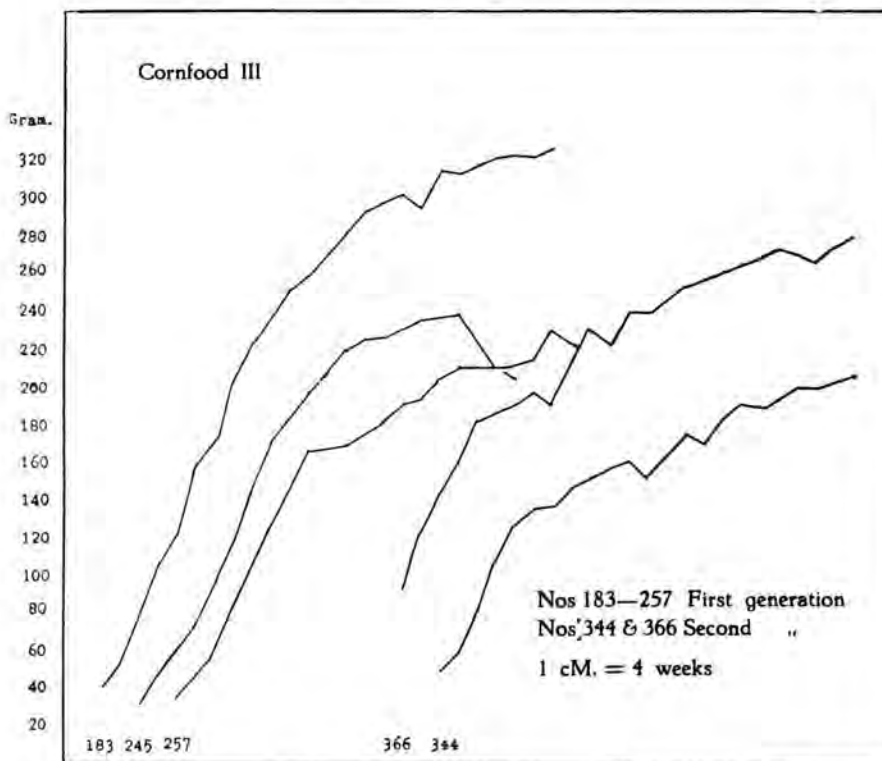
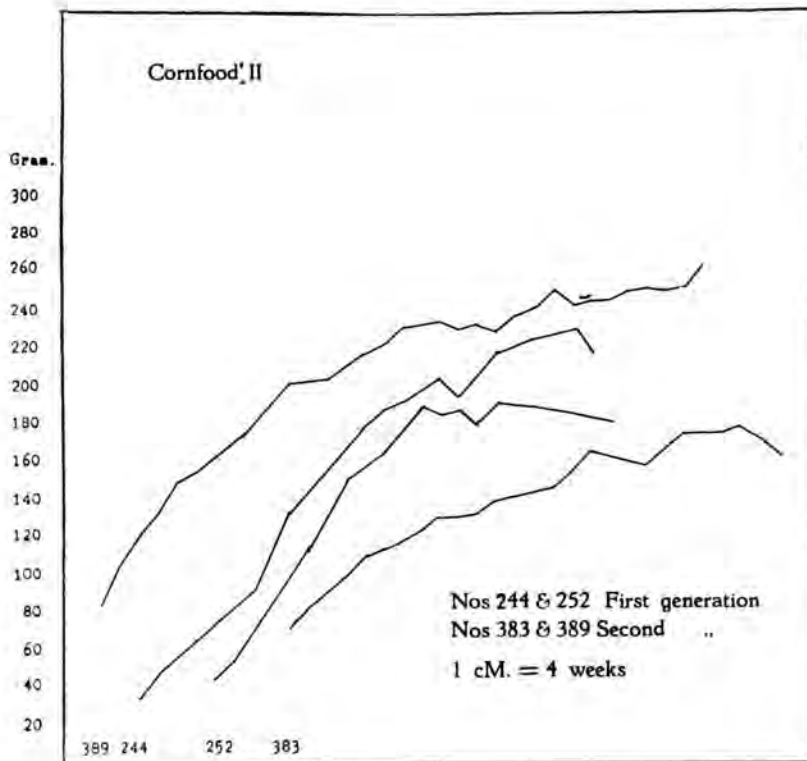


a priori, that in both sexes fertility will depend on the same factor. Then in every case it is to be examined which link in the chain of procreative processes is wrong and whether change of nutrition is able to restore normal reproduction.

In my own experiments on the occurrence of vitamins in different foods it struck me, that often rats did not propagate, although both sexes were confined in a same cage. So I came on studying fertility in relation to diet.

I fed rats on corn, to which cocoanut meal, peanut meal or meat meal had been added, with a little hardened fat, and a saltmixture composed of NaCl 35, KHPO_4 , 7 FeSO_4 3.5, CaCO_3 56, so that all three diets had fairly well the same content of albumen, fat and carbohydrate.

	Cornfood I	Cornfood II	Cornfood III
Corn (Maize)	500	500	500
Peanut meal	100		
Cocoanut meal		200	100
Meat meal			50
Hardenet fat	28	15	22.5
Saltmixture	7.5	8	7



Our normal food is : whole wheat meal 630, meat meal 20, suet 50, salt-mixture 13 and milk 500.

Young rats as soon as they were weaned came on one of the above diets and when about 4 months old were mated. The youngs kept the same food as their mothers. After weaning, sexes were separated till adulthood. The first generation grew well, those on diet I a bit slower than the others, as can be seen in the curves. The second generation also grew well.

Tables 1 and 2 give the results of matings for the first lots. Table 3 and 4 for the II and III. Table 5 gives a general survey of the three experiments.

The young, so far as they did not die, grew as well as their parents ; but matings between them were all infertile but one. Mating from the males of the experiment with females on normal food had no success. Mating of females on cornfood with males on normal food proved fertile, and they raised their youngs.

TABLE 1.
Cornfood I.
1st Generation.

Male N ^o .	Female N ^o .	Number of Young	Weaned
174	172	6	0
	172	0	0
	175	0	0
230	207	0	0
	219	10	6
243	185	11	10
	210	0	0
	260	2	2
	295	6	4
248	209	5	0
	209	0	0
	210	5	0
	210	6	2
	250	5	0
	250	5	3
	254	8	3
	260	6	5

Total 17 matings of which 5 infertile, number of young 75, whereof weaned 35.

We may take from these experiments, that the limiting factors controlling reproduction are others than those controlling growth, and that the demands for nutrition of the males are others than those of the females. I am not

TABLE 2.
Cornfood I with 1 0/0 cod liver oil.
2nd Generation.

Male N ^o .	Female N ^o .	Mated	Result
418	342	17/4 — 23/6	nihil
	394	" "	"
422	430	21/1 — 17/4	"
	426	" "	"
425	417	21/1 — 17/4	"
	421	" "	"
	398	17/4 — 23/6	"
	399	" "	"
427	431	17/4 — 25/5	"
	433	" "	"
428	415	21/1 — 17/4	"
	424	" "	"
	410	17/4 — 23/6	"
	411	" "	"
429	414	17/4 — 23/6	"
	434	" "	"

N.B. The females: 398, 399, 394, 410, 431, 433 and 434 got normal food

Females of second generation mated with males on normal food.

Female N ^o .	Male N ^o .	Mated	Number of young	Weaned
415	436	17/4 — 20/5	8	8
417	400	19/5 — 11/6	4	0
421	400	" "	6	4
424	436	17/4 — 18/5	7	5
426	340	17/4 — 28/5	5	5
430	340	17/4 — 26/6	0	0

6 matings: 1 infertile: 30 young: 22 weaned.

quite sure, that these differences are qualitative and not quantitative ones, though the former seems more likely.

The fact that cod liver oil does not promote reproduction excludes the antirachitic and perhaps the Avitamin, but I have some observations that

TABLE 3.
Cornfood II.
1st Generation.

Male N ^o .	Female N ^o .	Mated	Number of young	Weaned
244	253	24/6 — 15/7	6	5
	258	24/6 — 15/7	8	8
252	242	24/6 — 15/7	2	0
	246	24/6 — 15/7	6	6
	242	22/7 — 15/8	2	2

2nd Generation.

Male N ^o .	Female N ^o .	Mated	Number of young	Weaned
383	375	6/1 — 16/4	0	0
	388	6/1 — 16/4	0	0
	402	16/4 — 10/6	0	0
	405	16/4 — 10/6	0	0
389	373	6/1 — 4/2	1	0
	384	6/1 — 28/1	5	4
	373	16/4 — 8/5	5	5
	384	16/4 — 2/7	7	0

N.B. 402 and 405 got normal food.

Females on Cornfood II mated with males on normal food.

Female N ^o .	Male N ^o .	Mated	Number of young	Weaned
375	438	16/4 — 2/5	4	1
388	438	16/4 — 20/5	1	0

tend to show, that cod liver oil can not fully substitute butter in promoting growth and as the reactions of the E-vitamine, supposed by SURE and EVANS to be the reproduction controlling factor, are very similar to those of A-vitamin, prudence seems me still required.

TABLE 4.
Cornfood III.
1st Generation.

Male N ^o .	Female N ^o .	Mated	Number of young	Weaned
183	195	7/10 — 12/11	7	4
245	255	24/6 — 15/7	8	8
	256	24/6 — 29/7	9	8
257	247	24/6 — 15/7	7	8
	249	24/6 — 15/7	9	9

N.B. Female 182 mated with male on normal food N^o. 85 had 7 young, all weaned.

2nd Generation.

Male N ^o .	Female N ^o .	Mated	Number of young	Weaned
344	363	6/1 — 16/4	0	
	371	6/1 — 16/4	0	
	392	16/4 — 3/5	0	
	397	16/4 — 3/5	0	
366	348	6/1 — 16/4	0	
	356	6/1 — 16/4	0	
	395	16/4 — 25/6	0	
	401	16/4 — 25/6	0	

Females 392, 395, 397 and 401 got normal food.

Females on Cornfood III mated with males on normal food.

Female N ^o .	Male N ^o .	Mated	Number of young	Weaned
348	432	17/4 — 11/5	8	7
356	432	17/4 — 20/5	5	4
371	403	16/4 — 3/6	2	0

TABLE 5.

	Number of males	Number of females	Number of matings	Of which interfile	Number of young	Of which weaned	Young pro mating	Percent weaned
Normal food.....	17	29	52	4	365	319	7	87
Cornfood I:								
1 st generation.....	5	11	17	5	75	35	4.4	46 ^{1/2}
2 nd generation A.....	6	7	10	10	0	0	0	
" B.....	6	6	6	6	0	0	0	
" C.....	5 ¹⁾	7	7	2	30	22	4.3	71
Cornfood II:								
1 st generation.....	2	4	5	0	24	21	4.8	87
2 nd generation A.....	2	4	6	2	17	8	2.8	47
" B.....	2	2	2	0	4	1	2	25
Cornfood III:								
1 st generation.....	3	5	5	0	40	34	8	85
2 nd generation A.....	2	4	4	4	0	0	0	
" B.....	2	4	4	4	0	0	0	
" C.....	2	3	3	0	15	11	5	73

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Wageningen.*

¹⁾ Big figures mean rats on normal diet.

Physics. — "*On the difference of the fluorescence and the absorption spectra of the uranyl salts.*" By G. H. DIEKE and A. C. S. VAN HEEL. (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated at the meeting of June 27, 1925).

1. In 1922 Prof. EHRENFEST has pointed out the necessity to explain a sudden change appearing in the regularly formed spectra of the uranyl compounds, before one could think of solving the structure of these spectra. As is well known nearly all uranyl salts do fluoresce, and with a spectrum of very regular structure. This consists of three to eight groups having the same internal structure and appearing in the spectrum with a constant difference of frequencies. The absorption spectra of the same substances show quite an analogous structure, with the difference however that the frequency interval between the successive groups here has another, always smaller value. For one distinct salt this frequency interval is for example 830 per cm. for the fluorescence and 710 for the absorption.

For different salts these numbers can have a slightly different value, but they do not differ more than 5 per cent. This sudden difference in passing from fluorescence to absorption has to be solved. In the following it will turn out that such a difference must appear necessarily, when we do assume that the bands are to be ascribed to a simultaneous change of the electronic movement and of the oscillation of the nuclei, and that the oscillation energy for the two states of the electron are somewhat different.

2. As the uranium compounds not containing the UO_2 as radical neither fluoresce nor possess such regularly formed absorption spectra as those which *do* contain it, it seems to us not improbable that we may assume that the energy of the oscillations within this radical does play part at the emission and absorption of light.

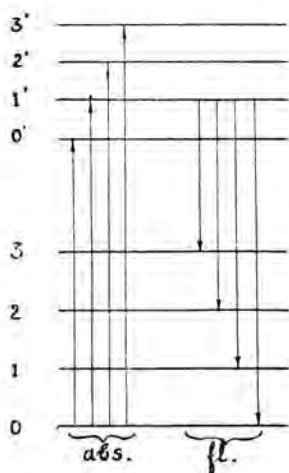
This oscillation energy will generally have a different value before and after the electronic jump, as is the case with the molecules emitting the ordinary band spectra.

In this manner we do arrive at the following scheme of niveau's.

For a non-excited molecule: a state 0 without oscillation energy; and states 1, 2, 3, etc. with respectively once, twice, thrice, etc. the energy of the fundamental oscillation.

For an excited molecule: a state 0' again without oscillation energy;

and states $1'$, $2'$, $3'$, etc. with respectively once, twice, thrice, etc. the oscillation energy in excited state.



In the figure these niveau's are schematically represented.

At low temperatures there are only molecules on niveau 0. Absorption then will take place from this niveau to the different upper niveau's, *the absorption bands will therefore show a frequency interval equal to the interval between the oscillation niveau's in excited state.* The corresponding lines are given in the figure.

From a definite excited niveau fluorescence will take place by jumping back to the different lower niveau's.

The frequency interval of the fluorescence bands will therefore correspond to the change of oscillation energy in non-excited state.

This should explain the plunge of the constant frequency interval in passing from fluorescence to absorption.

For convenience' sake we have assumed in the foregoing that in the states 0 and 0' no oscillation energy is present. Should this be the case then we ought to speak of *changes* of oscillation energy. One must confer to these changes the quantum numbers 1, 2, 3, etc., resp. $1'$, $2'$, $3'$, etc. in order to obtain the niveau's corresponding to these numbers.

This simple scheme does not suffice to explain the complete fluorescence and absorption spectrum of an uranyl salt. It has appeared to us however that a little extension suffices. We hope to publish before long about this subject.

In conclusion we will point out that the fact, that the frequency difference is constant in such a high degree, indicates that the oscillations are to a high degree harmonical.

Physics. — "*On the monochromatic excitation of fluorescence.* By A. C. S. VAN HEEL. (Communication from the Physical Laboratory at Leyden.) (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated at the meeting of June 27, 1925).

It is a good many years ago that the idea arose to continue the investigation on the fluorescence of the uranyl salts at low temperatures done by H. and J. BECQUEREL and H. KAMERLINGH ONNES in 1909 at Leyden. The war and the succeeding unfavourable circumstances did prevent for many years the execution of this project. Only in 1923 it came to the preparation of the intended measurements. From the first the old project was prominent to investigate the relation between the intensity of the fluorescence bands (better still of the components of these bands, that can indeed be separated sufficiently at hydrogen temperatures) and the wave length of the exciting band.

The importance of this investigation, which is from the purely experimental point of view highly interesting enough, is very increased by the considerations given by Prof. EHRENFEST in the "*Gedenkboek H. KAMERLINGH ONNES, 1922*".

Prof. KAMERLINGH ONNES had the kindness to invite me to help at the preliminary observations, while the definitive experiments should take place with bigger and better instruments on a larger scale and with greater precision. Meanwhile it appeared that with the provisional contrivement there could be obtained important results. Prof. BECQUEREL and Prof. KAMERLINGH ONNES were then willing enough with kind approval of Prof. DE HAAS to leave the subject to me. Here follows a preliminary communication of the results obtained up to now.

Concerning the work done in the range of years after 1909 we have to mention, that E. L. NICHOLS and his co-workers have published in the *Physical Review* a series of articles, containing a description of the fluorescence and absorption of uranyl salts at temperatures between 20° and -185° C. The regularities found by H. BECQUEREL have been found by them in all investigated cases.

The fluorescence consists of (at the utmost) eight bands, each of which consists of pl.m. five components, which components are separated at low temperatures and increased in number with many less regularly appearing bands. The interval in frequency scale between homologous components is constant over the whole of the fluorescence spectrum.

The absorption spectrum of these compounds too shows a similar regular structure. This too NICHOLS and his co-workers found confirmed. In contra-distinction however to what H. BECQUEREL formerly found,

they got the conviction that the interval appearing in the absorption spectra has another, always smaller value than the interval in the fluorescence spectra.

When one considers the spectra of one substance, one gets the impression, that every series of fluorescence lines is prolonged towards the violet in a corresponding absorption series, while the constant frequency interval plunges from $\Delta \frac{1}{\lambda} = \text{pl.m. } 82$ (λ expressed in mm.) to $\Delta \frac{1}{\lambda} = \text{pl.m. } 71$.

For this investigation I was allowed to dispose of the same crystal of autunite, that has served at the former experiments of Prof. BECQUEREL and also at those in 1909. The choice fell on this substance (double phosphate of uranyl and calcium) on account of the small number of components in every group of fluorescence and absorption, which renders superfluous the great monochromation necessary for the other substances, that do fluoresce with more lines. Low temperatures (liquid air) is wanted for the separation of the groups. In liquid hydrogen the phenomenon will be more sharply defined.

As a monochromator was used the instrument, described by Prof. ZEEMAN in Arch. Néerl., T. 27, p. 252. The aperture of the lenses is $f/2.2$. We were allowed to use a glass spectrograph of BUSCH (aperture $f/3$).

Results :

First there has been established, that a considerable fluorescence never can be excited by light that has not precisely the wavelength of one of the absorption lines. The extreme fluorescence band on the violet side is, as is known, at the same time the extreme absorption band on the red side. I call here this band 1, and number the fluorescence bands towards the red with 2, 3, etc. and the absorption bands towards the violet with 2', 3', etc. Band 1 might thus be called 1', too.

Now when the substance is illuminated by light of the wavelength of fluorescence band 2, then there is no fluorescence observable at all in the spectrum. When the crystal is illuminated by light of the wavelength of the reversible band 1, then there is fluorescence with the two fluorescence bands 2 and 3. It is not settled whether the reversible band emits in this case.

When one excites with the still more violet band 2', then the fluorescence of the bands 2 and 3 augments, the reversible band begins to emit and a still more red fluorescence band (4) appears.

Quite analogous phenomena are shown by the double sulphate of potassium and uranyl.

These observations have been recorded photographically at the temperature of liquid air. The observations in liquid hydrogen were done visually.

Finally I want to express my thanks for the use of the instruments and also of the kindness of the said professors.



Fig. 1. Fluorescence spectra of the double sulphate of potassium and uranyl at -185°C . Red to the left, violet to the right.

- a. The whole of the fluorescence spectrum, as excited by a broad range in the ultra-violet.
- b. Fl.-spectrum, excited by one ultra-violet absorption group (the reversible band 1 is not visible on the reproduction).
- c. Fl.-spectrum, excited by absorption group 2' (here too the yet present fluorescence group 1 is not visible on the reproduction).
- d. Fl.-spectrum, weakly appearing, as the exciting light lies between absorption groups.
- e. Fl.-spectrum, excited by the reversible group 1.
- f. Absence of fluorescence when the exciting light has the wavelenght of the fluorescence group 2.

Remark: at all excitements not only the strong, but also the weaker components of the fluorescence groups appeared.

Physics. — "*Measurements of the surface tension of liquid helium*".
Communication N^o. 179a from the Physical Laboratory, Leyden.
By A. TH. VAN URK, W. H. KEESOM and H. KAMERLINGH ONNES.

(Communicated at the meeting of October 31, 1925).

§ 1. *Method and apparatus.* In order to determine the surface tension of liquid helium in contact with its saturated vapour we used, as did KAMERLINGH ONNES and KUYPERS ¹⁾ in the case of hydrogen, the method

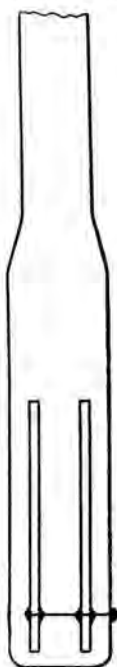


Fig. 1.

of the capillary elevation in a narrow tube. To diminish irregular pressure differences at the open ends of the capillaries these were made comparatively short (Fig. 1, c.f. Fig. 1, Comm. N^o. 142d). Also it appeared desirable to have an immediate control as to whether or not the measured rise was the true rise corresponding to the temperature used. It often happened that gas bubbles rose in the narrow tube, causing the meniscus to oscillate for a considerable time and then to remain stationary for some minutes at an entirely wrong height. By placing two capillaries of about the same diameter alongside one another in the same wide tube and by comparing the elevations in both, this uncertainty was eliminated. It is hardly to be expected that precisely the same disturbance to the elevation would appear in both tubes at the same time.

A platinum wire bearing two loops, in which the capillaries were fixed with a little Kothinsky cement, was fused into the wall of the wide tube.

§ 2. *Calibrations.* Two capillaries about 10 cms. long were chosen, one twice as wide as the other. Each capillary was calibrated several times by two different methods, namely, by filling with mercury threads of various lengths which were measured, the mercury used being weighed, and by placing the tube filled with mercury in a liquid (an approximately 10:1 mixture of chloralhydrate and glycerine) of the same refractive index, for Na-light, as glass and then measuring the diameter of the mercury thread with the micrometer eyepiece of a microscope.

The two calibrations of both tubes (of radius about 0,009 and 0,02 cms.) could not be made to agree to more than $\frac{1}{2}\%$. A calibration

¹⁾ Comm. N^o. 142d. These Proceedings 17, 525, 1914.

curve was drawn for each capillary from which the radius at the position of the meniscus could be read off. From each tube two pieces about 3 cms. long were taken to be placed alongside one another.

§ 3. *Observations.* The positions of the menisci in the capillary tubes (the top and the edge could not be distinguished) and the positions of the liquid in the wide tube, in the neighbourhood of the capillaries and somewhat further off, were measured. Besides these the tops of the tubes were also read to determine the positions of the menisci in relation to the tubes.

The corrected rise ' H ' was calculated from the rise ' h ' measured in a capillary tube placed inside a wider tube by introducing the following two corrections:

$$H = h + \frac{r}{3} + h'$$

where r is the inner radius of the capillary and

$$h' = \left(h + \frac{r}{3} \right) \frac{\frac{2d}{r} \frac{(R-r_1)^2}{(R-r_1)^2}}{1 - \frac{2d}{r} \frac{(R-r_1)^2}{(R-r_1)^2}} \quad ^1)$$

¹⁾ See J. E. VERSCHAFFELT, Leyden Comm. N^o. 18, These Proc. 1895. This correction is not properly applied in Communication N^o. 142d. For the there communicated measurements of *Hydrogen* we now can borrow the above corrections from the elevation in two concentric tubes as these have been more accurately calculated by a graphical method by VERSCHAFFELT, Bull. Acad. Roy. de Belg. Cl. d. Sc. 1921, p. 574. The following values for H , which are to be substituted for the values given in Table I of Communication N^o. 142d were obtained.

The corresponding values of ψ_σ are also given (c. f. Table II, Comm. N^o. 142d)

T	H	ψ_σ
20.40	1.694	1.910
18.70	1.883	2.1945
17.99	1.962	2.3195
16.16	2.169	2.631
14.68	2.324	2.860

(c. f. also J. E. VERSCHAFFELT, Comm. Phys. Lab. Ghent, N^o. 2, Wis- en Natuurkundig Tijdschrift 2, 231, 1925). In the formula of VAN DER WAALS $\psi_\sigma = A(1-t)^B$ the values of A and B become $A = 5.554$, $B = 1.119$, and the constant of EÖTVÖS $k_{E\ddot{O}} = 1.363$, and EINSTEIN's constant, 6.64×10^{-9} .

In the case of *helium* we have been unable to use the new calculations of the rise between two concentric tubes by VERSCHAFFELT, as the capillary constant of helium is small and the table given by him does not go far enough. However the difference lies within the experimental errors.

The combination of both corrections gives

$$H = \frac{h + \frac{r}{3}}{1 - \frac{2dr}{(R-r_1)^2}}.$$

We have applied this formula to the present case in which two tubes are placed in a wider tube; as the total correction h' amounts to 1% for the wider capillary, and only $1/2\%$ for the narrower, any error thus involved is negligible.

Corrections for the expansion of the glass have been neglected as they would certainly lie within the experimental error.

The temperature was calculated from the vapour pressure according to the formula given in Comm. N^o. 147b¹⁾.

§ 4. *Results.* The differences between the two values found for Hr at the same temperature amount to a maximum of 5%. It must be remembered that the largest rise was 5 mm. and that this had to be read through two vacuum vessels and then through the walls of two glass tubes.

The surface tension ψ_s and the molecular surface tension ψ_M (in ergs) can be calculated from the product Hr by means of the following formulae²⁾

$$\psi_s = (\varrho_l - \varrho_v) \frac{g}{2} \cdot Hr$$

$$\psi_M = \psi_s \left(\frac{M}{\varrho_l} \right)^{2/3}.$$

The results are shown in Figure 2. The points \odot and Δ refer to the measurements with the capillaries of radius 0.02 and 0.009 cms. respectively. The values of ψ_M given in table II have been interpolated by means of this graph. To them correspond the values given for $a^2 = Hr$, a being the capillary constant.

TABLE I.

T	ψ_M	a^2	T	ψ_M	a^2
4.20	0.98	0.00181	2.50	2.69	0.00419
4.00	1.19	211	2.00	3.08	477
3.50	1.68	280	1.50	3.22	496
3.00	2.19	350			

¹⁾ These Proceedings 18, 493, 1915.

²⁾ The densities ϱ_l and ϱ_v for helium were obtained from E. MATHIAS, C. A. CROMMELIN, H. KAMERLINGH ONNES and J. C. SWALLOW, these Proceedings 28, 526, 1925, Leyden Comm. N^o. 172b.

§ 5. Discussion.

From Fig. 2 it is seen that the line which represents the surface tension as a function of temperature has a curvature which first appears at 2.4° K. Above this temperature the line appears to be quite straight.

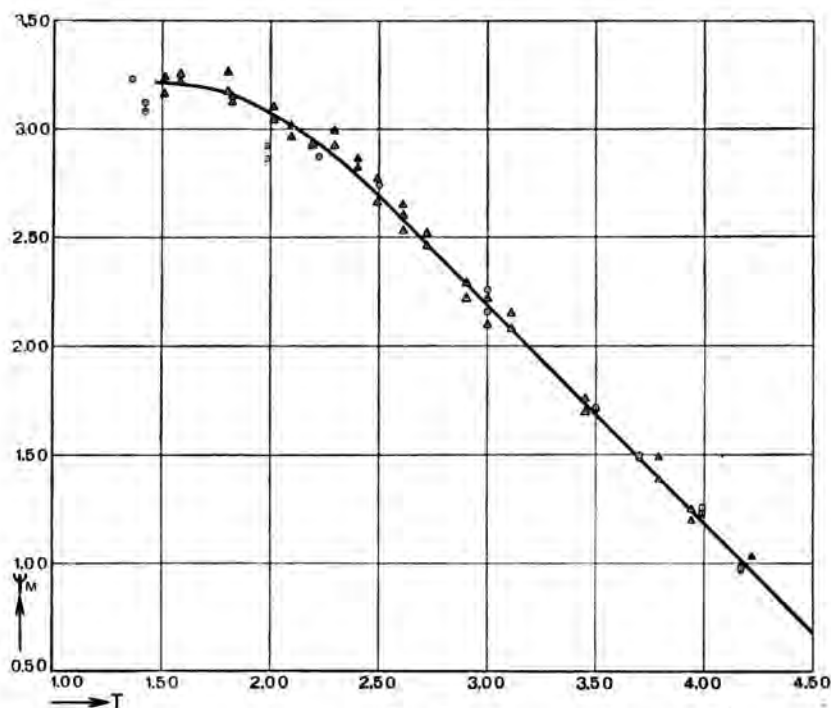


Fig. 2.

We have calculated the EÖTVÖS' constant¹⁾ for the straight portion and this amounts to about 1.0. Thus helium obeys the rule, stated by KAMERLINGH ONNES and KEESOM²⁾, according to which normal substances in this respect form a series in which the EÖTVÖS' constant increases with the critical temperature. According to this rule the constant for helium must be the smallest, which is actually the case.

The curvature just mentioned probably indicates, as does the maximum that is observed in the liquid density³⁾, a peculiarity in the molecular

¹⁾ $d\psi_M/dT$. See „die Zustandsgleichung“. *Enz. d. math. Wiss.* V. 10, Leyden Suppl. No. 23, § 37b.

²⁾ „Die Zustandsgleichung“, note 381.

³⁾ The observations of this phenomenon published up to now only indicate the existence of a maximum of the apparent density of liquid helium in a glass vessel. Here it can be further stated that measurements have been made in which a graduated silver scale was placed next to the glass scale of the reservoir in the helium bath and both scales compared with the aid of a cathetometer. No difference in the expansions of either scale could be recorded, from which it can be concluded that such a difference, if it exists, amounts to less than a thousandth part of the calculated density of the liquid helium. It is hardly

attraction. With regard to the former no such curvature is observed with the other so-called permanent gases. The surface tension of the latter, however, because of the appearance of the solid state, cannot be observed at such a low reduced temperature as is the case with helium.

We wish to acknowledge our very great indebtedness to Mr. G. P. NIJHOFF, who made part of the observations and to Miss A. F. J. JANSEN and Mr. J. VOOGD for their help in the temperature measurements.

possible that both substances undergo the same transformation at the same temperature; hence it follows that the maximum of the apparent density of the helium in a glass reservoir is due to the helium itself.

Physics. — *"Isotherms of di-atomic substances and their binary mixtures. XXXIII. Isotherms of oxygen between -40° C. and $-152^{\circ}.5$ C. and pressures from 3 to 9 atmospheres. (Communication N^o. 179b from the Physical Laboratory of the University of Leyden.)* By G. P. NIJHOFF and W. H. KEESOM.

(Communicated at the meeting of October 31, 1925).

1. *Introduction.*

A knowledge as accurate as possible of the first virial-coefficients, i.e. of B , afterwards of C , is important, as well in view of the calculation of gas-densities in the neighbourhood of the normal one, and the determination of corrections of the gas-thermometer, as in view of the fact, that in practice it is yet possible to infer for those coefficients some relations with molecular structure and forces, eventually the molecular volume and the moment of the molecular quadruplet or doublet, using simplifying assumptions that are fairly approximate.

For the determination of B are to be preferred measurements with gases in slightly compressed states, in which the influence of B is already important and that of C might be noticeable, but the following virial-coefficients have no influence. Since at very low temperatures, in the first place with substances with a low critical pressure, such states are reached at about atmospheric pressures, and on the other hand, at high pressures and with substances with higher critical pressures those states extend to pressures as high as some tens of atmospheres, for some gases those states exist at a given temperature-range with pressures of only some atmospheres. So we desired to complete the investigations of isotherms at low temperatures, done in Leyden at pressures from about 20 to 100 atmospheres, with measurements at pressures from 3 to 20 atmospheres, to fill up a gap between those first-mentioned and gas-thermometer measurements at the lower pressures.

In the second place precise measurements at those pressures are of importance with substances with a very low critical pressure, e.g. helium, because then one gets the same reduced pressures at which other gases (at higher pressures) have been studied, and so a comparison after the principle of the corresponding states will be possible.

To have some estimation of the precision that is to be reached in the pressure-domain mentioned, we began with measurements with oxygen, for which substance KAMERLINGH ONNES and KUYPERS¹⁾ determined the isotherms with pressures from 20 to 60 atmospheres and temperatures from

¹⁾ H. A. KUYPERS and H. KAMERLINGH ONNES, Arch. Néerl. sér. III A, 6, 277, 1923. Leyden. Comm. N^o. 165a, H. KAMERLINGH ONNES and H. A. KUYPERS. Leyden Comm. N^o. 169a.

20° C. to —117° C. We were able to extend the measurements down to —152°.5 C., before approaching condensation made us stop.

2. *The apparatus.*

a. *The oxygen* was prepared with the same apparatus as described in Leyden Comm. N^o. 165a ¹⁾).

b. *The piezometer.* For the arrangement we refer to Leyden Comm. N^o. 69 ²⁾). We calibrated a stem 108 cm. long, with a total volume of 108.6 ccm. A gas-reservoir of 137.8 ccm. capacity was blown on this stem. Thus it is possible to vary the densities in the piezometer reservoir rather widely. The same result could be reached by using instead of such a big stem a smaller piezometer reservoir; but then the accuracy would be less.

c. *The piezometer reservoir* had a capacity of 20.400 ccm., and was connected in the usual way by means of a steel capillary to the stem.

d. *The pressure measurements.* Pressures for these measurements varied from 9 to 3 atmospheres. They were measured first by means of the standard open manometer of KAMERLINGH ONNES ³⁾). In this manometer columns of mercury of a constant length of 3 meters are coupled in series by air transmission, and a first tube of variable length is added to fill continuously the 4 atm. intervals. All tubes are read with telescopes, and tenths of mm. estimated. To know the pressure of the gas in the piezometer one has to add the barometer pressure to the so measured pressure and to subtract from it the pressure of the mercury column from the top of the meniscus in the piezometer to that in the indicator glass ⁴⁾). With low pressures the difficulty arises, that the uncertainty (which is about 0.3 mm.) in reading the variable first tube, especially in cases where the mercury column happens to be very short, can give a relatively large error, which is not now compensated by the much larger accuracy (of 1/10.000) of the other tubes, as it is with greater pressures.

Also the inaccuracy in the reading of the mercury column in the piezometer, (where the height in the indicator-glass is estimated in $\frac{1}{10}$ mm.) was not to be neglected against the small pressures, which were now to be measured. Therefore the indicator glass was read with a small cathetometer, whereas the open tube of the open standard manometer was replaced by a small divided manometer, constructed after the model of the standard manometer, and joined parallel to the open tube. This small manometer could be read with a cathetometer. For greater simplicity the first tube of this small manometer was closed, to eliminate the reading of the barometer. The apparatus was constructed in the following way.

¹⁾ Arch. Néerl. sér. III A, 6, 277, 1923, Leyden Comm. No. 169 a.

²⁾ These Proceedings 3, 621, 1901.

³⁾ These Proceedings 1, 213, 1898, Leyden Comm. N^o. 44.

⁴⁾ The indicator-glass is given at C₃ in Plate I, these Proceedings 3, 621, 1901, Leyden, Comm. No. 69.

e. *The divided manometer for pressures from 1 to 4 atm.* Two tubes of mercury of a constant length of 115 cm. can be coupled in series and a third tube is affixed by means of which the pressure can be changed continuously. These tubes are connected, in the same manner as the open manometer, to a pressure tube, to which are also connected: a cock (K_1), to apply the pressure, a cock (K_2), to shut off the connection with the open manometer, and two cocks (K_3 and K_4), the first an ordinary outlet, the second connected with a small vacuum pump, for reducing the external pressure on the closed tube.

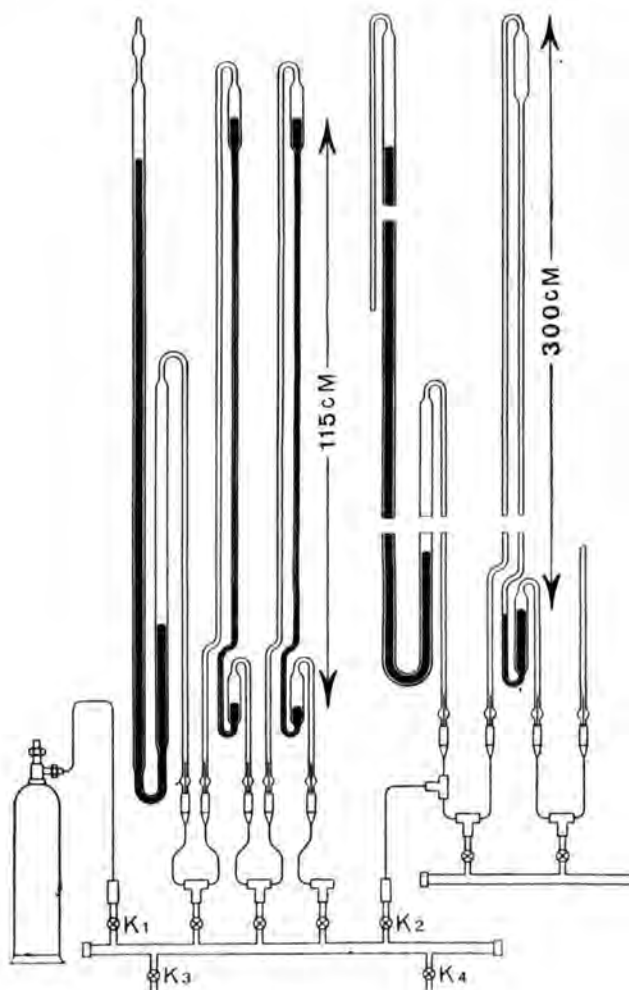


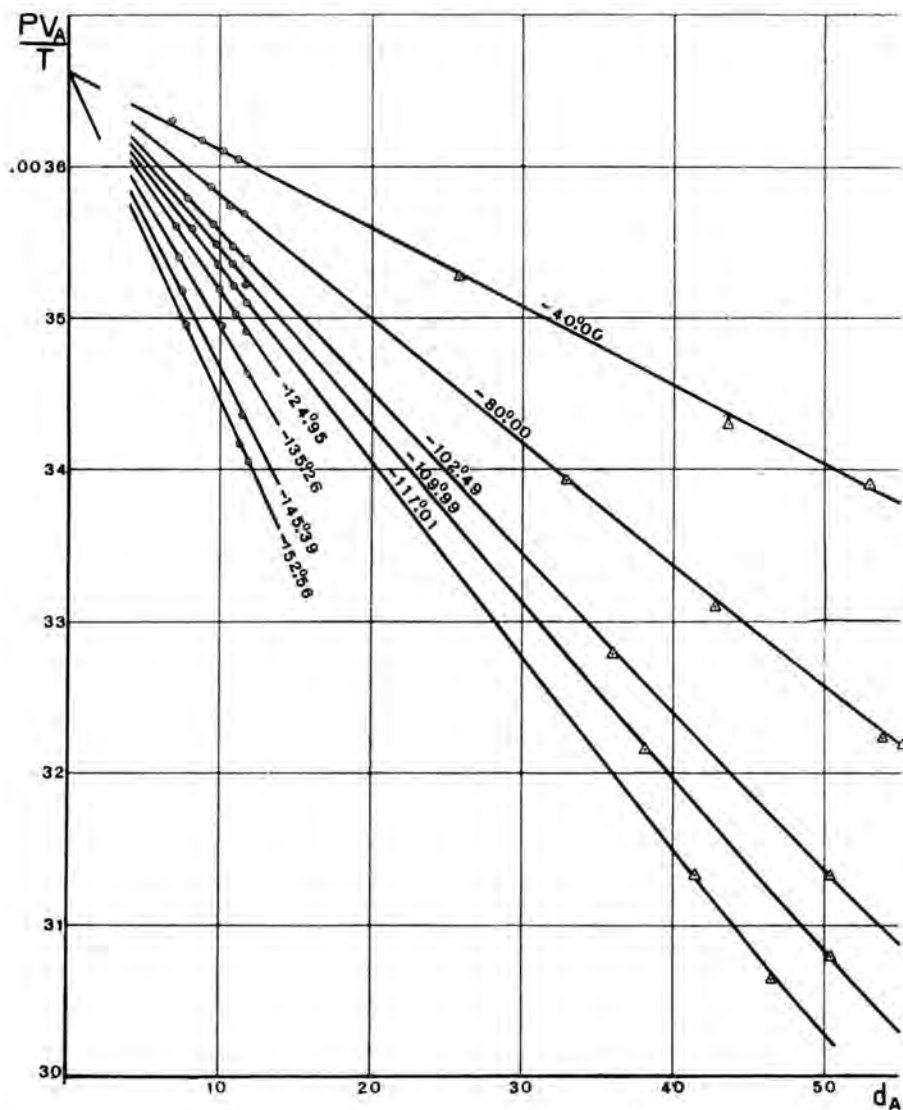
Fig. 1.

When measuring, one first sets the correct pressure on the open manometer, keeping the connection with the small manometer closed. From the length of the mercury column in the open tube of the standard manometer

we can calculate how much pressure to apply to the small manometer. The pressure in the latter can always be measured to an accuracy of one in 10.000, because the measurements are made with a cathetometer.

3. The measurements.

a. The *normal volume* was determined before and after the measurements in the way described in Leyden Comm. N^o. 78 ¹⁾. Because the volume of the upper part of the stem reaching outside the waterbath would be



- △ KAMERLINGH ONNES and KUYPERS.
- NIJHOFF and KEESOM.

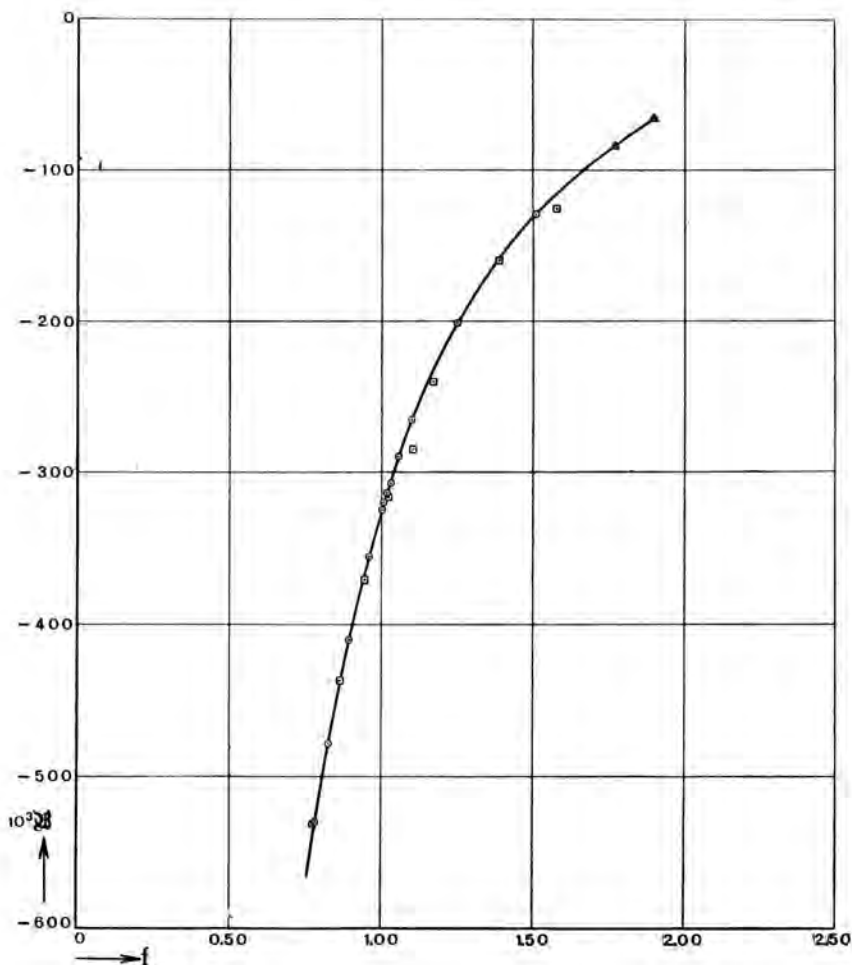
Fig. 2.

¹⁾ These Proceedings 4, 761, 1902.

disturbing for such a small gas reservoir, the whole stem was put in a separate waterbath, which was fed by a sidebranch from the same thermostat which kept the main waterbath at constant temperature. The temperature of the two baths agreed within $\frac{1}{100}$ of a degree.

b. The *temperatures* were obtained with a cryostat described in Leyden Comm. No. 83 ¹⁾, using methyl-chloride and ethylene.

4. *The results of the measurements* are given in the following tables.



△ KUYPERS and KAMERLINGH ONNES.

□ CATH and KAMERLINGH ONNES.

⊙ NIJHOFF and KEESOM.

Fig. 3.

¹⁾ These Proceedings 5, 502, 1903.

TABLE I.

Normal volumes before: 254.37
after: 254.32

θ	p	d_A	p^v_A	$\frac{p^v_A}{T}$	$p^v_{A \text{ obs.}} - p^v_{A \text{ calc.}}$
— 40.01	9.382	11.165	0.8403	0.003605	+ 0.00005
	8.559	10.169	8416	3611	+ 1
	7.385	8.756	8432	3618	0
	5.755	6.801	8462	3631	+ 5
— 80.00	7.918	11.490	6892	3569	+ 1
	7.300	10.576	6902	3574	— 4
	6.445	9.306	6926	3587	— 1
—102.49	7.029	11.650	6037	3539	+ 4
	6.507	10.752	6051	3547	+ 1
	5.783	9.519	6076	3562	+ 2
	4.759	7.795	6105	3579	— 0 ⁵
—109.99	6.684	11.634	5745	3522	+ 5
	6.218	10.781	5767	3536	+ 1 ⁵
	5.594	9.666	5788	3549	+ 0 ⁵
—113.94	6.501	11.616	5597	3517	0
	6.092	10.855	5613	3527	+ 1
	[5.470	9.695	5642	3545	+ 6]
—116.01	6.486	11.767	5512	3509	— 4
	6.008	10.855	5534	3523	0
	5.422	9.757	5557	3538	0
	4.506	8.055	5594	3561	+ 3
—116.03	4.533	8.101	5596	3563	+ 1
	3.841	6.839	5616	3576	— 1
—117.01	6.389	11.661	5478	3510	0
	5.965	10.854	5496	3521	+ 1
	5.385	9.760	5517	3555	— 1
	4.493	8.088	5555	3559	+ 2

TABLE I (Continued).

θ	d	d_A	$p\nu_A$	$\frac{p\nu_A}{T}$	$p\nu_{A \text{ obs.}} - p\nu_{A \text{ calc.}}$
-118.58	6.254	11.538	0.5421	0.003508	- 0.0001
	5.909 ⁵	10.876	5433	3516	- 3
	3.799	6.883	5520	3572	+ 1
-124.95	6.013	11.629	5171	3491	- 4
	5.688	10.961	5190	3503	+ 0 ⁵
	5.160	9.897	5213	3519	0
	3.715	7.042	5276	3561	+ 1
	2.882	5.422	5316	3588	+ 5
-135.29	5.599	11.732	4773	3463	- 1 ⁵
	4.838	10.045	4816	3495	+ 2
	3.550	7.277	4878	3540	- 1
-145.39	5.007	11.411	4387	3436	- 3
	3.375	7.513	4492	3518	+ 3
-152.56	4.854	11.827	4102	3405	- 1
	4.636	11.262	4117	3417	- 1
	3.251	7.716	4213	3496	0

In the last column the differences are given between the measured $p\nu_A$'s, and those calculated with help of the B_A 's of table II.

The points also are given on a $\frac{p\nu_A}{T}$, d_A -graph (fig. 2), where the points measured by KAMERLINGH ONNES and KUYPERS are appended as far as possible. They agree within the limits of accuracy ¹⁾.

In the second table we give a survey of the B -values, as calculated graphically from our measurements. For greater completeness we add those for 20° C. and 0° C. from Leyden Comm. No. 165a. All are given together with those of CATH and KAMERLINGH ONNES, as given by VAN AGT in Leyden Comm. No. 176c ²⁾, in another graph (fig. 3). They too agree within the limits of accuracy.

In conclusion we want to express our sincere thanks to those who helped

¹⁾ For greater clearness two isothermals are omitted in fig. 2, viz. -118° C. and -116° C. (-117° C. is given).

²⁾ These Proceedings 28, 687, 1925.

us by regulating the temperatures, especially Mr. J. VOOGD, who helped us with the measurements and the calculations.

TABEL II.

t	τ	A_A	$10^3 \cdot B_A$	$10^3 B$	\mathfrak{B}
+20° C.	1.8998 ⁵	1.07426	—0.80379	—0.74823	—65.846
0	1.7702	1.000952	0.95803	0.95712	84.229
—40.01	1.5109	0.85430	1.258	1.473	129.59
—80.00	1.2516	70773	1.619	2.288	201.31
—102.49	1.1058 ⁵	62530	1.885	3.014	265.24
—109.99	1.0572	59781	1.967 ⁵	3.291	289.60
—113.94	1.0316	58333	2.038	3.494	307.46
—116.01	1.0182	57574	2.051	3.562	313.50
—117.01	1.0117	57208	2.079	3.634	319.81
—118.58	1.0016	56632	2.090	3.690 ⁵	324.77
—124.95	0.9603	54298	2.192	4.037	355.27
—135.29	0.89324	50508	2.355	4.663	410.32
—145.39	0.82777	46806	2.545	5.437	478.50
—152.56	0.78129	44178	2.660	6.021	529.87

$$T_k = 154.27 \quad p_k = 49.713^1) \quad B = \frac{B_A}{A_A} \quad \mathfrak{B} = \frac{p_k}{RT_k} \cdot B = 88.0024 B.$$

¹⁾ For the critical data see: These Proceedings 13, 939, 1911. Leyden Comm. No. 117.

Physics. — *"Further experiments with liquid helium. C A. On the properties of supraconductive metals in the form of thin films."* By G. J. SIZOO and H. KAMERLINGH ONNES. (Comm. N^o. 180a from the Physical Laboratory at Leyden.)

(Communicated at the meeting of October 31, 1925).

§ 1. In the report of KAMERLINGH ONNES to the IVth Conseil-Solvay (April 1924) a preliminary communication was made on the results of an investigation, at that time not yet considered as finished, concerning the behaviour of supraconductive metals in the form of thin films.

Though we intended to continue and to repeat with more accuracy these experiments, the difficulties which arose as well as the necessity of other researches made it impossible for us to work out this plan. However we consider the results obtained, notwithstanding their uncompleteness, important enough to be communicated here in their quantitative form.

The original plan to investigate extremely thin films, a few $\mu\mu$ thick for example, had soon to be given up, as such very thin lead or tin films, obtained by evaporation or cathode sputtering, showed the phenomenon of agglomeration or coalescence in such a high degree, that their electrical resistance increased very quickly with the time and soon reached an infinite value.

In the literature on the properties of thin metallic films this phenomenon is repeatedly mentioned ¹⁾.

The impact of the particles in the course of one or more days could be followed easily with the aid of a microscope. Keeping the films at liquid air temperature appeared to decrease the speed of the agglomeration process. Still it remained so inconvenient, that we decided to investigate first only thicker films. All measurements to be communicated here, are therefore made with films of a thickness of 0.3—0.5 μ , obtained by cathode sputtering. Even the resistance of these thicker films appeared to increase with the time, though in a much smaller degree than that of the very thin ones. The thickness could be determined by weighing.

For the resistance measurements it was necessary to apply four contacts to the film. For that purpose the four corners of the glassplate, on which the film had to be deposited were first sputtered with a thick layer of the metal, the rest of the plate being covered with mica.

Four wires of the same metal, with flattened ends, were then fixed to the four corners by means of little copper clamps.

The glassplate provided in this way with contacts and leads, was then

¹⁾ E.g. L. R. KOLLER. Physical properties of thin metallic films. Phys. Rev. XVIII (1921) p. 221.

placed again in the sputtering jar, to apply on it the film of the required thickness.

The sputtering took place in a glass bell jar which contained a cathode of the metal to be sputtered and which was placed on a copper plate as anode. The jar was filled with hydrogen.

The resistances were always measured by comparing the potentials at the end of the unknown and a known resistance placed in series with each other. This was done with a compensation apparatus, free from thermo-effects, or when this apparatus was in use for other measurements, with a set in which the deflections of a galvanometer were proportional to the mentioned potentials. With the measurements in liquid helium the films were placed in the heliumcryostat shown in Leyden Comm. N^o. 124c (1911), fig. 4¹⁾.

The temperatures were calculated with the aid of the formula of Leyden Comm. N^o. 147b, (1915) p. 33²⁾ from the vapour pressures of the helium-bath, which were read on a closed mercury manometer.

§ 2. The greater part of the measurements are made with tin films. Of one of them the temp. coeff. of the electrical resistance between 0° and 100° C. was determined. It was found to be 0.0034. Of another film the change of the resistance in the region between roomtemperature and helium temperatures was followed. Of course these measurements could not be made in one day. In consequence of this fact connected with the process of the change in resistance, the results can only give a rough survey of the way in which the resistance of the film depends on the temperature. They are sufficient though to show immediately the great difference between the behaviour of these films and that of ordinary tinwires.

The results of these measurements are given in table I. The low

TABLE I.

Date	T	$W_{T_{PI}}$
18—V—1922	roomtemp.	9 Ω
19—V—1922	4°.22 K.	1.96 ..
15—VI—1922	83.04	5.19 ..
15—VI—1922	90.18	5.46 ..
17—VI—1922	114.36	6.51 ..
21—VI—1922	228.55	10.93 ..
22—VI—1922	roomtemp.	13.55 ..

¹⁾ These Proceedings 14, 1911. p. 682.

²⁾ These Proceedings 18, 1915, p. 507.

temperatures were obtained by means of suitable cryostat liquids in the way generally used in the Leyden laboratory and measured with calibrated platinum thermometers.

At helium temperatures a number of measurements were carried out with the films Tp I, Tp II and Tp II'. In the first place the temperatures of the "vanishing point" of each film were determined. These appeared to be different for different films and also for the same film (Tp II') on different data.

TABLE II.

Date	p_{helium} in mm Hg	T	$W_{T_{pI}}$	$\frac{W}{W_k}$
18 — V — 1922		roomtemp.	9 Ω	1.
19 — V — 1922	760	4.20 ₀	1.96 ..	0.218
	480	3.76 ₄	1.964 ..	0.2182
	444	3.69 ₈	1.817 ..	0.2019
	424	3.66 ₈	1.518 ..	0.1686
	404	3.62 ₀	0.408 ..	0.0453
	390	3.59 ₂	0.0031 ..	0.00035
	387	3.58 ₆	0.00014 ..	0.00015
	386	3.58 ₄	0.00000 ..	0.00000

TABLE III.

Date	p_{helium} in mm Hg	T	$W_{T_{pII}}$	$\frac{W}{W_k}$
8 — VI — 1922		roomtemp.	32 Ω	1.
9 — VI — 1922	485	3.56 ₀	3.480 ..	0.1088
	450	3.70 ₈	3.486 ..	0.1089
	430	3.67 ₂	3.486 ..	0.1089
	410	3.63 ₂	3.480 ..	0.1088
	390	3.59 ₂	3.510 ..	0.1097
	370	3.55 ₀	3.380 ..	0.1057
	350	3.50 ₈	2.893 ..	0.09041
	330	3.46 ₂	0.304 ..	0.00950
	310	3.41 ₈	0.008 ..	0.00024

TABLE IV.

Date	Helium in mm. Hg	T	$W_{T_{pl}}$	$\frac{W}{W_k}$
15 — VI — 1922		roomtemp.	110 Ω	1.
16 — VI — 1922	760	4.20 K	15.17 ..	0.1274
	370	3.55 ₀	14.85 ..	0.1248
	350	3.50 ₈	10.37 ..	0.0871
	345	3.49 ₆	7.81 ..	0.0656
	340	3.48 ₄	4.41 ..	0.0371
	330	3.46 ₂	0.80 ..	0.0067
	310	3.41 ₆	0.00 ..	0.0000
29 — VI — 1922		roomtemp.	121 Ω	1.
16 — VI — 1922	420	3.65 ₂ K	15.81 ..	0.1307
	400	3.61 ₂	15.81 ..	0.1307
	380	3.57 ₀	15.64 ..	0.1293
	370	3.55 ₀	15.32 ..	0.1266
	360	3.52 ₈	13.46 ..	0.1112
	350	3.50 ₆	7.59 ..	0.0627
	340	3.48 ₄	1.02 ..	0.0084
	330	3.46 ₂	0.003 ..	0.0003
	320	3.44 ₀	0.000 ..	0.0000

But they were always lower than the "vanishing point" of ordinary tinwires, namely by about 0.1° to 0.2° K.

In the tables II, III and IV the results of these measurements are given.

To make it possible to unite them all in one figure (Fig. 1) the resistances of the films are all divided by the value of the resistance measured at room-temperatures, on the day before that on which the measurements in liquid helium were carried out. As a matter of course, the absolute accuracy of these quotients, in the figure and the tables called $\frac{W}{W_K}$, is small. The temperatures at which the resistance has half disappeared ("vanishing-point") are given in table V for these three films as well as for the resistance coil Sn-1922-M, made of extruded tinwire ¹⁾. The density of the current through the film is also given. This is calculated as if the current

¹⁾ Diss. W. TUYN, Leiden 1924 p. 8.

TABLE V.

Date	Name of the resistance	$T_{1/2}$	Density of the current
	Sn-1992-M	$3^{\circ}.74_6$ K.	
19 — V — 1922	T_{pI}	3.63_6	2.5 amp./mm. ²
9 — VI — 1922	T_{pII}	3.48_4	0.17 ..
16 — VI — 1922	$T_{pII'}$	3.49_6	0.25 ..
30 — VI — 1922	$T_{pII'}$	3.50_6	0.25 ..

distributes itself uniformly through the whole section of the film. The influence of the density is clear from the inclinations of the lines in fig. 1. The question arises whether the low "vanishing-point" is due to thinness of the film or to its granular structure. The fact that the vanishing-point of the film $T_{pII'}$ appeared to change with time supports the last suggestion. This change might be connected with the change in structure ("aging") which is clear from the increase of the resistance.

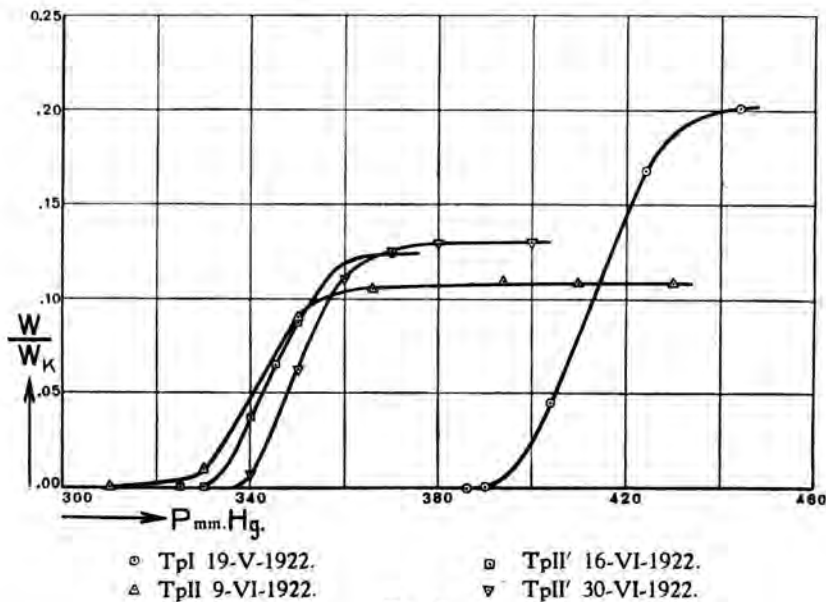


Fig. 1.

§ 3. With the tinfilm some measurements were further carried out concerning the disturbance of the supraconductivity by a magnetic field.

Though these investigations are only to be considered as of an orienting nature, they were a sufficient basis for concluding that the threshold value of the field for these films cannot greatly differ from that for tin

in the form of extruded wires. For example, with the film T_{pII}' a magnetic field of 55 gauss, directed parallel to the direction of the current through the film was sufficient to bring back the resistance of the film to the half value, at the temperature of 3°.42 K. For a time the required fieldstrength at this temperature amounts to about 45 gauss.

Lastly for one of the films the threshold value of the current could be determined roughly at two temperatures. It was found to be 0.16 Amp. at 3°.44 K. and 0.80 Amp. at 2°.78 K. The thickness of this film was about 0.5 μ , the breadth 15 mm., thus the section about 0.01 mm². So it was of the same order of magnitude as that of the tinwires, mentioned in Leyden Comm. No. 133d¹⁾. For these tinwires threshold values of the current are given which are also of the same order of magnitude as those found with this tinfilm.

This result thus is not in agreement with the suggestion of SILSBEE²⁾, namely that thin metallic films should have an abnormally high threshold value of the current, in consequence of the small value of the magnetic field of a current sent through a thin film.

Rather than to reject the hypothesis of SILSBEE about the connection of the threshold values of the current and the magnetic field, which is strongly supported by the measurements of W. TUYN³⁾, we are apt to consider as false the supposition about the uniform distribution of the current through the film. Besides it is difficult to form an idea about the roll, which the granular structure of the film plays in this connection.

§ 4. Besides tin other supraconductors have not been investigated. Some measurements are made with bismuth films. Namely it was known⁴⁾ that bismuth did not become supraconductive at 4°.25 K., but it had not yet been investigated at lower temperatures. As a bismuth film was easily to obtain while the drawing and winding of bismuth wires gives considerable difficulty because of the fragility of the wire, the resistance of some bismuth films was determined at helium temperatures. The material was electrolytic bismuth.

In the whole region of the temperatures obtainable with liquid helium the resistance of these films remained practically constant. Even at 1°.24 K. supraconductivity did not appear.

¹⁾ These Proceedings 16, 1914, p. 673.

²⁾ F. B. SILSBEE. Journal Wash. Ac. of Sc. Vol. VI. (1916) p. 597.

³⁾ Diss. Leiden 1924. Cap. II.

⁴⁾ Leyden Comm. N°. 142b (1914). These Proceedings 17, 1914. p. 520.

Physiology. — „Ueber die nervöse Natur und das Vorkommen der sogenannten interstitiellen Zellen (CAJAL, DOGIEL) in der glatten Muskulatur.“ (Aus dem Laboratorium für Embryologie und Histologie in Utrecht, Dir. Prof. J. BOEKE.) Von B. I. LAWRENTJEW, Kasan. (Communicated by Prof. J. BOEKE.)

(Communicated at the meeting of November 28, 1925).

In der vorliegenden Mitteilung will ich über einige interessante Tatsachen berichten, die ich bei der Untersuchung des feineren Baues des peripheren autonomen Nervensystems zu beobachten Gelegenheit hatte, und die meines Erachtens eine selbständige Bedeutung haben.

Es handelt sich um die sogen. interstitiellen Zellen von CAJAL und DOGIEL, deren Natur bis jetzt bei weitem nicht aufgeklärt war. Bekanntlich lassen sich in den Wandungen des Verdauungskanals vieler Wirbelthiere ausser den typischen Nervenzellen des AUERBACHSchen und MEISSNERSchen Plexus mit Hilfe von Methylenblau oder Silberimpregnation kleine spindelförmige oder dreieckige Zellen mit dünnen langen varikösen Fortsätzen nachweisen, die in grosser Anzahl zwischen den Muskelschichten, in der Periferie der Nervenganglien und Blutgefässe, in der Mucosa und Submucosa eingelagert sind. Diese von CAJAL im Jahre 1889 entdeckten Zellen waren seitdem stets der Gegenstand aufmerksamer Beobachtungen vieler Forscher. In der Literatur finden wir zwei sich widersprechende Ansichten über die Natur dieser Elemente.

RAMON Y CAJAL weist auf Grund seiner zahlreichen Beobachtungen und der Untersuchungen von LA WILLA auf das Vorhandensein eines neurofibrillären Apparates in den interstitiellen Zellen hin, der sich in einigen Fällen besser mit Silber imprägnieren lässt als in den typischen Zellen des AUERBACHSchen und MEISSNERSchen Plexus. Das Vorhandensein von Neurofibrillen, die variköse Form der Fortsätze und die mit den Nervenzellen übereinstimmende Färbbarkeit mit Methylenblau sind nach der Meinung von CAJAL und LA WILLA unzweifelhafte Beweise der nervösen Natur der interstitiellen Zellen. CAJAL und LA WILLA beschreiben diese Zellen als eine Reihe nicht mit einander verbundener Neurone — „neurones sympathiques interstitielles“. Die Fortsätze dieser Zellen scheinen nach CAJAL mit den glatten Muskelfasern und den LIEBERKÜHNschen Drüsen in Verbindung zu stehen.

Es muss aber bemerkt werden, dass es weder CAJAL, noch LA WILLA gelungen ist, einen Zusammenhang der interstitiellen Zellen mit den übrigen Nervelementen des sympathischen Nervensystems nachzuweisen. Ueber die Endigungen der Fortsätze der interstitiellen Zellen drückt sich CAJAL ebenfalls sehr vorsichtig aus (CAJAL 1911, S. 934).

Hierbei sei erwähnt, dass PAUL SCHULTZ in 1895 sehr genau und ausführlich interstitielle Zellen im Darm, in der Harnblase und in den Harnleitern des Frosches und vieler Säugethiere beschrieben hat. Er beobachtete die Endigungen der Fortsätze der interstitiellen Zellen in der glatten Muskulatur und spricht sich entschieden für die nervöse Natur dieser Zellen aus.

Nach ERIK MÜLLER sind die interstitiellen Zellen echte Nervelemente deren Ursprung er auf Grund seiner zahlreichen embryologischen Untersuchungen sogar feststellt. Die interstitiellen Zellen entstehen aus der Keimanlage des sympathischen Nervensystems, während die grosse Mehrzahl von Nervenzellen des AUERBACHSchen und MEISSNERSchen Geflechts im Magen und Dünndarm aus der Keimanlage des Nervus Vagus sich entwickeln. Im Magen der Embryone von *Squalis acantias*, sowie im Magen von Hühnerembryonen beobachtete MÜLLER alle Entwicklungsstadien dieser Zellen. Die langen Fortsätze dienen zur Anastomose der Zellen unter einander. Innerhalb der Zellen und ihrer Fortsätze verlaufen Neurofibrillen verzweigen sich in der glatten Muskulatur und in der Schleimhaut. Es gelang MÜLLER nicht an den interstitiellen Zellen einen pericellulären Apparat nachzuweisen. Nach MÜLLER sind die interstitiellen Zellen ein syncytiales System, das für den Darmtraktus spezifisch ist. Indem er diesem System eine spezielle physiologische Funktion zuschreibt, findet er in demselben viel Gemeinsames mit peripheren Nervenetzen, die BETHE 1895 in der Froschzunge beschrieb.

DOGIEL wies mit Hilfe der Methylenblaufärbung die interstitiellen Zellen im Darm, im Unterhautbindegewebe, in der Gallenblase, im Centrum tendineum des Zwerchfells von Säugetieren nach und lieferte eine Reihe sehr schöner direkt klassischer Abbildungen. Nichtsdestoweniger konnte DOGIEL weder Neurofibrillen in diesen Zellen nachweisen noch einen Zusammenhang derselben mit den Nervenfasern feststellen. Auf Grund seiner Untersuchungen spricht er sich entschieden für die bindegewebige Natur der interstitiellen Zellen aus, ebenso wie HUBER.

MARTIN HEIDENHAIN schliesst sich nach Zusammenfassung der Ergebnisse dieses Streites vollkommen der Ansicht DOGIELS an, indem er erklärt, dass gar kein Grund vorliege, den interstitiellen Zellen den Charakter von Nervelementen zuzuschreiben.

Bei Untersuchungen über den Bau der Nervengeflechte in der glatten Muskulatur, welche ich in Anschluss an den Untersuchungen von VAN ESVELD über die Elemente des sympathischen Plexus von AUERBACH und MEISSNER anstellte, erzielte ich ebenso wie VAN ESVELD mittels Methylenblaufärbung wiederholt sehr schöne Bilder der interstitiellen Zellen und war mit DOGIEL geneigt, dieselben für Bindegewebszellen zu halten, zumal nach Kenntnissnahme der Arbeit TELLO's, der argentophile Fasern in Bindegewebszellen nachwies. Erst nach Anwendung der BIELSCHOWSKY Methode in der Modifikation von GROSS war ich genötigt, meine Ansicht über die interstitiellen Zellen radikal zu ändern.

Als Untersuchungsobjekt dienten mir die Speiseröhre, der Magen, Darm und die Harnblase von Ratten, Mäusen, Kaninchen und Katzen.

Bij gelungener Impregnation nach der BIELSCHOWSKY-GROSS Methode erhält man sehr schöne Bilder der Nervenverzweigung in der glatten Muskulatur, in der Mukosa und Submukosa der erwähnten Organe. Fertigt man einen Flächenschnitt im Gebiet der Submukosa des Magens oder Darms an, so sieht man bei mässiger, sogenannter elektiver Impregnation das vielfach beschriebene Geflecht schichtweise über einander gelagerter markloser Nervenfasern, die bis in die Mukosa reichen. In jedem Nervenstämmchen kann man scharf imprägnierte Nervenfäden von verschiedener Dicke sehen, die meist ausserordentlich dünn sind. Sehr charakteristisch ist die Lage der Kerne in diesen Nervenstämmchen, die nicht ausserhalb, sondern innerhalb dieser Nervenstämmchen liegen, so dass die Nervenfäden (Neurofibrillenbündel) die Kerne von allen Seiten umgeben. Dasselbe Bild kann man mittels jeder beliebigen Silberimpregnationsmethode erhalten. (CAJAL, GOLGI, RANSON usw.) Der Vorzug der Methode BIELSCHOWSKY's besteht hauptsächlich darin, dass man die Imprägnierung nach Belieben verstärken kann, und dann treten sehr interessante Einzelheiten hervor. Betrachtet man z.B. den Kreuzungspunkt der geschilderten Nervenstämmchen, so kann man, wie aus der Abbildung (I) zu ersehen ist, beobachten, dass die Nervenfäden (Neuro-



Abb. 1.

Kaninchen, Magen, Submukosa. Kreuzungspunkt des Nervengeflechtes. BIELSCHOWSKY.

fibrillenbündel) innerhalb des Protoplasmageflechtes liegen, von dem nach allen Richtungen Protoplasmastränge verlaufen. Das Protoplasma dieser Stränge ist mit Silber imprägniert, was doch nicht hindert, den Verlauf der Zarten Nervenfäden zu verfolgen. Es ist sehr merkwürdig, dass an einem solchen Kreuzpunkte die Nervenfäden (Neurofibrillen-

bündel) nicht direkt aus einem Stämmchen ins andere übergehen, sondern häufig einen verwickelten Weg einschlagen: sie machen wiederholte Biegungen, kehren zu ihrem Ausgangspunkt um und bilden um die Kerne dieser Protoplasmaanhäufung eine Art Flechtwerk. Ob hierbei ein wirkliches Netz entsteht, oder ob sich die Nervenfasern nur kreuzen, ist ausserordentlich schwer zu entscheiden. Es ist nur vollkommen klar, dass die Nervenfasern (Neurofibrillenstränge) innerhalb des Protoplasmas liegen. Es kann hier von einer Anlagerung der Neurofibrillen oder Axone an die SCHWANNschen Zellen keine Rede sein, denn wie sollten sich bei einer blossen Anlagerung die Geflechte um die Kerne herum bilden? Die Imprägnierung kann noch verstärkt werden; dann wird das Protoplasma der Stränge und der Kreuzungspunkte noch dunkler, die zarte wabige Struktur des Protoplasmas wird gut sichtbar und die Nervenfasern werden kaum erkennbar.

Man kann schliesslich durch Wechseln der Intensität der Imprägnierung alle möglichen Uebergänge erzielen — von einer scharfen Imprägnierung der Nervenfasern allein bis zur Imprägnierung des Protoplasmas und an demselben Geflecht bald das imprägnierte Protoplasma, bald die in demselben liegenden Nervenfasern beobachten.

Somit sehen wir in der Submukosa und Mukosa des Magens und Darmes ein Protoplasmasyncytium, in welchem Nervenfasern eingelagert sind. Ich gebrauche absichtlich die Bezeichnung *Nervenfasern*, um den Vorwurf zu entgehen, den MARTIN HEIDENHAIN der Auffassung HELD's macht. Die Frage ob wir hier einen Komplex von Neurofibrillen oder ein sogen. Kabelsystem vor uns haben, bin ich zur Zeit nicht imstande zu beantworten. Es ist wohl möglich dass hier, wie HERINGA bei der Untersuchung der Nervenendigungen am Vogelschnabel gezeigt hat, eine Unterscheidung der einzelnen Axone nicht gelingt, so dass man in diesem Syncytium nur von miteinander zusammenliegenden, wahrscheinlich aus verschiedenen Axonen herkömlichen Neurofibrillenbündeln sprechen konnte¹⁾. Fast dasselbe Verhalten finden wir in der Muscularis propria der Speiseröhre, des Magens, des Darmes und Muscularis der Harnblase. Längs den dünnen bindegewebigen Scheidewänden verlaufen Nervenstämmchen, von denen Zweige zur glatten Muskulatur abgehen. Auch hier sind diese Stämmchen nichts anderes als Protoplasmastränge, zuweilen von flacher Form, in denen Kerne eingelagert sind, die immer innerhalb des Stranges liegen.

Die für die Mukosa und Submukosa typischen Kreuzungspunkten finden wir hier nicht vor. Von diesen Nervenstämmchen gehen meist unter einem rechten Winkel feinste Bündel von Nervenfasern ab, die zu den glatten Muskelzellen ziehen. Bei genügender Imprägnierung kann man auch hier ganz klar sehen, dass die Fasern innerhalb eines sehr feinen Stranges liegen, der die unmittelbare Fortsetzung des Grundstämmchens

¹⁾ HERINGA schlägt für einen solchen Fall den Namen Neuroplasmabahn vor.

bildet. Die Protoplasmaschicht ist hier sehr dünn, im weiteren Verlauf wird sie aber wieder dicker und hier sehen wir einen ovalen oder zuweilen auch fast runden Kern. Diese Kerne lassen sich gewöhnlich stärker imprägnieren als die Kerne von den glatten Muskelfasern und nehmen meist eine intensiv schwarze Farbe an. Die Nervenfasern gehen um den Kern von der einen oder von beiden Seiten herum und verzweigen sich dann nach allen Seiten unter einem weit stumpfen Winkel, indem sie aber stets innerhalb des feinen Protoplasmafortsatzes bleiben, und sobald sie eine bestimmte glatte Muskelfaser erreichen, bilden sie in derselben eine motorische Endigung. Ist das Protoplasma um einen solchen Kern genügend intensiv imprägniert, so hat das ganze Gebilde das Aussehen einer spindelförmigen oder dreieckigen Zelle mit feinen langen nach verschiedenen Richtungen verlaufenden Fortsätzen, d.h. wir haben eine typische interstitielle Zelle CAJAL's und DOGIEL's vor uns!

Ebenso wie in der Submukosa gelang es mir auch hier alle möglichen Abstufungen der Imprägnierung zu erzielen. Man kann nur die Neurofibrillen (meines Erachtens sind wir jetzt durchaus berechtigt, von Neurofibrillen zu sprechen) imprägnieren, dann sieht man nur, dass sie dicht an den Kern herankommen und ihn umgeben. Man kann auch gleichzeitig das Protoplasma und die Neurofibrillen imprägnieren, wie auf der Abbildung (2) zu sehen ist. Ebenso wie an den Kreuzungspunkten der



Abb. 2.

Harnblase, Ratte, *T. muscularis*.

Interstitielle Zelle. Man kann intraprotoplasmatische Neurofibrillen bis zur Endigung verfolgen. BIELSCHOWSKY-Meth.

Submukosa gehen die Neurofibrillen häufig nicht direkt in die Fortsätze über, sondern bilden eine Art Geflecht. Bei starker Imprägnierung endlich, bei der das wabige Protoplasma sich dunkel färbt, sehen wir das typische Bild der interstitiellen Zellen, wie sie mittels der Methylenblaufärbung dargestellt werden und u.a. von VAN ESVELD beschrieben werden.

DOGIEL hat vollkommen recht — die interstitiellen Zellen anastomosieren mit einander vermittels ihrer Protoplasmafortsätze, ebenso recht hat aber auch RAMON Y CAJAL wenn er sagt, dass im Protoplasma der Zellen und in ihren Fortsätzen Neurofibrillen enthalten sind, deren Verlauf sich leicht bis zu den motorischen Endigungen in der glatten Muskelfasern verfolgen lässt. Die intraplasmatische Lage der Neurofibrillen lässt sich



Abb. 3.

Ratte, Harnblase.

In dem Protoplasma der grossen interstitiellen Zelle quergeschnittene Neurofibrillenbündel als Pünktchen sichtbar.

BIELSCHOWSKY-Meth.

vollkommen klar auf Querschnitten beweisen wie aus Abbildung (3) zu ersehen ist, wo man sieht, dass die Neurofibrillenbündel mitunter so nahe dem Kerne anliegen, dass in demselben zuweilen eine Einbuchtung zu bemerken ist.

In dieser kurzen Mitteilung übergehe ich eine ganze Reihe Einzelheiten ebenso wie einen genauen Vergleich der erhaltenen Bilder mit den Angaben in der Literatur, indem ich hoffe, zu dieser Frage in einer anderen Arbeit über die Innervation der glatten Muskulatur, die demnächst veröffentlicht werden soll, zurückzukehren.

Hier wollte ich nur in Anschluss an die ebenfalls in diesen Proceedings beschriebenen Mitteilungen VAN ESVELD's über die Elemente des sympathischen Plexus von AUERBACH und MEISSNER meine Beobachtungen über die interstitiellen Zellen kurz referieren.

Ich beschränke mich nur auf folgende kurze Zusammenfassung der Ergebnisse.

In der glatten Muskulatur, in der Mukosa und Submukosa des Verdauungskanal der Säugetiere finden wir grosse protoplasmatische Syncytien, in denen ein System von Neurofibrillen enthalten ist.

Die Protoplasmaanhäufungen mit ihren Kernen und Strängen bilden ein abgeschlossenes und ununterbrochen verlaufendes Gebilde — Lemmoblasten nach der Terminologie HELD's — bis zu den terminalen Nervenendigungen. Die interstitiellen Zellen sind das letzte Glied dieser Leitungsbahn; ihre Fortsätze begleiten die Neurofibrillen bis zu den Endverzweigungen und Endigungen in den glatten Muskelfasern. Es ist durchaus verständlich, dass diese Endglieder, diese eigentümlichen Lemmoblasten überall dort gefunden werden, wo Endigungen des autonomen Nervensystems vorhanden sind: in der glatten Muskulatur, in den Drüsen und Gefässen, wie DOGIEL tatsächlich nachgewiesen hat. Ich bin vollkommen überzeugt, dass vollkommen analoge Bilder des Verlaufs der Neurofibrillen innerhalb der interstitiellen Zellen sich in jedem beliebigen Organ, im unmittelbaren Zusammenhang mit den Endigungen des autonomen Nervensystems werden darstellen lassen. Wir sehen auch, dass die in der letzten Zeit durch die Arbeiten BOEKE's und HERINGA's

glänzend weiter entwickelte Auffassung HELD's, nach der die Neurofibrillen der Spinalnerven bis zu ihren terminalen Verzweigungen in einer Kette von Lemmoblasten verlaufen, eine schöne Bestätigung durch die Art der Nervenendigungen des autonomen Nervensystems findet.

Wie sind die oben geschilderten Kreuzungspunkte und die interstitiellen Zellen zu deuten, in denen, wie wir sehen, die Neurofibrillen einen recht komplizierten Weg durchmachen, indem sie eine Art von Geflecht bilden? Wird in diesen Punkten die Nervenversorgung verändert, sind diese Bahnen nur einfache Reizleitungen? Ich bin vollkommen überzeugt, dass diese hochinteressante und wichtige Frage durch das Experiment zu lösen ist, an das ich jetzt herantreten werde.

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Mathematics. — „Sur les points accessibles des ensembles fermés” ¹⁾.

By PAUL URYSOHN †. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of November 28, 1925).

1. Désignons par E_n l'espace euclidien à n dimensions et soit F un ensemble fermé quelconque situé dans E_n . Nous dirons qu'un point a de F est accessible s'il existe dans E_n un arc simple \overline{ba} , aboutissant au point a et dont tous les autres points sont étrangers à F . Nous dirons que a est accessible au sens étroit s'il est possible de supposer, dans la définition précédente, que \overline{ba} soit un segment rectiligne.

Le but de cette note est de démontrer la proposition suivante.

THÉORÈME. — Quel que soit l'ensemble fermé F situé dans l'espace E_n , l'ensemble L resp. L_d des points de F qui sont accessibles, resp. accessibles au sens étroit, cet ensemble est toujours un ensemble (A) de Souslin ²⁾.

Nous montrerons en outre par des exemples que (au moins au cas $n \geq 3$) ce théorème ne peut pas être précisé davantage.

2. Commençons par prouver que l'ensemble L est toujours un ensemble (A).

Désignons comme d'habitude par $S(\xi, \varepsilon)$ l'intérieur de la sphère (n -dimensionnelle) de centre ξ et du rayon ε . Nous dirons que la sphère $S(\xi, \varepsilon)$ est canonique si elle vérifie les conditions suivantes:

1° toutes les coordonnées du point ξ et le nombre ε sont rationnels,

2° ξ appartient à $E_n - F$.

3° $S(\xi, \varepsilon)$ a des points communs avec F .

L'ensemble de toutes les sphères canoniques étant évidemment dénombrable, rangeons-les d'une façon quelconque en une suite bien déterminée:

$$(1) \quad S_1, S_2, \dots, S_{i_1}, \dots$$

(i_1 étant un entier positif quelconque).

Supposons construites toutes les sphères $S_{i_1 i_2 \dots i_k}$, où i_1, i_2, \dots, i_k prennent indépendamment l'un de l'autre toutes les valeurs entières et positives.

Une $S_{i_1 i_2 \dots i_k}$ étant donnée, soient

$$(2) \quad S_{i_1 i_2 \dots i_k 1}, \quad S_{i_1 i_2 \dots i_k 2}, \text{ etc.} \quad S_{i_1 i_2 \dots i_k i_{k+1}}, \text{ etc. in inf.}$$

¹⁾ Les résultats formant le travail ci-dessus furent établis par PAUL URYSOHN dans les derniers mois de l'année 1923. Ils ont été communiqués à cette même époque à la Société Mathématique de Moscou. La présente rédaction a été faite par PAUL ALEXANDROFF (Moscou); les figures sont dues à D. VAN DANTZIG (Amsterdam).

²⁾ Voir pour la définition des ensembles (A) la note de SOUSLIN (Comptes Rendus t. 164, séance du 8 janvier 1917).

toutes les sphères canoniques contenues dans $S_{i_1 i_2 \dots i_k}$ et vérifiant en outre les deux conditions que voici:

4^o le rayon $r_{i_1 i_2 \dots i_{k+1}}$ de $S_{i_1 i_2 \dots i_{k+1}}$ est inférieur à la moitié du rayon $r_{i_1 i_2 \dots i_k}$ de $S_{i_1 i_2 \dots i_k}$

5^o les centres $c_{i_1 i_2 \dots i_k}$ et $c_{i_1 i_2 \dots i_{k+1}}$ de $S_{i_1 i_2 \dots i_k}$ et $S_{i_1 i_2 \dots i_{k+1}}$ peuvent être joints par une ligne polygonale $A_{i_1 i_2 \dots i_{k+1}}$ située dans

$$(E_n - F) \cdot S_{i_1 i_2 \dots i_k}.$$

Les sphères $S_{i_1 i_2 \dots i_k}$ se trouvent ainsi définies par induction quels que soient les nombres naturels k, i_1, i_2, \dots, i_k . Désignons par M l'ensemble (A) défini par le système déterminant $\{S_{i_1 i_2 \dots i_k}\}$.

Démontrons que l'ensemble M coïncide avec L .

Soit a un point quelconque de M . Il existe, d'après la définition de M au moins une suite d'entiers positifs

$$i_1, i_2, \dots, i_k, \dots$$

telle que

$$(3) \quad a = \prod_{k=1}^{\infty} S_{i_1 i_2 \dots i_k}.$$

L'ensemble

$$(4) \quad a + \sum_{k=3}^{\infty} A_{i_1 i_2 \dots i_k}$$

est évidemment fermé; il a avec $A_{i_1 i_2}$ au moins le point $c_{i_1 i_2}$ en commun. Soit d_1 le premier point de l'ensemble (4) qu'on rencontre en parcourant $A_{i_1 i_2}$ dans le sens de c_{i_1} à $c_{i_1 i_2}$. Désignons par Π_1 le segment $\overline{c_{i_1} d_1}$ du polygone $A_{i_1 i_2}$. Le point d_1 est nécessairement différent de a (puisque $a \in F$ en même temps que $d_1 \in A_{i_1 i_2} \subset E_n - F$); il en résulte que d_1 appartient au moins à un $A_{i_1 i_2 \dots i_k}$, $k \geq 3$.

Supposons que nous ayons construit une ligne polygonale simple $\Pi_s = \overline{c_{i_1} d_s} \subset E_n - F$ de façon que $d_s \neq a$ est le seul point commun à Π_s et à l'ensemble fermé

$$(4_s) \quad a + \sum_{k=h(s)}^{\infty} A_{i_1 i_2 \dots i_k}$$

où $h(s)$ est un certain entier non inférieur à s (pour $s=1$ on a $h(1)=3$). Comme d_s est différent de a , il existe un premier indice $k_0 \geq h(s)$ tel que

$$d_s \in A_{i_1 i_2 \dots i_{k_0}} - c_{i_1 i_2 \dots i_{k_0}}.$$

Considérons l'ensemble fermé

$$(4'_s) \quad a + \sum_{k=k_0+1}^{\infty} A_{i_1 i_2 \dots i_k}$$

ayant avec $A_{i_1 i_2 \dots i_{k_0}}$ au moins le point $c_{i_1 i_2 \dots i_{k_0}}$ en commun.

Soit d_{s+1} le premier point de l'ensemble $(4'_s)$ qu'on rencontre sur $A_{i_1 i_2 \dots i_{k_0}}$ en allant de d_s à $c_{i_1 i_2 \dots i_{k_0}}$. Comme $A_{i_1 i_2 \dots i_{k_0}}$ est étranger à F ,

d_{s+1} appartient à un au moins $A_{i_1 i_2 \dots i_k}$, $k \geq k_0 + 1$. Soit $h(s+1)$ le plus petit parmi les nombres $k \geq k_0 + 1$ tels que $d_{s+1} \in A_{i_1 i_2 \dots i_k}$. Posons

$$(5) \quad \Pi_{s+1} = \Pi_s + \overline{d_s d_{s+1}}$$

où $\overline{d_s d_{s+1}}$ est le segment de $A_{i_1 i_2 \dots i_{k_0}}$ aux extrémités d_s et d_{s+1} .

Il est évident que d_{s+1} est le seul point commun à Π_{s+1} et à l'ensemble

$$(4_{s+1}) \quad a + \sum_{k=h(s+1)}^{\infty} A_{i_1 i_2 \dots i_k}$$

on a en outre

$$h(s+1) \geq k_0 + 1 \geq h(s) + 1 \geq s + 1.$$

En procédant ainsi par induction on obtient une suite infinie de lignes polygonales simples:

$$\Pi_1 \subset \Pi_2 \subset \dots \subset \Pi_s \subset \dots, \quad \Pi_s = \overline{c_{i_1} d_s} \subset E_n - F$$

Comme le diamètre de $\sum_{j=1}^{\infty} \overline{d_j d_{j+1}}$ et la distance $\varrho(d_s, a)$ deviennent infiniment petits avec $\frac{1}{s}$, l'ensemble fermé $a + \sum_{s=1}^{\infty} \Pi_s$ est immédiatement homéomorphe à un segment rectiligne; il n'a d'ailleurs avec F que le seul point a en commun. Ce dernier point est donc accessible et l'inclusion $M \subset L$ est ainsi démontrée.

3. Pour démontrer l'inclusion inverse $L \subset M$, considérons un point accessible quelconque de l'ensemble F . Soit a ce point et $\overline{ab_0}$ un arc simple agrégé à $(E_n - F) + a$.

On peut toujours supposer que $\overline{ab_0}$ soit une „ligne polygonale généralisée” c. à d. que

$$(7) \quad \overline{ab_0} = a + \sum_{i=0}^{\infty} \overline{b_i b_{i+1}}$$

où $\overline{b_i b_{i+1}}$ sont des segments rectilignes convergents vers le point a (donc de longueur tendant vers 0 avec $\frac{1}{i}$) et tels que $\overline{b_i b_{i+1}}$ et $\overline{b_k b_{k+1}}$, $i < k$, n'ont aucun point commun, si $k > i + 1$, et ont le seul point b_{i+1} en commun, si $k = i + 1$.¹⁾

En déplaçant légèrement les points b_i , il est facile d'obtenir un arc

¹⁾ Soient en effet, $\overline{ab_0}$ un arc simple quelconque n'ayant avec F que le point a en commun, et

$$b_0, b_1, b_2, \dots, b_n, \dots$$

une suite infinie des points de $\overline{ab_0}$ tendant vers a . On peut évidemment joindre b_i et b_{i+1} par une ligne polygonale $\Lambda_{i+1} \subset E_n - F_1$ très voisine de l'arc correspondant $\overline{b_i b_{i+1}}$ de $\overline{ab_0}$.

Un raisonnement absolument analogue à celui du numéro précédent permet alors d'extraire du continu $a + \sum_{i=1}^{\infty} \Lambda_i$ un arc simple de la forme (7).

simple de la forme (7) dont les „sommets” b_i ($i = 0, 1, 2, \dots$) ont toutes leurs coordonnées rationnelles. Nous supposons donc que (7) vérifie cette condition supplémentaire. Désignons enfin par $\overline{ab_i}$ le segment $\overline{ab_i}$ de l'arc simple (7).

Considérons maintenant une sphère $S(b_0, \varepsilon_0)$ d'un rayon rationnel ε_0 surpassant le diamètre de $\overline{ab_0}$. La sphère $S(b_0, \varepsilon_0)$ étant évidemment canonique, elle est une certaine S_{i_1} de la suite (1).

Supposons choisie une $S_{i_1 i_2 \dots i_k}$ telle que les deux conditions suivantes soient vérifiées:

1). $c_{i_1 i_2 \dots i_k}$ est un „sommets” b_{m_k} déterminé de la „ligne polygonale généralisée” (7).

2). $S_{i_1 i_2 \dots i_k} \supset \overline{ab_{m_k}}$.

Soit alors m_{k+1} le premier entier vérifiant la condition:¹⁾

$$(8) \quad \delta(\overline{ab_{m_{k+1}}}) < \frac{1}{2} \varrho(\overline{ab_{m_k}}, E_n - S_{i_1 i_2 \dots i_k})$$

Désignons par ε_{k+1} un nombre rationnel quelconque supérieur à la première et inférieur à la seconde partie de l'inégalité (8).

$S(b_{m_{k+1}}, \varepsilon_{k+1})$ est une sphère canonique contenue dans $S_{i_1 i_2 \dots i_k}$ puisque ε_{k+1} est inférieur à

$$\frac{1}{2} \varrho(\overline{ab_{m_k}}, E_n - S_{i_1 i_2 \dots i_k}) < \frac{1}{2} \varrho(b_{m_{k+1}}, E_n - S_{i_1 i_2 \dots i_k}).$$

On a de plus

$$\varepsilon_{k+1} < \frac{1}{2} \varrho(\overline{ab_{m_k}}, E_n - S_{i_1 i_2 \dots i_k}) < \frac{1}{2} \varrho(b_{m_k}, E_n - S_{i_1 i_2 \dots i_k}) = \frac{1}{2} r_{i_1 i_2 \dots i_k}$$

(où $r_{i_1 i_2 \dots i_k}$ est le rayon de $S_{i_1 i_2 \dots i_k}$).

Le segment $\overline{b_{m_k} b_{m_{k+1}}}$ de l'arc simple (7) est une ligne polygonale joignant le centre de $S_{i_1 i_2 \dots i_k}$ avec celui de $S(b_{m_{k+1}}, \varepsilon_{k+1})$. Cette ligne polygonale est étrangère à F ; d'après 2) elle est contenue dans $S_{i_1 i_2 \dots i_k}$. Les deux conditions 4° et 5° sont donc réalisées par la sphère $S(b_{m_{k+1}}, \varepsilon_{k+1})$, de sorte qu'elle est une $S_{i_1 i_2 \dots i_k i_{k+1}}$ déterminée. $S_{i_1 i_2 \dots i_k i_{k+1}}$ réalise enfin les deux conditions 1) et 2) ci-dessus: en effet, son centre est le point $b_{m_{k+1}}$; d'après la définition de ε_{k+1} , la sphère $S_{i_1 i_2 \dots i_k i_{k+1}}$ contient de plus l'arc simple $\overline{ab_{m_{k+1}}}$.

En procédant ainsi par induction on obtient une „chaîne régulière”

$$S_{i_1}, S_{i_1 i_2}, \dots, S_{i_1 i_2 \dots i_k}, \dots$$

de sphères canoniques auxquelles le point a est intérieur.

¹⁾ Où $\varrho(A, B)$ désigne, d'une façon générale, la distance entre les deux ensembles A et B , tandis que $\delta(C)$ est le diamètre de l'ensemble C .

On a donc

$$a \in \prod_{k=1}^{\infty} S_{i_1 i_2 \dots i_k}$$

ce qui exprime que le point a fait partie de l'ensemble M . L'inclusion $L \subset M$ et par suite l'identité $L = M$ se trouve ainsi démontrée. L'ensemble L est donc un ensemble (A).

4. Démontrons maintenant que l'ensemble L_d est lui aussi un ensemble (A). Comme L_d est l'ensemble de tous les points a de F accessibles par des segments rectilignes \overline{ab} , ($\overline{ab} \cdot F = a$), on a évidemment l'identité

$$L_d = \sum_{m=1}^{\infty} L_d^{\mu},$$

où L_d^{μ} est l'ensemble de ceux-là parmi les points a de L_d , pour lesquels il existe un segment \overline{ab} de longueur $\geq \frac{1}{\mu}$.

Il suffit donc de prouver que tout ensemble L_d^{μ} est un ensemble (A).

Pour arriver à ce but, appelons „paire canonique” $\Psi = (P, T)$ un couple de parallélépipèdes n -dimensionaux rectangulaires P et T jouissant des propriétés suivantes:

1°. Les sommets de P et de T ont toutes leurs coordonnées rationnelles.

2°. P et T sont adjacents, c. à d. ils ont une face $(n-1)$ -dimensionnelle et ils n'ont aucun autre point en commun. L'arête de T perpendiculaire à cette face commune est de longueur $\geq \frac{1}{\mu}$.

3°. P possède des points communs avec F tandis que T est situé dans $E_n - F$.

L'ensemble de toutes les paires canoniques étant évidemment dénombrable, nous le supposons rangé en une suite bien déterminée

(9) $\Psi_1, \Psi_2, \dots, \Psi_{i_1}, \dots$ (i_1 est un nombre naturel quelconque).

Nous supposons d'ailleurs que Ψ_{i_1} soit formé de P_{i_1} et T_{i_1} , tout en remarquant qu'un même parallélépipède P ou T peut figurer plusieurs fois respectivement dans la suite des P_{i_1} et dans la suite des T_{i_1} .

Supposons choisies, parmi les paires (9), toutes les paires $\Psi_{i_1 i_2 \dots i_k} = (P_{i_1 i_2 \dots i_k}, T_{i_1 i_2 \dots i_k})$, où i_1, i_2, \dots, i_k prennent toutes les valeurs entières et positives. (Pour $k=1$ on a toutes les paires (9)).

Choisissons une $\Psi_{i_1 i_2 \dots i_k}$ déterminée et considérons toutes les paires canoniques $\Psi = (P, T)$ telles que les relations suivantes aient lieu simultanément:

$$\left. \begin{aligned} (10) \quad & \delta(P) < \frac{1}{2} \delta(P_{i_1 i_2 \dots i_k}) \\ (11) \quad & P \subset P_{i_1 i_2 \dots i_k} \\ (12) \quad & P + T \subset P_{i_1 i_2 \dots i_k} + T_{i_1 i_2 \dots i_k} \end{aligned} \right\}$$

Les $\Psi = (P, T)$ ainsi définies seront désignés par

$$(13) \quad \Psi_{i_1 i_2 \dots i_k-1}, \quad \Psi_{i_1 i_2 \dots i_k, 2}, \dots, \quad \Psi_{i_1 i_2 \dots i_k, i_{k+1}}, \dots$$

et on posera par définition

$$(14) \quad \Psi_{i_1 i_2 \dots i_k, i_{k+1}} = (P_{i_1 i_2 \dots i_k, i_{k+1}}, T_{i_1 i_2 \dots i_k, i_{k+1}}).$$

Désignons par N l'ensemble (A) défini par le système déterminant $\{P_{i_1 i_2 \dots i_k}\}$.

Je dis que N est identique à L_d^μ .

5. Soit d'abord a un point quelconque de N . Il existe alors une suite de nombres naturels $i_1, i_2, \dots, i_k, \dots$, telle que $a = \prod_{k=1}^{\infty} P_{i_1 i_2 \dots i_k}$. On voit de suite d'après la condition 2° du n° 4 et les relations (10) et (12), que la suite des parallélépipèdes

$S_{i_1}, S_{i_1 i_2}, \dots, S_{i_1 i_2 \dots i_k}, \dots$ (où l'on a posé $S_{i_1 i_2 \dots i_k} = P_{i_1 i_2 \dots i_k} + T_{i_1 i_2 \dots i_k}$)

est décroissante et admet comme partie commune un segment rectiligne A de longueur $\geq \frac{1}{\mu}$. D'après la condition 3° l'ensemble non vide $A.F$

est contenu, quel que soit k , dans $P_{i_1 i_2 \dots i_k}$; il se réduit donc au point a . Comme évidemment ce point n'est pas intérieur à A (en vertu de (10)), A est un segment \overline{ab} , dont tous les points à l'exception de a sont étrangers à F . Le point a est donc accessible par le segment A d'une longueur $\geq \frac{1}{\mu}$, c. à d. que $a \in L_d^\mu$ et par conséquent $N \subset L_d^\mu$.

6. Soit maintenant a un point quelconque de L_d^μ . Il existe un segment rectiligne $\overline{ab} \subset (E_n - F) + a$, d'une longueur $\geq \frac{1}{\mu}$. Si la longueur de \overline{ab} était précisément égale à $\frac{1}{\mu}$, on pourrait toujours prolonger un peu ce segment au-delà de b sans rencontrer aucun point de F . On peut donc supposer que la longueur de \overline{ab} est supérieure à $\frac{1}{\mu}$.

Cela posé, soit c un point de \overline{ab} assez voisin de a pour que \overline{cb} soit encore de longueur supérieure à $\frac{1}{\mu}$ (voir la fig. 1, faite pour le cas $n = 2$, d'ailleurs immédiatement applicable au cas général).

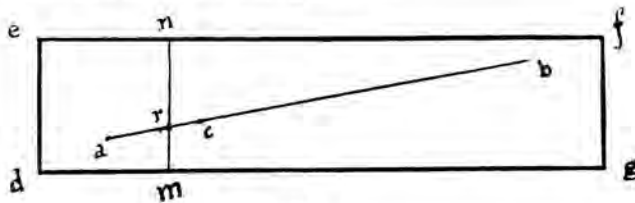


Fig. 1.

Il existe un parallélépipède „rationnel” (c. à d. dont les sommets ont toutes leurs coördonnées rationnelles), à n dimensions $defg$ (voir toujours la figure) contenant le segment \overline{ab} et situé tout entier dans un voisinage assez restreint de \overline{ab} pour qu'en menant par un certain point r de \overline{ac} , un hyperplan $(n-1)$ -dimensionnel mn perpendiculaire à l'arête dg on obtienne un parallélépipède $mngf$ dépourvu de points de F et dont l'arête mg a une longueur $\geq \frac{1}{\mu}$. On peut en outre supposer que $mngf$ et $denm$ soient des parallélépipèdes rationnels. On s'aperçoit aussitôt que les deux derniers parallélépipèdes forment une paire canonique, soit Ψ_{i_1} , avec $P_{i_1} = (denm)$ et $T_{i_1} = (mngf)$.

Supposons déjà construite une paire canonique

$$\Psi_{i_1 i_2 \dots i_k} = (P_{i_1 i_2 \dots i_k}, T_{i_1 i_2 \dots i_k})$$

telle que $S_{i_1 i_2 \dots i_k} = P_{i_1 i_2 \dots i_k} + T_{i_1 i_2 \dots i_k} \supset \overline{ab}$.

Il existe (voir la fig. 2).

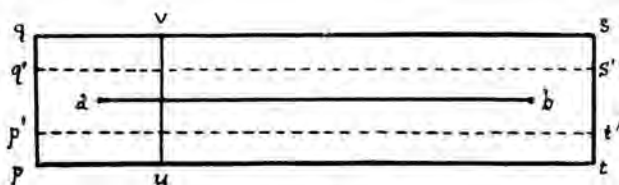


Fig. 2.

un parallélépipède $pqrst$ contenu dans $S_{i_1 i_2 \dots i_k}$ et assez voisin d' \overline{ab} pour qu'un hyperplan $(n-1)$ -dimensionnel uv , perpendiculaire à l'arête pt et assez rapproché de pq découpe de $pqrst$ un parallélépipède $pquv$ contenu dans $P_{i_1 i_2 \dots i_k}$ et de diamètre inférieur à $\frac{1}{2} \delta(P_{i_1 i_2 \dots i_k})$.

Nous supposons de plus que le parallélépipède $pqrst$ ait son arête pt parallèle à la direction du segment \overline{ab} .

On peut évidemment supposer que le parallélépipède $vust$ soit étranger à l'ensemble F : dans le cas contraire on n'aurait en effet qu'à remplacer $pqrst$ par un parallélépipède $p'q's't'$ plus mince encore (c. à d. situé dans un voisinage plus restreint du segment \overline{ab}) et jouissant des mêmes propriétés par rapport à \overline{ab} .

Il ne nous reste que de déplacer légèrement nos parallélépipèdes afin de les transformer en parallélépipèdes possédant toutes les propriétés signalées et dont les sommets aient en outre toutes leurs coördonnées rationnelles. Une des propriétés en question sera en général mise en défaut par cette dernière opération: après son déplacement le parallélépipède $pqrst$ ne possédera plus d'arête parallèle à \overline{ab} : il sera changé de direction, d'ailleurs aussi peu qu'on voudra.

Le couple des parallélépipèdes $pquv$ et $vust$ forme (comme on le

voit aussitôt) une paire canonique; cette paire canonique vérifie de plus les relations (10), (11), (12), elle est donc une $\Psi_{i_1 i_2 \dots i_k i_{k+1}}$, avec $(pquv) = P_{i_1 i_2 \dots i_k i_{k+1}}$ et $(vust) = T_{i_1 i_2 \dots i_k i_{k+1}}$. L'inclusion $S_{i_1 i_2 \dots i_k i_{k+1}} \supset \overline{ab}$ se trouve réalisée, ce qui permet de poursuivre indéfiniment le raisonnement d'induction ci-dessus.

On définit ainsi de proche en proche les nombres naturels

$$i_1, i_2, \dots, i_k, \dots$$

vérifiant la condition $a \in P_{i_1 i_2 \dots i_k}$; il en résulte que $a \in N$.

L'identité des deux ensembles N et L_d^μ , et par conséquent notre proposition entière, se trouvent ainsi démontrées.

7. Passons maintenant à la construction de quelques exemples se rattachant intimement au théorème que nous venons de démontrer.

Faisons d'abord la convention suivante. Nous désignerons dans ce n^0 par $I_{i_1 i_2 \dots i_k}$ (où k, i_1, i_2, \dots, i_k sont des nombres naturels quelconques) l'ensemble de tous les nombres irrationnels (positifs) dont le développement en fraction continue commence par

$$\frac{1}{i_1} + \frac{1}{i_2} + \frac{1}{i_3} + \dots + \frac{1}{i_k} + \dots$$

Nous désignerons aussi par $a_{i_1 i_2 \dots i_k}$ et $b_{i_1 i_2 \dots i_k}$ respectivement la borne inférieure et supérieure de l'ensemble $I_{i_1 i_2 \dots i_k}$.

Supposons maintenant donné, dans l'espace tridimensionnel ordinaire, un système de coordonnées cylindriques z, r, φ .

Considérons sur l'axe Oz un ensemble (A) non-mesurable B quelconque agrégé à l'intervalle $0 < z < 1$ et défini par un système déterminant formé d'intervalles $A_{i_1 i_2 \dots i_k} = (a_{i_1 i_2 \dots i_k}, b_{i_1 i_2 \dots i_k})$. Nous supposons de plus (ce qui est possible pour tout ensemble (A)) qu'on ait toujours $A_{i_1 i_2 \dots i_k} \supset A_{i_1 i_2 \dots i_{k+1}}$ et que la longueur de l'intervalle $A_{i_1 i_2 \dots i_k}$ tende vers 0 avec $\frac{1}{k}$.

Désignons par H le domaine formé de tous les points dont les coordonnées vérifient l'ensemble des inégalités suivantes:

$$(15) \quad \frac{1}{2} < r < 1; \quad 0 < \varphi < 1; \quad 0 < z < 1$$

De même, quels que soient les entiers positifs k, i_1, i_2, \dots, i_k , désignons par $H_{i_1 i_2 \dots i_k}$ l'ensemble de tous les points dont les coordonnées vérifient simultanément les relations

$$(16) \quad \frac{1}{k+2} < r \leq \frac{1}{k+1}, \quad a_{i_1 i_2 \dots i_k} < \varphi < b_{i_1 i_2 \dots i_k}, \quad a_{i_1 i_2 \dots i_k} < z < b_{i_1 i_2 \dots i_k}.$$

Posons

$$(17) \quad G = H + \sum_{k=1}^{\infty} \left(\sum_{i_1=1}^{\infty} \cdots \sum_{i_k=1}^{\infty} H_{i_1 i_2 \dots i_k} \right),$$

$$(18) \quad F = E_3 - G.$$

On voit immédiatement que F est un ensemble fermé. Une analyse facile montre que les deux ensembles L et L_d coïncident dans notre cas et que l'ensemble de ceux-là parmi les points accessibles de l'ensemble F , qui sont situés sur l'axe Oz est précisément l'ensemble (A) que nous venons de placer sur cette axe. Par conséquent, la partie commune à l'ensemble L et à l'ensemble de tous les points de l'axe Oz est non-mesurable B ; il en résulte que l'ensemble $L = L_d$ est lui-même non-mesurable B .

Nous avons ainsi construit un exemple d'un ensemble fermé situé dans l'espace ordinaire et pour lequel les deux ensembles L et L_d sont non-mesurables B .

La question, si un pareil ensemble existe dans le plan, reste ouverte ¹⁾. Ainsi, du moins pour le cas $n \geq 3$, on ne peut pas remplacer dans l'énoncé de notre théorème l'affirmation que L ou L_d soient des ensembles (A) , par une affirmation plus précise.

8. Notre théorème ne pouvant pas être précisé, on pourrait peut-être songer à le généraliser, c. à d. à appliquer le même énoncé à une classe d'ensembles plus vaste que celle des ensembles fermés. Pour montrer que cela aussi est impossible, nous allons donner un exemple d'un ensemble G_3 pour lequel l'ensemble des points accessibles resp. accessibles au sens étroit n'est point un ensemble (A) .

Cette construction se fera d'ailleurs dans le plan euclidien E_2 .

Supposons donné dans le plan E_2 un système xOy de coordonnées rectangulaires. Désignons par Φ l'ensemble de tous les points situés à l'extérieur et sur la frontière du carré $Q = [(0,0), (0,1), (1,0), (1,1)]$ et soit Ψ l'ensemble de ceux-là parmi les points intérieurs à Q dont l'ordonnée n'appartient pas à l'ensemble parfait de Cantor (= ensemble des nombres réels situés sur $[0,1]$ et dont le développement triadique peut être fait sans utiliser le chiffre 1).

Désignons enfin par D un sous-ensemble (A) non-mesurable B de l'ensemble parfait de Cantor P , placé sur le segment $0 \leq y \leq 1$ de l'axe Oy .

D'après les résultats connus de SOUSLIN et de MM. LUSIN et SIERPIŃSKI l'ensemble D est une projection orthogonale d'un ensemble H du type G_3 , situé dans le carré Q . Par une contraction effectuée dans la seule direction de l'axe Ox on transforme H en un ensemble H_n de

¹⁾ Cette question a été posée par l'auteur en 1923 (dans sa communication à la Société Mathématique de Moscou).

points dont les ordonnées sont restées les mêmes, tandis que les abscisses ont leurs valeurs contenues entre $x = \frac{1}{2n}$ et $x = \frac{1}{2n+1}$.

L'ensemble

$$K = \Phi + \Psi + \sum_{n=1}^{\infty} H_n$$

est un ensemble G_δ : en effet, Φ étant fermé et Ψ ouvert, ces deux ensembles sont évidemment des G_δ ; quant à $\sum_{n=1}^{\infty} H_n$, cet ensemble est somme d'une infinité dénombrable d'ensembles G_δ situés dans des régions du plan deux à deux séparées, il est donc aussi un ensemble G_δ ; par conséquent K est somme de trois ensembles G_δ ; il entre donc encore dans la même classe d'ensembles.

On voit de suite que tout point accessible de K situé sur l'axe Oy appartient à l'ensemble parfait P , tout en étant étranger à l'ensemble D .

Or tout point de $P-D$ est évidemment accessible au sens étroit, de sorte qu'on a, pour l'ensemble K :

$$Y.L = Y.L_d = P - D$$

(en désignant par Y l'ensemble de tous les points de l'axe Oy).

L'ensemble $P-D$ n'étant pas un ensemble (A) (dans le cas contraire les deux ensembles $P-D$ et D seraient mesurables B), il en est de même pour les ensembles L et L_d , c. q. f. d.

Mathematics. — "*Zur allgemeinen Dimensionstheorie*". By L. TUMARKIN.
(Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of November 28, 1925.)

1. Zweck der vorliegenden Bemerkungen ist festzustellen, dass *wesentliche*, bisher nur für *abgeschlossene* Teilmengen eines kompakten metrischen Raumes bewiesene *dimensionstheoretische Sätze* für *beliebige* Teilmengen eines kompakten metrischen Raumes, also nach einem bekannten URYSOHNschen Satze ¹⁾, für jeden separablen ²⁾ metrisierbaren, d.h., einem in Erweiterung eines URYSOHNschen Theorems von TYCHONOFF bewiesenen Metrisationssätze ³⁾ zufolge, für einen beliebigen regulären ⁴⁾, dem II. Abzählbarkeitsaxiome ⁵⁾ genügenden topologischen Raum gelten. Ausserdem gebe ich einen ganz neuen Satz, der die Dimensionstheorie beliebiger separabler metrisierbarer Räume auf die Untersuchung allein *vollständiger* metrischer Räume zurückführen lässt.

2. Den eigentlichen Kern meiner ganzen Untersuchung bildet ein Hilfsatz, der nichts anderes als eine direkte Verallgemeinerung des bekannten HEINE-BOREL-LEBESGUESchen Ueberdeckungssatzes ist, und zu dessen Formulierung ich eine Hilfsdefinition brauche.

Definition. — Es sei M irgend eine im kompakten metrischen Raume R liegende Menge, und \mathfrak{P} ein die Menge M als Vereinigungsmenge besitzendes System (beliebiger Mächtigkeit) von Mengen G , von denen jede ein Gebiet (rel. M) ⁶⁾ ist. Dann soll das Mengensystem \mathfrak{P} eine *kanonische Ueberdeckung* der Menge M heissen, sobald es folgender Bedingung genügt:

¹⁾ "Jeder separable ²⁾ metrisierbare topologische Raum ist einer Teilmenge eines (und desselben) kompakten metrischen Raumes homöomorph"; bewiesen in "Der Hilbertsche Raum u.s.w.", Math. Ann. 92.

²⁾ Separabel heisst ein Raum falls er eine abzählbare dichte Teilmenge enthält (FRÉCHET).

³⁾ P. URYSOHN, "Zum Metrisationsproblem", Math. Ann. 94; TYCHONOFF, Math. Ann. 95.

⁴⁾ Ein topologischer Raum heisst regulär (ALEXANDROFF—URYSOHN, "Zur Theorie der topologischen Räume", Math. Ann. 92) falls jede Umgebung eines beliebigen Punktes die abgeschlossene Hülle einer gewissen Umgebung desselben Punktes enthält.

⁵⁾ HAUSDORFF, Grundzüge der Mengenlehre, Leipzig 1914, S. 263.

⁶⁾ HAUSDORFF, op. cit. SS. 215. u. 240. Ueber weitere Bezeichnungen und Terminologie siehe z. B. die Einleitung zum URYSOHNschen "Mémoire sur les multiplicités Cantorienes" (Fund. Math. VII, SS. 49–64).

falls ξ ein beliebiger Häufungspunkt der Menge M ist, so gibt es eine positive Zahl ε und ein zu \mathfrak{P} gehörendes G von der Beschaffenheit, dass

$$M \cdot S(\xi, \varepsilon) \subset G$$

ist.

Nun lautet unser Hilfssatz folgendermassen:

Ueberdeckungssatz. Falls eine kanonische Ueberdeckung \mathfrak{P} einer beliebigen *Teilmenge* M eines *kompakten metrischen Raumes* R vorliegt, so ist die Menge M bereits in *endlich vielen Gebieten* dieser Ueberdeckung enthalten.

Durch systematische Anwendung dieses Satzes lassen sich unter wiederholter Benutzung der in den Kapiteln IV—VI des URYSOHNschen „Mémoire sur les multiplicités Cantorienes I“ (Fund. Math. VII u. VIII) dargestellten Methoden der Reihe nach folgende Sätze beweisen:

I. Falls M eine im kompakten metrischen Raume R liegende Menge, und ξ irgend ein Punkt des Raumes R ist, so ist $\dim(M + \xi) = \dim M$.

II. Falls R ein beliebiger separabler metrisierbarer Raum von der endlichen Dimension $n > 0$ ist, so ist die Menge $K_n(R)$ aller Punkte, in denen R die Dimension n hat, in sich dicht⁷⁾.

Desgleichen lassen sich verschiedene sonstige Sätze der Theorie der Dimensionskerne auf den Fall beliebiger separabler metrisierbarer Räume übertragen. Die Menge $K_n(R)$ kann in unsrem Falle allerdings auch abzählbar sein⁸⁾.

Weitere Sätze (die sich immer durch Kombination der URYSOHNschen Beweismethoden mit unsrem Ueberdeckungssatze und dem Satze I ergeben) sind folgende:

III. Die BROUWERSche Dimensionsdefinition ist mit der URYSOHN—MENGERSchen Definition für alle metrisierbaren separablen Räume äquivalent⁹⁾.

IV. Falls R ein beliebiger metrisierbarer separabler Raum ist, und daselbst ein höchstens abzählbares System von (rel. R) abgeschlossenen, höchstens n -dimensionalen Mengen gegeben ist, so ist die Vereinigungsmenge aller dieser Mengen höchstens n -dimensional¹⁰⁾.

⁷⁾ Dieser Satz wurde für kompakte Räume ausgesprochen von URYSOHN (C. R. 175, S. 442), und bewiesen von URYSOHN (Fund. Math. VIII) sowie von Menger (Math. Ann. 95).

⁸⁾ Dies zeigt sich an einer von SIERPINSKI konstruierten Menge (Fund. Math. II, S. 81); eine nähere Untersuchung dieses Falles findet sich bei Menger (Wiener Ber. 133, S. 442).

⁹⁾ Diese Äquivalenz wurde hinsichtlich kompakter sowie kondensierter Räume bewiesen von BROUWER (diese Proceedings 27, S. 635); für die ersteren Räume kann sie übrigens als Korollar eines URYSOHNschen Lemmas („Mémoire sur les multiplicités Cantorienes“, Ch. VI, § 5, lemme I, Fund. Math. VIII) betrachtet werden.

¹⁰⁾ Für kompakte Räume wurde dieser Satz ausgesprochen von URYSOHN (C. R. 175, S. 442), und bewiesen von URYSOHN (Fund. Math. VIII), sowie von Menger (Monatshefte f. Math. u. Phys. 34).

Aus IV ergibt sich (genau wie der entsprechende Satz im URYSOHNschen Mémoire, Kap. VI)

V. *Jeder n -dimensionale metrisierbare separable Raum lässt sich als Vereinigungsmenge von $n+1$ zueinander fremden nulldimensionalen Mengen darstellen.*¹¹⁾

Da die Umkehrung von V noch von URYSOHN selbst bewiesen war, so ist die Dimension (im Falle wo sie endlich ist) für beliebige metrisierbare separable Räume um 1 weniger als die kleinste Zahl der nulldimensionalen Mengen, die zum Aufbau des Raumes notwendig sind. Diese Zahl ändert sich übrigens nicht, wenn man eventuell auch zueinander nicht fremde nulldimensionale Mengen zulässt.

Auf den Satz V fussend, kann man mit Hilfe eines LAVRENTIEFFschen Satzes¹²⁾ folgendes beweisen:

VI. *Jede (in einem separablen vollständigen Raume R liegende) Menge M ist in einer G_δ -Menge derselben Dimension wie M enthalten.*

Aus einem ALEXANDROFFschen Satze¹³⁾ ergibt sich dann sofort

VII. *Jeder separable metrisierbare Raum R ist einer Teilmenge eines, dieselbe Dimension wie R besitzenden, vollständigen metrischen Raumes \tilde{R} homöomorph.*

Indem wir die dem Raume R homöomorphe Teilmenge von \tilde{R} durch R^* bezeichnen, kann es vorkommen (wie Beispiele zeigen) dass $\tilde{R}-R^*$ notwendig von positiver Dimension ist.

Es sei hier nur auf diese Tatsache hingewiesen, an die, wie man sofort einsieht, interessante Problemstellungen anknüpfen.

Eine ausführlichere Darstellung der soeben besprochenen Ergebnisse habe ich am 4. Oktober 1925 der Moskauer Mathematischen Gesellschaft vorgelegt; sie erscheint übrigens demnächst in den „Mathematischen Annalen“.

¹¹⁾ C. R. 175, S. 442, sowie Fund. Math. VIII.

¹²⁾ LAVRENTIEFF, Contribution à l'étude des ensembles homéomorphes. Fund. Math. VI (der Satz lässt sich unmittelbar auf in vollständigen Räumen gelegene Mengen übertragen).

¹³⁾ P. ALEXANDROFF, Sur les ensembles de 1^{re} classe et les espaces abstraits (C. R. 178).

Mathematics. — "*Über stetige Abbildungen kompakter Räume*". By PAUL ALEXANDROFF. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of November 28, 1925).

1. Wir wollen im folgenden eine topologische Eigenschaft (d. h. Eigenschaft eines topologischen Raumes) eine *starke* Eigenschaft nennen, falls aus ihrer Geltung für irgend einen topologischen Raum R folgt, dass sie gleichzeitig in jedem topologischen Raume $R^* = f(R)$, der ein stetiges Bild des Raumes R ist, erfüllt ist ¹⁾.

So sind die Eigenschaften eines topologischen Raumes bzw. kompakt, bikompakt, zusammenhängend zu sein, starke topologische Eigenschaften, ebenso wie z. B. die Eigenschaft eine abzählbare dichte Teilmenge zu besitzen.

Dagegen gehört weder das 1. Abzählbarkeitsaxiom, noch, wie Herr TYCHONOFF durch scharfsinnige Beispiele gezeigt hat, das 2. Abzählbarkeitsaxiom, noch irgendeines der Trennungsaxiome (also insbesondere weder Regularität noch Normalität), noch Metrisierbarkeit, noch verschiedene Kombinationen dieser Verhältnisse zu den starken Eigenschaften. Auch braucht, sogar im Falle dass die beiden Räume, R und sein stetiges Bild R^* , kompakt sind, keineswegs die Bildmenge F^* einer in R abgeschlossenen Menge F in R^* abgeschlossen zu sein.

Das Verhalten der topologischen Räume zu stetigen Abbildungen darf also nicht als ein selbstverständliches betrachtet werden; es bedarf vielmehr einer sorgfältigen Untersuchung.

2. Ich will hier einige Ergebnisse dieser Untersuchung für den Fall der kompakten Räume mitteilen ²⁾. Es gelten zuerst die Sätze:

1. Falls R ein bikompakter ³⁾ topologischer Raum und R^* ein stetiges

¹⁾ Der Ausdruck "topologischer Raum" wird überall in dieser Arbeit in dem von HAUSDORFF (Grundzüge der Mengenlehre, Leipzig 1914) gebrauchten Sinne gemeint. Das Gleiche gilt von den übrigen topologischen Begriffen: stetige Abbildung, Abzählbarkeitsaxiome, Zusammenhang u.s.w. Vgl. über Bezeichnungen auch die Einleitung zum URYSOHNschen "Mémoire sur les multiplicités Cantoriennes", I. Teil (Fund. Math. VII, SS. 49—64). Man könnte auch in einem festen Raume R gelegene Mengen betrachten, und dann eine Eigenschaft dieser Mengen stark nennen, falls sie für jede (in R gelegene) stetige Bildmenge einer Menge M erfüllt ist, sobald sie für die Menge M selbst zutrifft.

So ist z. B. für einen Euklidischen Raum die Eigenschaft einer Menge, eine beschränkte abgeschlossene oder auch eine (A) -Menge zu sein eine in bezug auf diesen Raum starke Eigenschaft.

²⁾ Eine ausführliche Darstellung der den Inhalt dieser Voranzeige bildenden Sätze erscheint demnächst in den „Mathematischen Annalen“.

³⁾ Vgl. P. ALEXANDROFF u. P. URYSOHN, Zur Theorie der topologischen Räume, Math. Ann. 92.

Bild von R ist, so ist auch R^ bikompakt und jeder abgeschlossenen Teilmenge von R entspricht eine abgeschlossene Teilmenge von R^* ⁴⁾.*

II. *Die Eigenschaft eines topologischen Raumes, kompakt und metrisierbar zu sein, ist eine starke Eigenschaft.*

3. Die bikompakten Räume verhalten sich besonders einfach, und zwar lässt sich jeder topologische Raum R^* , der ein stetiges Bild des bikompakten Raumes R ist, direkt aus abgeschlossenen Teilmengen des Raumes R erbauen.

Das geschieht mit Hilfe folgender Erklärung:

DEFINITION. Die Zerlegung $R = \Sigma X$ des topologischen Raumes R in zueinander fremde abgeschlossene Mengen X heisst stetig, falls folgende Bedingung erfüllt ist: es sei X_0 eine beliebige der Mengen X , und G irgend ein die Menge X_0 enthaltendes Gebiet. Dann gibt es ein die Menge X_0 ebenfalls enthaltendes Gebiet G_0 von der Art, dass jede Menge X unserer Zerlegung in G enthalten ist, falls sie zu G_0 nicht fremd ist.

Jede stetige Zerlegung

$$(1) \quad R = \Sigma X$$

eines topologischen Raumes R induziert einen neuen Raum R^* (der im allgemeinen ein FRÉCHETScher H -Raum ist), und zwar erhält man den Raum R^* indem man alle Punkte jeder Menge X_0 zu einem "Punkte" x_0^* identifiziert, und als Umgebung $U(x_0^*)$ die Gesamtheit aller "Punkte" x^* betrachtet, für die die entsprechenden Mengen X in einem (beliebigen) die Menge X_0 enthaltenden Gebiete G (des Raumes R) gelegen sind ⁵⁾.

Es gilt nun folgender Satz:

III. *Ein stetige Zerlegung eines bikompakten topologischen Raumes R induziert stets einen bikompakten topologischen Raum R^* . Der Raum R^* ist dabei ein stetiges Bild von R .*

Falls umgekehrt R^ ein stetiges Bild des bikompakten topologischen Raumes R ist, so erhält man eine stetige Zerlegung*

$$R = \Sigma X$$

von R , indem man durch X die Menge aller Punkte von R bezeichnet, die in einen und denselben Punkt x^ von R^* abgebildet werden.*

4. Der Satz III gilt insbesondere für kompakte metrische Räume, und erlaubt den Begriff einer topologischen Eigenschaft stetiger Zerlegungen eines solchen Raumes festzustellen: so kann man z. B. eine stetige

⁴⁾ Den zweiten Teil dieses Satzes habe ich zuerst nur für dem 1. Abzählbarkeitsaxiom genügende Räume bewiesen: Herr VEDENISSOFF hat mich auf die allgemeine Gültigkeit dieses Satzes aufmerksam gemacht.

⁵⁾ So induziert z.B. die stetige Zerlegung einer kompakten Punktmenge R eines Euklidischen Raumes in ihre „Stücke“ als Raum R^* eine kompakte nirgends dichte Punktmenge des Linearkontinuums (vgl. BROUWER, diese Proceedings, April 1911).

Zerlegung (1) eines gegebenen Raumes R n -dimensional nennen, falls der durch diese Zerlegung induzierte Raum R^* n -dimensional ist. Insbesondere ist folgender Satz leicht zu beweisen:

IV. *Die Zerlegung eines beliebigen kompakten metrischen Raumes in die Menge seiner Komponenten ist eine stetige nulldimensionale Zerlegung.*

5. Es sei endlich folgender Fundamentalsatz erwähnt:

V. *Jeder kompakte metrische Raum ist ein stetiges Bild einer (beliebigen) perfekten nulldimensionalen Menge (also z. B. der CANTORSchen Dreiteilungsmenge).*

Die Sätze II, III und V liefern zusammen das folgende Ergebnis:

Einen kompakten metrischen Raum definieren, sagt genau so viel aus, wie eine stetige Zerlegung der CANTORSchen perfekten Menge angeben.

6. Ich möchte zum Schluss auf folgendes Problem hinweisen. Es scheint sehr plausibel zu sein, dass jeder kompakte metrische Raum, für den eine stetige nulldimensionale Zerlegung in höchstens n -dimensionale abgeschlossene Mengen vorhanden ist, auch selbst höchstens n -dimensional ist. Zuzufolge des Satzes IV würde die positive Lösung dieses Problems u. a. bedeuten, dass jeder n -dimensionale kompakte Raum ein n -dimensionales Kontinuum enthält, was eine URYSOHNSche Vermutung, die für die gesamte Dimensionstheorie von grosser Wichtigkeit zu sein scheint, beweisen würde.

Man könnte natürlich auch weitere Probleme an die obigen Entwicklungen anknüpfen.

Zusatz bei der Korrektur. Wie ich soeben ersehe, behandelt Herr R. L. MOORE in seiner Arbeit: "Concerning upper semicontinuous collections of continua" (Amer. Trans. 27 (1925), pp. 416—428) einen Begriff, der sich mit dem obigen Begriff der stetigen Zerlegung für den Fall metrischer Räume mit Kontinuen als Zerlegungseinheiten im wesentlichen deckt. Da aber Herr MOORE sich a. a. O. auf ebene Kontinua beschränkt, so kommen seine Resultate mit den meinigen nicht weiter in Berührung.

Mathematics. — "*Ueber Zerlegungen kompakter metrischer Räume in zueinander fremde abgeschlossene Mengen.*" By L. TUMARKIN.
(Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of November 28, 1925.)

Herr P. ALEXANDROFF hat den Begriff der stetigen und insbesondere der stetigen nulldimensionalen Zerlegung eines kompakten metrischen Raumes in zueinander fremde abgeschlossene Mengen ¹⁾ eingeführt und ein sich darauf beziehendes Dimensionsproblem ²⁾ aufgestellt. Im folgenden will ich die positive Lösung dieses Problems mitteilen. Es handelt sich also um den Beweis des folgenden Satzes:

I. *Falls eine stetige nulldimensionale Zerlegung des kompakten metrischen Raumes R in zueinander fremde, abgeschlossene, höchstens n -dimensionale Mengen X vorliegt, so ist der Raum R höchstens n -dimensional.*

Der Beweis dieses Satzes stützt sich auf folgenden Hilfssatz:

Es sei L ein separabler metrischer nulldimensionaler Raum;

$$\Phi_1, \Phi_2, \dots, \Phi_s$$

ein System von zueinander fremden, in L abgeschlossenen Teilmengen des Raumes L ; endlich,

$$G_1^0, G_2^0, \dots, G_s^0$$

ein System von Gebieten (rel. L), die so beschaffen sind, dass

$$L = \sum_{m=1}^s G_m^0 \text{ und } G_m^0 \supset \Phi_m \text{ (für alle } m, 1 \leq m \leq s)$$

ist. Dann lassen sich s zueinander fremde, den Bedingungen

$$L = \sum_{m=1}^s G_m \text{ und } G_m^0 \supset G_m \supset \Phi_m$$

genügende Gebiete (rel. L) bestimmen.

Nachdem dieser Hilfssatz bewiesen ist, betrachten wir den durch die gegebene Zerlegung von R induzierten, aus Punkten $x^* \in X$ gebildeten kompakten nulldimensionalen Raum R^* .

Es sei nun ε eine beliebige positive Zahl, und X eine beliebige der

¹⁾ P. ALEXANDROFF, "Ueber stetige Abbildungen kompakter Räume", im gleichen Band dieser Proceedings, S. 997. Es sei auf diese Arbeit auch wegen Terminologie und Bezeichnungen hingewiesen.

²⁾ Siehe die unter ¹⁾ zitierte Arbeit, namentlich § 6.

Mengen, in die R zerlegt ist. Es existiert³⁾ eine $(\varepsilon, n+1)$ -Überdeckung⁴⁾

$$(1) \quad \Phi_X^1, \Phi_X^2, \dots, \Phi_X^{k_X}$$

jeder Menge X , und eine positive Zahl σ_X , die so klein ist, dass das Mengensystem

$$(2) \quad \bar{S}(\Phi_X^i, \sigma_X), \quad 1 \leq i \leq k_X$$

von der Ordnung $\leq n+1$ ist⁵⁾, und ausserdem $\delta\{\bar{S}(\Phi_X^i, \sigma_X)\} < \varepsilon$ bleibt.

Es sei X_0 eine beliebige der Mengen X . Wir bezeichnen durch $G_{x_0}^*$ das im Raume R^* gelegene Gebiet, das aus allen denjenigen x^* gebildet ist, denen in $S(X_0, \sigma_{X_0})$ enthaltene Mengen X entsprechen.

Der ganze Raum R^* wird dann durch endlichviele Gebiete G_{x^*} überdeckt. Es seien

$$G_{x_1^*}, G_{x_2^*}, \dots, G_{x_s^*},$$

diese Gebiete. Indem wir die $G_{x_i^*}$, $1 \leq i \leq s$, als G_i^0 und die Punkte x_i^* als Φ_i des Hilfssatzes betrachten, und diesen Hilfssatz anwenden, erhalten wir in R^* die Gebiete

$$G_1^*, G_2^*, \dots, G_s^*.$$

die zueinander fremd sind und den Bedingungen

$$x_i^* \subset G_i^* \subset G_{x_i^*}^* \quad (1 \leq i \leq s)$$

genügen. Die G_i^* sind aber gleichzeitig in R^* abgeschlossen. Die ihnen entsprechenden Mengen $F_i \subset R$ sind also in R abgeschlossen und zueinander fremd. Ausserdem ist

$$X_i \subset F_i \subset S(X_i, \sigma_{X_i}).$$

Indem wir durch F_{ik} die Mengen

$$F_{ik} = F_i \cdot \bar{S}(\Phi_{X_i}^k, \sigma_{X_i}), \quad 1 \leq k \leq k_{X_i}, \quad 1 \leq i \leq s$$

bezeichnen, erhalten wir, wie leicht ersichtlich, eine $(\varepsilon, n+1)$ -Überdeckung des Raumes R (mittels der Mengen F_{ik}). Da ε beliebig klein genommen werden konnte, ergibt sich unser Satz I direkt aus einem URYSOHN'schen Satze.⁵⁾

Aus dem Satze I und einem Resultate Herrn ALEXANDROFF's⁶⁾ ergibt sich nun sofort folgende Lösung eines vorhin von URYSOHN gestellten Problems:

II. Jeder endlichdimensionale kompakte metrische Raum enthält ein Kontinuum von der gleichen Dimension.

³⁾ Siehe hierzu das Kapitel V des URYSOHN'schen "Mémoire sur les multiplicités Cantoriniennes" (Fund. Math. VIII), sowie den einschlägigen Aufsatz von Menger (Monatshefte für Math. u. Phys. 34).

⁴⁾ Eine $(\varepsilon, n+1)$ -Überdeckung der Menge X ist ein Mengensystem (1), wobei die Φ_X^i ($1 \leq i \leq k_X$) abgeschlossen, und so beschaffen sind, dass

$$\sum_{i=1}^{k_X} \Phi_X^i = X, \quad \delta(\Phi_X^i) < \varepsilon,$$

ist, und es keinen Punkt gibt, der mehr als $n+1$ unter den Mengen (1) angehört.

⁵⁾ Vgl den unter ³⁾ zitierten URYSOHN'schen Mémoire.

⁶⁾ Die unter ¹⁾ zitierte Arbeit, Satz IV.

