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JOHANNES MÜLLER :—: AMSTERDAM

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KONINKLIJKE AKADEMIE VAN WETENSCHAP  
TE AMSTERDAM.

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PROCEEDINGS OF THE MEETING  
of Friday May 24, 1907.

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Proceedings Royal Acad. Amsterdam. Vol. X.

**Palaeontology.** — “*On fossil Trichechids from Zealand and Belgium.*” By Mr. L. RUTTEN. Communicated by Prof. C. E. A. WICHMANN.

(Communicated in the meeting of March 30, 1907).

Last summer a fisherman found opposite the village of Breskens in the West Scheldt a large skull, which Dr. S. SCHOUTEN secured for the Geological Institute of Utrecht University.

The fragment belongs to an old Trichechus, but differs in some respects from the now living Walrus. On closer examination it appeared that the skull must be of the tertiary Trichechus Huxleyi, of which until now only tusks were known, found in the “Red Crag” of Suffolk. These were described by RAY LANKESTER. Of the skull the description will be given here.

The plan suggests itself to compare the fragment first with the walrus of recent times and then with the already known fossil Trichechids.

1. *Description of the skull and comparison with the walrus.*

The most conspicuous point about the skull is its remarkably good state of preservation. It has this in common with some remains of diluvial mammals, also found in the river Scheldt. The skull, to be sure, arrived here in several pieces, but the broken edges were absolutely fresh and all parts fit perfectly together. Probably the fossil only broke when it was being dredged. As to completeness the skull leaves nothing to be desired, since only parts of the nasal, maxillary and frontal bones, part of the vomer, the conchae and a few teeth are wanting. The skull was filled with a fine-grained grey clay; the outer wall of the cranium was overgrown with Balanids and Bryozoa. Although the fossil is very heavy, a chemical analysis of a little piece of bone revealed nothing particular. It still contains pretty much organic matter and consists for the rest especially of CaO and P<sub>2</sub>O<sub>5</sub>, while a small quantity of ferric hydroxide colours the bone dark brown.

That our Trichechus is full-grown, is proved by the fact that all sutures are absent and by the strong development of all ridges.

As material for comparison we had at our disposal 24 recent skulls and 26 pairs of tusks. Very unpleasant was the great variability of the recent walruses. Certain characteristics vary so strongly in different individuals that with the limited material one always remains uncertain whether the analogous characteristic in the fossil lies within

the limit of variation of the recent animals. It will appear that in most respects the fragment approaches the old walruses, but that the tusks deviate considerably from those of the living animals.

Looking at the hind side of the fossil skull, one is at once struck by its relatively great height. This is caused by the strong development of the mastoid process and by a high ridge on the lambda suture (*crista lambdoidea*).

Dividing the height of the skull and that of the mastoid process by the breadth of the skull, we obtain two quotients, which for the fossil are greater than for the walrus. In determining these quotients the height of the mastoid process was measured by the vertical distance between the lower edge of the foramen magnum and the base of the mastoid process. The differences found are small, however; for this characteristic the fossil stands consequently at the end of the variation series of the walrus. The strong relief on the mastoid process and the extraordinary size of the *crista occipitalis externa* as well as of the *crista lambdoidea* are characteristics which the fossil skull has in common with some old walruses.

Small deviations are also found in the vicinity of the foramen magnum. The *canalis hypoglossi* always opens with the walrus into the inside of the condyli of the cranium with two openings at each side, whereas the fossil only shows a single small opening. But this characteristic has not much value, since the aperture of the *canalis hypoglossi* always varies strongly. The foramen magnum is much more flattened dorsoventrally with the fossil than with the walrus, but this too is a very variable characteristic. Comparable numbers are here obtained again when the breadth of the foramen magnum is divided by its height. The condyli occipitales are in the fossil less strong than normally and present a shuttle-like appearance, while in the walrus they project more and more when we proceed upwards; also they here project above the upper edge of the foramen magnum, while there they remain below its upper edge.

Of all these small differences the shape of the condyli and of the foramen magnum have the greatest importance, while the height-ratios and the aperture of the *canalis hypoglossi* are of less value.

The base of the skull shows no more differences with the walrus than the back part. The length of the two skulls compared with their breadth, agrees entirely. The first difference concerns the position of the foramen lacerum and of the *canalis alisphenoidens*. These namely lie close behind each other with the walrus, while with the fossil they are separated by a rather massive bony lamella, extending from the *os petrosum* towards the pterygoid process. Also

the cup for the joint of the lower jaw is very broad and the result of this is again that the pterygoid processes have approached each other closely. Further changes appear at the frontal side of the skull-base by the size of the alveoles of the tusks.

The alveolar outer wall shows a lateral projection as with the walrus, only slightly more massive; the distance between the two projections is consequently also somewhat greater than with the walrus. We divide this distance again by the breadth of the skull: the fossil lies at the end of the variation series of the walrus. But the size of the tusk-alveoles produces still another difference. It causes namely the rows of teeth to be squeezed together, so that the distance of the two incisors, compared with the breadth of the skull, is extremely small. But this also occurs with some old walruses. Moreover the lower side of the upper jaw differs in shape: in the walrus it is broad and hollowed, in the fossil narrow and flat.

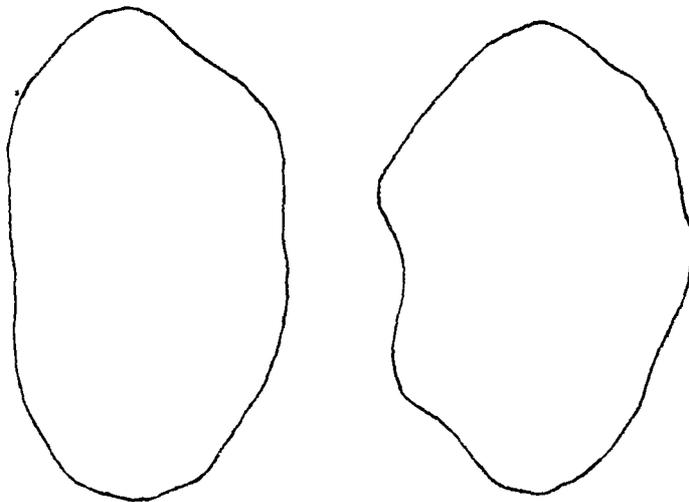
The lateral face of the skull presents in more than one respect a great difference with the walrus, namely in the shape of the tusks. In all the former properties the fossil approached the old walruses and if also the tusks had little deviated from theirs, the reasons for making a distinction would have been rather feeble. But this is not the case. The curvature of the tusks is with the fossil much stronger than with the walrus. If we determine the radius of curvature of all the tusks, we find it in the fossil to be 27 centimetres, for the walrus never under 38 cms. It must be noted that such a small radius of curvature only occurs with young, female walruses with relatively weak teeth. In older animals, however, with which we must compare our skull, the radius of curvature was never under 45 cms. and mostly over 50 cms. Whereas in the former properties the fossil resembles the old walruses, it deviates very strongly from them in regard to the shape of the tusks. Also the tusks are more elegant and the right tooth shows deep longitudinal grooves.

From the tusks we may also draw a conclusion as to the age of the animal. With young individuals the pulp cavity is very deep; with advancing age it gradually fills with osteodentine. With the fossil now the pulp cavity only had a depth of 3,5 cm. Also the thickness of the tusks is greater in the middle than at the base, which points to the period of strongest growth for the teeth being passed.

Again the considerable corrosion of the teeth point to an elderly individual.

If we now summarise the results of the comparison of the fossil with the walrus, we may state:

That the fossil skull belongs to a walrus-like animal, whose in general differs only little from recent animals as to strength of



Cross-section of the base of the tusks of *Trichechus Huxleyi*.  
Found near Breskens in the West Scheldt.

lopment, but deviates entirely from them by the shape of the

It is a pity that for comparative anatomy the value of the ment is nil, for it presents many properties of *Trichechus*, s the strong crista occipitalis externa, the big mastoid process a massive bulla ossea still more typically than the recent animal

## 2. Comparison of the skull with already known fossil *Trichec*

Fossil remains of *Trichechids* are known from North-An England and Belgium. Also skulls of *Trichechus rosmarus* have described from the subsoil of Paris (17), Hamburg (10) and C (25), but it has been proved that they were carried there by The North-American finds seem to belong to the pleistocen miocene (21). The tertiary skull deviates in the number of 1 from *Trichechus rosmarus* (8); the pleistocene remains are id with *Trichechus rosmarus*, although DE KAY has classed a fragment from Accomac County in Virginia under a fossil s *Trichechus virginianus*.

The English fossils were first found in the "Red Crag" of S where, however, they are in a secondary "Lagerstätte"; pr they belong to the older pliocene. (19). Later they have also found in the "Cromer Forest Beds" (32). They are only distinguished from the tusks of walruses by strong curv

smaller thickness and deeper longitudinal grooves. Also RAY LANKESTER is of opinion that in general they are bigger than those of the walrus, although the maximum size of the two is the same. So these tusks show a very good agreement with those of the Zealand fossil.

The Belgian Trichechids, occurring in the "Crag" of Antwerp, have been described by P. J. VAN BENEDEN in a work of splendid get up (26). The only pity is that the contents do not harmonise at all with the exterior, since to a dangerous imagination more scope has been given than to accurate description and careful criticism. When the fortifications round Antwerp were dug, fossil remains of Pinnipedia were found in very different places and at different times: they were treated by VAN BENEDEN in the following manner:

"Voici, comment nous avons procédé: Après avoir réuni tous les os de phoque, . . . nous avons réuni tous les os de même nature c'est à dire, les humérus, les fémurs etc. . . . Après cette première opération nous avons reparti les os longs après leur taille, ayant devant nous les mêmes os des espèces vivantes. Si l'on considère, que la plupart des pièces se répète plusieurs fois, il n'est pas difficile, . . . d'établir parmi eux des groupes génériques et spécifiques. Quand cette opération est faite pour les os comme les humérus et les fémurs, . . . on leur rapporte les autres os, en se guidant d'abord d'après leur dimension . . . . Nous avons alors étalé les humérus, les fémurs, les vertèbres etc. des diverses espèces européennes et nous nous sommes assurés, de quelles espèces vivantes nos phoques fossiles se rapprochent le plus. En répétant la même opération pour les autres os, nous sommes arrivés ainsi à composer nos espèces et à en établir un certain nombre avec une certitude entière."

Hence when VAN BENEDEN had established a new species by means of a single bone, he added to this bone what fitted best in size, a method which theoretically has some good points, but which in practice, with the very incomplete Antwerp material, presents so many difficulties, that the determinations of VAN BENEDEN must *a priori* be received with some misgivings. In any case, only the first piece of bone, on which a species was founded, may be regarded as having been definitely determined; all the other bones, added to it, must be critically re-examined.

VAN BENEDEN describes three species of Trichechids, which he refers to three genera. Of these *Trichechus rosmarus* is supposed to be diluvial; the two others, *Trichecodon Koninekii* and *Alachtherium Cretsii* are tertiary.

Of the common walrus only a scaphoid and an incomplete vertebra are described: "qui ont été quelque temps confondues . . . avec les

animaux quaternaires terrestres. On les avait placés à côté de Rhinocéros”!

The genus *Trichechodon* was based on a small fragment of a tusk which has now even been lost and of which a cast only is left at Brussels. This strongly rounded fragment, however, is not typified by a single characteristic, and so it will always be impossible to ascertain whether later remains really belong to it. But in this way the genus *Trichechodon* loses any right of existence and the bones, referred to it, must be regarded as undetermined.

*Alachtherium* is first mentioned in an oration of Viscount du Bus. Of this *Trichechid* only half a mandible was known then. Also in this case VAN BENEDEEN has added to this lower jaw a whole series of bones from the neighbourhood of Antwerp. Among these also a fragment of a skull occurs, of which VAN BENEDEEN gives the following description, accompanied by some large, but not very happy illustrations.

“En comparant la tête d'*Alachtherium* avec celle du Morse, nous voyons des différences fort grandes dans la disposition de certains os. Vu par devant, le crâne est beaucoup plus élevé et les parties latérales, formées par le temporal surtout, sont plus étendues en dehors et en dessous. Il en résulte, que par la partie supérieure, le crâne se rapproche plus de celui des Otaries et par les parties latérales de celui des Morses. Le crâne est brisé en avant de manière que la boîte est restée entière, et les os frontaux ne prennent qu'un faible part à la formation de la cavité cranienne. Le crâne, vu par la face postérieure, montre l'os occipital s'élevant verticalement très haut comme dans certaines Otaries adultes et les parties latérales et inférieures, formées par le temporal, sont très massives en même temps qu'elles descendent fort bas. Les deux condyles sont brisés. . . . Vu sur le côté, le crâne présente l'aspect d'un casque; il est beaucoup plus élevé que dans le Morse et la conformation de toutes les régions est complètement différente. . . . Tout le dessus du crâne est aplati et une bordure véritable sépare cette région supérieure en avant des os de la face, sur le côté des os des tempes. Les pariétaux sont fort bien indiqués au devant de l'occipital et sont disposés de manière à ressembler au premier abord, à des os nasaux”.

Not to mention a few inaccuracies, the differences with the walrus might have been indicated in less vague a manner, so that a new comparison does not seem superfluous:

Looking at the skull in front, we notice several differences with the walrus, which all have led to an alteration in the shape of the parietal. For with the walrus this bone is clearly convex at both sides while with *Alachtherium* a concavity is found which only fo

a small part must be ascribed to decrease in size of the cranium. It is chiefly caused by the development of a gigantic crista lambdoidea and by the big mastoid process, as well as by the form of both. The crista lambdoidea namely by its size draws the parietal upwards and since in a median direction it extends far to the front, it exerts this influence over a great part of the circumference of the parietal. The strongly developed mastoid process, especially by its frontal position, draws the lower edge of the parietal and the upper edge of the squamosum outwards and therefore has the same effect at the lower side of the parietal as the crista lambdoidea at the upper and posterior side: the two together produce the concave shape of the parietal. While now the strong development of the crista lambdoidea and the increase in height of the mastoid process also cause an increase in height of the skull as compared with the walrus, it is at the same time broadened by the frontal position of the mastoid processes. For these are placed with the walrus in a slanting forward direction and are also smaller than with *Alachtherium*. So we cannot wonder that the absolute height and breadth of the skull exceed the corresponding dimensions of the walrus, but that their ratio lies within the limit of variation of recent animals.

Other differences with *Trichechus rosmarus* are found at the base of the skull. With the walrus a very large bulla ossea extends from the external edge of the basioccipital and basisphenoid as far as the mastoid process and as far forwards as the fossa glenoidea; a more or less distinct groove separates this bulla ossea, in a rostral and a caudal part. With *Alachtherium*, however, the bulla ossea is very small and in this respect it deviates distinctly from the *Trichechus* type. Corresponding to some extent to this circumstance the fossa glenoidea lies far backwards in *Alachtherium*: the space between the articulation and the mastoid process is very small. While now with the walrus the fossa glenoidea extends on the jugal process of the squamosum, so that above it the squamosum rises in a slanting upward direction, with *Alachtherium* it lies far less free and in front of it the squamosum rises steeply. We shall see later on that this is of importance when dealing with the mandibles to which the cranial fragment was said to correspond by VAN BENEDEN.

A further difference is found at the border between basioccipital and basisphenoid. Not to mention a frontally diverging crista and a roughness on the occipital on both sides behind it, these bones pass gradually into each other in the walrus. In *Alachtherium* the outside of the sphenoccipital suture is strongly thickened; a real knob has formed which only at the left side has been preserved. The back of

the basisphenoid now rises at the left to a great height against knob and, instead of following the cranial base normally, it is situated here almost sagittally: the complete basisphenoid must consequently have shown a deep median groove. Analogous changes have occurred at the basioccipital, which towards the knob shows a deep concavity. By this the angle between basisphenoid and basioccipital has become more acute than in the walrus.

In order to compare the back of the skull with that of the walrus we placed the fragment in such a position that the upper edge of the parietal has a slight forward inclination, as this is also the case in a walrus skull, placed on the table without tusks.

Then with both the basisphenoid rises slightly in a forward and the basioccipital in a backward direction, so that their positions may be considered as corresponding.

With *Alachtherium* the outline of the posterior part of the skull then shows one important change, caused by the strong cristae lambdoidea and the broad mastoid processes. For this causes the back of the skull to consist of a narrow supra-occipital and a very broad temporal part, a phenomenon which also with old walrus is sometimes indicated to some extent, but never so strongly as with *Alachtherium*. Moreover *Alachtherium* has a very small cranium: the bones are uncommonly thick. Further in *Alachtherium* the cristae lambdoidea runs in a median direction far to the front and even shows a tendency to pass into a sagittal ridge. As compared with the walrus this phenomenon becomes very striking by the complete absence of the crista occipitalis externa. Where consequently with old walruses the occipital superius is strongly convex by the mass of crista occipitalis, it shows with *Alachtherium* a deep median fossa. Compared with *Trichechus* the hind skull of *Alachtherium* thus shows three modifications: absence of the crista occipitalis externa, size of the mastoid processes, and shape of the crista lambdoidea. The differences at the side of the skull are not very great and we are certainly not justified in stating, as VAN BENEDEN does: that la conformation de toutes les régions est complètement différente. Especially with the skulls of old male walruses *Alachtherium* shows many points of resemblance and it would almost appear as if VAN BENEDEN had only a small material for comparison at his disposal in his description.

The many changes which the skull of *Alachtherium* shows when compared with the skull of *Trichechus*, have not deprived it, though, of its *Trichechid* character. But there are three phenomena which bring it nearer the *Otaridæ*: the smallness of the bulla ossea,

absence of the crista occipitalis and the tendency of the crista lambdoidea to develop on the skull into a sagittal ridge<sup>1</sup>).

What reasons had v. BENEDEK to coordinate the cranial fragment to the mandible on which Alachtherium is based? He does not state them anywhere:

“On ne possédait d'abord de ce curieux Amphitérien d'autre os que le maxillaire . . . . Nous rapportons à ce même animal . . . ., le crâne que nous représentons . . . ., les vertèbres cervicales etc. etc. . . . La forme du maxillaire inférieur indique une conformation toute particulière de tous les os en face . . . .”

The question now is whether on the contrary it cannot be shown that cranial fragment and mandible do not belong to each other. This seems indeed to be the case:

The lower jaw deviates strongly from that of Trichechus and points in fact to a “conformation toute particulière de tous les os en face”. But as the hind skull of Alachtherium does entirely conform to the Trichechus type, it is unjustifiable to assume for the lacking part an entirely deviating shape, only in order to be able to fit the skull to the lower jaw.

The hind skull has much more massive and coarse bones than Trichechus, the mandible on the other hand is larger than that of the walrus, but of a much more elegant and fine build: also in their structure skull and lower jaw have consequently opposite characters. Also the lower jaw is too big for the cranial fragment. For the cranium belongs to an old animal and so the lower jaw should certainly not be much too big for the skull. If we now divide two dimensions of the walrus and of Alachtherium, we find:

	Walrus	Alachtherium	Alacht. : Walrus
distance of the fossae glenoideae	13.5	14.5	107
length of the mandible	24.7	35.7	144

Hence we here obtain again such abnormally great differences of two dimensions between the walrus and Alachtherium that the otherwise considerable analogy of the skulls does not permit us to ascribe mandible and skull to one species. The principal argument, however, is found in the shape of cranium and mandible.

We saw that with Alachtherium the fossa glenoidea has a much less free situation than with Trichechus. With the latter the mandible has a short, vertical coronoid process, which consequently easily finds a place in front of the squamosum. The lower jaw of Alach-

<sup>1</sup>) J. A. ALLEN (30) states about Trichechus obesus that this also has a small bulla ossea.

therium, on the other hand, shows a long coronoid process, which has a backward and slightly inward direction, and which on account of the un-free situation of the articulation of the cranial fragment must inevitably come in collision with the squamosum; hence the two bony pieces cannot possibly belong together.

So we may conclude that the skull described as Alachtherium does not belong to this species. No more can it belong to Trichecodon, since this genus must disappear from literature. So it must be regarded as undetermined.

Finally the "Musée d'Histoire naturelle" at Brussels possesses still another Trichechid skull, floated ashore near Heyst and considered to be diluvial. It is the cranium of a very old male: the sutures have all disappeared and the tusks are almost entirely used up. The preservation is exactly as that of the Zealand fossil: the bones have turned brown and the teeth entirely black; the skull is very heavy and perhaps has become partly siliceous. Besides its shortness and a strong development of the alveoles of the tusks, the fossil shows no differences with the walrus: these two characteristics however, give it a very square appearance. But these small differences give us no right to regard the skull as a new species: it seems to be an ordinary *Trichechus rosmarus*. After having dealt with the known skulls, we must assign a place in the system to the Zealand fossil and to the Antwerp hind skull. They belong to different species. The resemblance of the tusks of *Trichechus Huxleyi* with those of the Zealand cranium was already pointed out. The curvatures of the tusks of *Trichechus Huxleyi*, drawn by RAY LANKESTER, are:

21, 27, 30, 38, > 50, > 50 cms.

Hence they agree much better with the Zealand tusks than with those of the walrus. Also the cross-sections of the tusks show analogies and so we may safely class the Zealand skull under *Trichechus Huxleyi*.

If we ask what age must be attributed to the skull from the Scheldt, we must bear in mind that the good state of preservation precludes a long transport. Hence the skull must have been dislodged out of the bottom of the river. What sort of soil do we find there? Formerly already Dr. DE MAN has described remains of diluvial terrestrial mammals (35), which were also fished from the Scheldt and partly even very near the spot where also the *Trichechus* was found (36). Now it is very improbable that the *Trichechus* and the terrestrial mammals come from the same layer, since both are well preserved. In the year 1879 Dr. SEELHEIM published some profiles:

of Zealand, based on borings and showing that in the West Scheldt occasionally tertiary layers occur. Since it is of course impossible to indicate the precise layer from which the fossil got free, yet it appears that the skull may belong to the tertiary pleiocene. Also in this respect it would correspond to *Trichechus Huxleyi*.

The cranial fragment from Antwerp does not belong to *Trichechus Huxleyi*, since it deviates considerably from the Zealand skull. Hence it must be a new species. It does not seem desirable to establish a new genus for a fragment, showing so much analogy with *Trichechus*. The name of this *Trichechid* may be, after the spot where it was found:

#### *Trichechus Antverpiensis*.

The recent walrus skulls from the "Rijks Museum voor Natuurlijke Historie" at Leyden and from the Zoological collections of the University at Utrecht and Amsterdam were placed at my disposal through the kindness of Dr. F. A. JENTINK and Profs. A. A. W. HUBRECHT and MAX WEBER. At Brussels I was enabled by the kindness of Dr. L. DOLLÉ to study the fossil and recent material of the "Musée royal d'Histoire naturelle de Belgique". Finally I have to thank Prof. WICHMANN who lent me the fossil for description and without whose assistance I should certainly not have succeeded in collecting all the literature.

#### FIGURES.

- Figs. 1. 3. 5. Hind view, base and side of the skull of *Trichechus Huxleyi*.  
Find: opposite Breskens in the West Scheldt.  
Figs. 2. 4. 6. Hind view, base and side of the skull of *Trichechus Antverpiensis*.  
Find: near Antwerp.

#### LITERATURE ON FOSSIL TRICHECHIDS.

1. 1823. CUVIER. Ossements fossiles 2e éd. 1e partie p.264, 2e partie p.521.
2. 1828. MITCHILL, SMITH and COOPER. Discovery of the fossil Walrus in Virginia. Ann. Lyceum of Nat. Hist. of New-York II p. 271.
3. 1834. R. HARLAN. Critical notices of various organic Remains, hitherto discovered in North America. Edinb. New. Phil. Journ XVII p. 360.
4. 1835. R. HARLAN. Physical and medical Researches p. 255.
5. 1839. H. DUCROTAY DE BLAINVILLE. Ostéographie, II, p 45 et 49.
6. 1843. CH. LYELL. Edinb. New. Phil. Journ. p. 187.
7. 1842—1843. CH. LYELL. Proc. geol. Soc. IV p. 31.
8. 1844. CH. LYELL. On the tertiary strata of the Island of Marthas Vineyard. Amer. Journ. of Sc. XLVI. p. 319.

L. RUTTEN. On fossil Trichechids from Zealand and Belgium.



Fig. 1.



Fig. 2.



Fig. 3.



Fig. 4.



Fig. 5.



Fig. 6.

Proceedings Royal Acad. Amsterdam. Vol. X.

Number.	f	1	2	3	4	5	6	7	♀ 8	9	10	11	12	13	14	♂ 15	♀ 16	17	18	♂ 19	♀ 20	21	22	23	24	25	♀ 26	27	h	H	H	H	H	H	H
Height . . . . . I	24.0	19.0	16.7	16.8	16.5	14.9	16.4	19.2	15.0	23.9	16.8	18.4	19.3	14.5	19.7	16.0	16.3	20.4	20.1	15.7	16.8	22.4	—	—	—	21.3	16.4	18.8	22.0						
Breadth . . . . . II	31.8	28.0	26.0	25.9	24.7	22.7	24.1	27.8	22.1	34.8	24.3	27.6	30.5	21.5	28.5	26.0	23.6	31.2	28.0	23.2	24.4	30.3	—	—	—	32.5	25.4	29.4	30.2						
Height occip. sup . III	11.9	8.6	—	8.5	7.4	—	7.9	9.9	7.5	9.4	7.3	—	9.3	6.7	9.0	9.5	8.6	9.5	9.1	7.9	7.3	9.0	—	—	—	10.6	8.5	10.0	—						
Height for. magnum IV	4.3	4.5	—	4.1	4.0	—	4.1	3.4	4.3	5.4	4.1	—	3.9	4.6	4.2	3.6	3.9	3.4	4.2	4.5	5.0	4.5	—	—	—	4.4	4.0	4.0	—						
Breadth for. magnum V	5.4	4.5	—	4.0	4.4	—	3.8	3.8	4.1	5.4	4.1	—	4.3	4.6	4.6	3.0	4.4	3.7	3.9	4.1	5.0	4.2	—	—	—	4.6	5.0	4.5	—						
Length . . . . . VI	39.5	36.6	33.6	33.6	32.4	—	31.7	35.8	30.4	42.0	32.2	—	37.0	30.5	37.5	35.0	33.7	37.0	37.7	32.5	33.0	41.0	—	—	—	38.0	33.5	37.5	38.0						
Curvature of the tusk, exterior edge } VII	26.0	—	49.0	>50	47.0	>50	—	>50	43	45	>50	48	>50	>50	45	37	37	>50	47	33	38	>50	43	46	>50	>50	40	47	>50	21	27	30	38	>50	>50
The same, interior edge } VIII	28.0	—	>50	>50	>50	>50	—	>50	45	50	>50	>50	>50	>50	>50	39	35	>50	40	33	38	>50	47	50	>50	>50	42	>50	>50						
Distance of the processus praeorbitales } IX	22.0	16.5	14.8	16.8	14.2	12.5	15.0	18.9	13.4	23.0	14.5	16.9	18.3	12.3	17.4	16.0	12.8	18.3	18.2	13.6	12.2	20.2	—	—	—	21.0	13.6	17.7	21.4						
Distance of the incisors X	2.7	3.8	3.0	3.6	3.9	3.6	3.2	3.0	3.7	3.2	3.4	3.2	3.1	3.0	3.8	3.2	3.8	3.5	3.8	3.4	3.2	2.6	—	—	—	1.8	3.2	3.3	2.7						
I/II × 100% . . . . .	75.5	67.9	64.2	64.0	66.8	65.6	68.0	69.0	71.9	68.7	69.1	66.7	63.3	65.5	69.1	62.4	69.1	65.4	69.6	67.7	68.0	73.9	—	—	—	65.5	64.5	63.9	73.2						
III/II × 100% . . . . .	37.4	30.7	—	32.8	30	—	32.8	35.0	33.9	27.0	30.0	—	30.5	31.2	31.6	35.7	36.4	30.5	31.5	34.1	29.9	—	—	—	—	32.6	33.3	39.0	—						
V/IV × 100% . . . . .	125.6	100	—	97.0	95.5	—	92.7	111.5	95.9	100	100	—	110.3	100	100.5	108.3	112.8	108.8	80.5	91.1	100.0	93.3	—	—	—	104.5	108.6	112.5	—						
IX/II × 100% . . . . .	69.2	61.8	56.9	64.9	57.5	55.1	62.2	60.8	60.7	66.1	60.0	61.7	60.0	57.2	61.1	60.2	51.2	58.7	63.0	58.5	50.0	66.7	—	—	—	64.3	53.5	50.0	70.9						
X/II × 100% . . . . .	8.5	13.6	11.6	13.0	15.8	15.8	13.3	10.8	16.7	9.2	14.0	11.6	10.2	14.0	13.3	12.0	10.1	11.2	13.1	14.7	13.5	8.6	—	—	—	5.5	12.6	11.2	8.0						
VI/II × 100% . . . . .	124.2	131.7	129.2	129.7	131.2	—	131.5	128.4	137.6	120.7	132.5	—	121.3	141.5	128.1	131.5	142.8	148.6	130.5	140.5	135.2	135.3	—	—	—	146.9	131.8	127.5	125.8						

All the measures are in centimeters.

f = *Trichechus Huxleyi* from the Scheidt, Nr. 1—6 are walrus skulls from the Zoological Collection of Utrecht University.

Nr. 7—24 are walrus skulls from the State Natural History Museum at Leiden and from the collection of *Natura Artis Magistra* at Amsterdam.

Nr. 25—27 are walrus skulls from the Musée d'Histoire naturelle at Brussels. h is the skull of HEYST

H are tusks of *Trichechus Huxleyi* (29), drawn by RAY LANKESTER.

9. 1845. CH. LYELL. Travels in North America I p. 257—258.
10. 1845. K. G. ZIMMERMANN. Brief an den Geheimrath v. Leonhard. Neues Jahrb. f. Min. p. 73. (The here described walrus skull from the subsoil of Hamburg seems to have been carried there by man; Communications of Prof. C. GOTTSCHÉ).
11. 1847. GIEBEL. Fauna der Vorwelt. I. p. 232.
12. 1851. AGASSIZ. Proceed. Amer. Assoc. f. the Adv. of science. p. 252, 348.
13. 1853. EICHWALD. Lethaea rossica. 3. p. 890.
14. 1853—1856. BRONN. Lethaea geognostica. Thl. 6. p. 786.
15. 1853. PICTET. Paléontologie I. p. 233.
16. 1857. J. LEIDY. Notice on the Remains of the fossil walrus on the coast of the United States. Transact. Phil. Soc. Philadelphia New Series. vol. XI. p. 83.
17. 1858. GRATIOLET. Bull. Soc. géol. de France. 2e série. V.
18. 1859. P. GERVAIS. Zoologie et Paléontologie française. IIe éd. p. 275.
19. 1865. E. RAY LANKESTER. On the Sources of the Mammalian Fauna in the Red Crag and on the Discovery in that Deposits of a new Mammal, allied to the Walrus. Proc. Geol. Soc. XXI. p. 233—232.
20. 1867. Vicomte DU BUS. Sur quelques mammiferes du Crag d'Anvers. Bull. Acad. roy. Belgique. 2e serie 24. p. 562—577.
21. 1869. J. LEIDY. The extinct Fauna of Dakota and Nebraska Journ. Acad. Nat. Science of Philadelphia VII. p. 416.
22. 1869. LE HON. L'Homme fossile. p. 304.
23. 1871. P. J. v. BENEDEN. Les Phoques de la mer Scaldisienne. Bull. Acad. roy. Belgique. 2e série 32. p. 5—18.
24. 1876. P. J. v. BENEDEN. Les Phoques du bassin d'Anvers. Bull. Acad. roy. Belgique. 2e série T. 41. p. 783—812.
25. 1876. SCHAAFHAUSEN. Trichechus rosmarus in Coln. Sitz. Ber. Niederrh. Ges. f. Natur- und Heilk. S. 427.
26. 1877. P. J. v. BENEDEN. Description des ossements fossiles des environs d'Anvers I. Pinnipedia Ann. Musée d'Hist. Nat. de Belg. T. I.
27. 1878. W. DAVIS. On a collection of pleistocene Mammals, dredged off the Eastern Coast. Geol. Mag. (2). V. p. 97. 98.
28. 1880. E. T. NEWTON. Notes on the Vertebrata of the preglacial Forest Beds of the Coast of England. Geol. Mag. (2). VII. p. 152—159.
29. 1880. E. RAY LANKESTER. On the Tusks of the fossil Walrus found in the Red Crag of Suffolk. Transact. Linn. Soc. (Zoology) (2). II. p. 213—221.
30. 1880. J. A. ALLEN. History of North American Pinnipeds U. S. Geol. Survey. Miscellaneous Publications 12.
31. 1880. E. RAY LANKESTER. Journ. Linn. Soc. (Zoology) XV London, p. 144—146.
32. 1881. E. T. NEWTON. The vertebrata of the pliocene Deposit of Britan. Mem. Geol. Surv. of the United Kingdom, p. 17—18
33. 1891—1893. K. ZITTEL. Handb. d. Paläontologie IV p. 680—685,
34. 1898—1899. TROUËSSART. Catalogus Mammalium p. 375—376.

## LITERATURE ON THE FINDS OF TRICHECHUS HUXLEYI.

- 35 1875. J. C. DE MAN. Beenderen van den mammoth en van het uitgestorven rund, opgevischt in den omtrek van Zeeland. Arch. Zeeuwsch Genootsch. der Wetensch. III 2. p. 101—127.
- 36 1878. J. C. DE MAN. Een elandshoren, opgevischt in de Schelde. Mededeeling over eenige beenderen, in of nabij Zeeland gevonden. Arch. Zeeuwsch Gen. III 3. p. 1—22.
- 37 1879. F. SEELHEIM. Grondboringen in Zeeland. Verhand. Kon. Akad. der Wetenschappen Afd. Natuurk. Amsterdam.
- 38 1880. J. C. DE MAN. Derde Mededeeling over in de Schelde gevonden beenderen. Arch. Zeeuwsch Genootsch. V. 1. p. 161—170.

**Anatomy.** — “*On the existence of cartilaginous vertebrae in the development of the skull of birds*”. By Prof. J. W. VAN WIJHE.

(Communicated in the meeting of April 26, 1907).

It is a well-known fact that at a certain stage of development the notochord in all vertebrates extends forward as far as the hypophysis cerebri and backwards as far as the tip of the tail.

Over the whole length of the trunk and also in the occipital region of the head the dorsal part of the mesoderm is separated into segments or somites.

In the lower vertebrates: Selachians and Petromyzontes, the somites are not restricted to the occipital region, but extend forward as far as the hypophysis, i.e. equally far as the notochord.

The greater part of the voluntary muscular system is formed from the somites and in Amphioxus the segmentation of this muscular system is permanent and distinct from the anterior to the posterior end of the body.

The original function of the somitic muscles of the Chordates existed in my opinion<sup>1)</sup> in the to and fro movement of the notochord and so of the whole body during swimming.

In the Craniotes this muscular system is interrupted in the region of the auricular organ and in my opinion the presence of the auricular capsule is the cause of this. This capsule, which also encloses the organ for equilibrium, needed a firmer attachment than could be afforded by the connective tissue and found it in the parachordal cartilage, through the stiffness of which the muscular fibres in this region could no longer operate and consequently disappeared, partly even in their origin.

<sup>1)</sup> Cf. VAN WIJHE “Ueber die Homologisirung des Mundes und die primitive Leibesgliederung der Wirbelthiere.” PETRUS CAMPER, Vol. IV. 1906.

The effect of this was also felt in the region in front of the auricular organ, but here part of the somitic muscles remained on account of a change of function. They became attached to the here developing eye-ball and now served for the movement of this latter and no longer for the movement of the whole body. This was accompanied by far-reaching shiftings, which can still be followed in the individual development.

The cartilaginous skeleton forms a system which appears only late in the development of the vertebrates and long after the appearance of the muscular system. As soon as the first cartilage may be observed, the muscular system in the head has undergone the changes here indicated. In the auricular region the somitic muscles have degenerated; partly they were not even indicated; in the region in front of the auricular organ they have entirely changed in place and shape and have entered into the service of the eye-ball. Only in the region behind the auricular organ — the occipital region — the myotomes — generally numbering three — still stand in the original order, like the myotomes of the trunk.

Head and trunk are separated in the ontogeny — although the border is later somewhat shifted in a caudal direction — already before the cartilaginous spinal chord appears, and I see no reason for assuming that this separation should not have taken place also in phylogeny before the appearance of the spinal chord.

The segmentation of the spinal chord depends on that of the muscular system. The body of a vertebra is not formed opposite the middle of a myotome, but opposite the border of two successive myotomes. BALFOUR has given the explanation of this at first sight curious phenomenon: the first muscular fibres occupy the whole length of a myotome and lie laterally of the tissue, surrounding the notochord. Now it is no more than natural that the solid points of attachment which in this tissue are formed for the muscular fibres, namely the origin of the vertebral bodies, are formed opposite the borders of two successive myotomes.

If we now ask where the appearance of vertebral bodies in the head must be expected, the answer must be that this cannot be in the auricular region, since here the myotomes have disappeared at the time of the appearance of the cartilage. No more can this be the case in the region in front of the auricular organ, for here the myotomes have entirely altered their place and have entered into the service of the eye-ball.

Only in the occipital region one would expect the appearance of two or three vertebrae. Yet until recently nobody has observed them

here, although this region has been investigated not only by the method of sectional series, but also by the methylene blue method, by which the investigation is so much easier. By this method Dr. NOORDENBOS did not find them in the vertebrate skull any more than myself in the skull of Selachians.

Instead of vertebrae we found the well-known parachordal cartilage accompanying the notochord in the occipital and auricular regions.

Certain authors have indeed spoken of the origin of vertebrae in the occiput, but the parts observed by them, were not cartilaginous but only badly outlined cell-heaps, not deserving the name of vertebrae.

So I was greatly surprised when my former assistant, Mr. F. SONIES, discovered by the methylene blue method two cartilaginous vertebral bodies in the occiput of embryos of the chick of the sixth breeding day and of ducks in a corresponding stage.

It will be asked how it is possible that these vertebrae have not been long known, since the embryos of the chick form the classical material for investigation in all embryological laboratories. The answer is that they were not discovered because the stage, in which they appear, is of so very short duration. One has to hit the moment in which the cartilage appears in the first two vertebrae of the neck. Before the cartilage appears in the remaining vertebrae, the two occipital vertebrae have already coalesced with the parachordal cartilage.

It is impossible to indicate the hour of the breeding day, since the development of the different eggs varies too much. By taking a large quantity of material, however, it is always possible to obtain the desired stage. It would require an immense expenditure of time to work all this material by the sectional method. With the methylene blue method, however, one is ready in a few days.

So the parachordal cartilage of birds does not originally form a morphological unity. With SONIES we may distinguish two parts in it: an anterior praevertebral part, situated in a region where the myotomes are degenerate or abortive and a posterior or vertebral part, occurring in the shape of two vertebral bodies, which soon coalesce with the anterior part.

Corresponding to these two vertebral bodies later also two vertebral arches appear on each side, which soon coalesce, but the locality of which remains indicated by two openings for the two roots of the nervus hypoglossus.

For further particulars and for several new discoveries about the development of the cartilaginous skull and the spinal column of

birds, I refer to the academical thesis of Mr. SONIES, which is now going through the press and will soon be published, also in "Petrus Camper". I will only mention that the small polar cartilage, discovered by NOORDENBOS in mammals and which also appears in Selachians, was found by SONIES also in birds.

**Microbiology.** — "*On Lactic acid fermentation in milk*". By Professor Dr. M. W. BEIJERINCK.

(Communicated in the meeting of April 26, 1907).

In milk left to itself, which in consequence of spontaneous infection, contains the more generally distributed germs, with certain regularity some special floras are observed, whose composition is chiefly controlled by two factors: temperature and oxygen pressure. If the latter is very slight, that is, if the microbes of the milk are reduced to more or less anaërobic conditions, the floras become simple of composition and produce certain fermentations. The three principal of these are the Aërobacter-, the Butyric acid- and the Lactic acid fermentations, of which the two first-are always characterised by the evolution of hydrogen and carbonic acid, whilst in the lactic acid-fermentations, which may occur under different forms, beside the lactic acid, no gas at all, or carbonic acid only is formed. Sometimes this fermentation is accompanied by a vigorous slime formation, which slime consists of the swollen cell walls of the inferred lactic acid ferments.

For domestic purposes the lactic acid fermentation should be considered as useful; both the others as noxious.

The fermentation experiment the dairy industry applies to judge of the purity of milk has for its object to determine the commonness or the rarity of the germs of Aërobacter and of the butyric acid ferment. To this end a high standing glass is filled with milk, placed in a water bath of 40° C. and it is observed whether any fermentation gas is evolved, and if so, after how much time. In good milk this production of gas does not occur because then the lactic acid ferments develop so quickly that the other microbes are expelled. Artificially the Aërobacter fermentation is easily obtained by infecting non-acidified milk with faeces, soil or canal water and cultivating at about 37° to 40° C. After 6 to 12 hours production of gas is observed originating from *Aërobacter coli* or more rarely from *A. aërogenes*. The nature of the thereby obtained varieties changes with the temperature.

At temperatures beneath 40° the Aërobacter fermentation, after

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lasting some hours, is replaced by a butyric acid fermentation which again, after some time is succeeded by a lactic acid fermentation. Externally the *Aërobacter* and the butyric acid fermentations cannot be distinguished, but this can be done easily with the microscope.

If 3 to 5 % chalk is added to a culture in a stoppered bottle at 35° to 40° C., the butyric acid fermentation can go on longer, and by early transplanting, likewise in milk with chalk and with exclusion of air, check the development of lactic acid ferments, without, however, quite dispelling them.

Microscopically the butyric acid fermentation may be recognised by the long, thin, at neutral reaction highly motile rods, sometimes mixed with elongated or more rounded clostridia, colouring blue by iodium, all belonging to the species *Granulobacter saccharobutyricum*.

To accumulate from such a crude butyric acid fermentation in milk the lactic acid ferments, which hardly ever lack there, it will suffice to transplant some drops into milk without chalk, and, if necessary, to repeat this after the butyric acid fermentation, which always sets in at first, is finished. Whether this be done in open or closed bottles or tubes, at 37° to 40° C., lactic acid rods of the genus *Lactobacillus* will be seen to appear, which by repeated transplantations completely dispel the butyric acid ferments.

If in these experiments instead of using fresh, unheated infection material, the soil, water, or faeces are previously heated to 80° or 95°C., by which only spore-forming microbes can develop in the milk, the fermentations of *Aërobacter* and the lactic acid ferments do not arise, their germs producing no spores, but a butyric acid fermentation is obtained, from which the aërobic spore-formers may be dispelled by repeated transplantation at exclusion of air.

### 1. *Properties of the active lactic acid ferments.*

As many bacteria of the most different groups can produce lactic acid it seems not superfluous to indicate what are the characteristics of the lactic acid ferments proper.

The active forms of dairy industries, yeast manufactories, distilleries, tanneries, and breweries, although joined by transitions, may be practically classified into the physiological genera *Lactococcus*, *Lactobacillus* and *Lactosarcina*, of which the two first only occur in the dairy products<sup>1)</sup>.

<sup>1)</sup> In the chief floras of milk- and dairy products occur, to my knowledge, no species of *Lactosarcina*. When EMMERLING asserts to have found a yellow *Sarcina* in Armenian mazun (Centralbl. f. Bacteriologie, 2<sup>te</sup> Abt. Bd. 4, p. 418, 1898), this can only have been a common infection from without. Also in butter sarcine species may accidentally occur but they do not belong to the chief flora, which consists of lactic acid ferments and lipophili.

They are always immotile, no-spore forming bacteria, which bear drying very well and which, by heating to 65° or 75° C., in which they just remain alive, while these temperatures are deadly to most other non sporeproducers, may be separated from these ("lacticisation"). They require for nitrogenfood peptones, such as are found in milk, malt extract, or other juices of plant- or animal origin, and for carbon food certain sugars, which may differ for different species. They do not peptonise proteids and, thus, do not liquefy gelatine; the secreted lactic acid can dissolve a certain quantity of caseine, but chemically this substance remains unchanged. These circumstances regulate their distribution in nature, where they are by no means general, but may rapidly multiply, especially under the influence of man. They are, however, found in the soil and can, by methods mentioned below, be accumulated and cultivated in a condition of pureness.

They are always more or less distinctly microaërophilous, some species or varieties can, however, grow very well at the air; other forms cannot and behave as real anaërobics. Access or absence of air is commonly of no consequence to the acid formation, but in the yeast industry a species is used, which at full atmospheric pressure produces no acid, and in the dairy industry are also forms which display the same property.

Always, even on good nutrient media, to which belong in particular maltextract agar, and milk- or whey-agar, the growth of the colonies remains limited, especially if the air and the produced acid can act simultaneously. If the acid is neutralised by chalk the growth of the colonies at the air may also become important. Yet, in most cases, the recognition of these ferments may repose on the smallness of their colonies compared with those of other bacteria.

Catalase is constantly absent, and hereupon an excellent diagnosis can be based, for which it is only necessary that a culture plate, on which all kinds of bacteria may occur, be flowed with strongly diluted hydrogensuperoxyd which is by all microbic species, except the lactic acid ferments, indifferently whether they belong to *Lactococcus*, *Lactobacillus* or *Lactosarcina*, changed into a scum of little oxygen bubbles.

Even the lately described<sup>1)</sup> large celled *Sarcina*, which in consequence of continued research I now consider as identic with the stomach sarcine (*Sarcina ventriculi*), and whose acid producing power is very slight, — i. e. 3 c.c. of normal acid per 100 c.c. of

<sup>1)</sup> These Proceedings 25 Februari 1905. Archives Néerlandaises T. 1 and 2. T. 11, p. 200, 1906.

maltextract or glucose broth, — does not at all decompose hydrogen superoxyd.

If we consider how generally catalase is met with in the animal and vegetable kingdom, as also in the microbes, its very absence in the lactic ferments appears in a peculiar light.

All active lactic acid ferments from milk invert sugar (invertase reaction) and can more or less easily decompose esculine and indican (emulsine reaction). The reaction on esculine is demonstrated by introducing, for example, 0.1% of this substance and a few drops of ferric citrate solution into whey agar or whey gelatin. Streaks drawn on it of species which decompose esculine produce intensely brown or black diffusion fields of esculetiniron, brown at more alkaline, black at more acid reaction, so that the lactic acid ferments become recognisable by the black fields in the midst of which their colonies are placed <sup>1)</sup>. So long as esculine is present it is recognised by the magnificent blue fluorescence of the whole plate at feeble alkaline reaction. Indican may be used in a corresponding way but then no iron salt is wanted as the indoxyl produced from the glucosid oxidises of itself at the air to indigo blue. The lactic acid ferments decompose these two glucosides, slowly indeed, yet these reactions are very characteristic and useful. Amygdaline is not decomposed by the lactic acid ferments. <sup>2)</sup>

To the most remarkable properties of the lactic acid ferments belongs their power of reducing levulose to mannite, <sup>3)</sup> which latter substance may even in concentrated nutrient solutions be recognised by its ready cristallisation at evaporation. A single drop dried on the object glass, commonly gives at microscopical investigation full certainty as to the existence of this reaction.

The lactic acid ferments thereby strongly contrast with the so nearly allied vinegar bacteria, in as much as the latter do just the reverse, i. e. they change by oxidation mannite into levulose.

Like so many other bacteria the lactic acid ferments possess, also with regard to various pigments, a strongly reducing power,

<sup>1)</sup> The knowledge of this extremely sensitive reaction, which has been applied for years in my laboratory, I owe to my colleague Mr. H. TER MEULEN.

<sup>2)</sup> Amygdalin is decomposed with much more difficulty by the action of microbes in general than the other glucosides named in the text. Moulds mostly decompose it into amygdalinate of ammonium; beer yeast into amygdalonitril glucosid and glucose. Splitting under production of bitter almond oil, hydrocyanic acid and glucose I detected hitherto only with *Saccharomyces apiculatus* and with the anaërobic ferment of butyric acid fermentation, *Granulobacter saccharobutyricum*.

<sup>3)</sup> Ferments lactiques de l'industrie. Archives Néerlandaises 1901. KAYSER, Fermentation lactique. Annales de l'Institut agronomique 1904.

as is easily shown by inoculation into deep test-tubes of boiled milk coloured with litmus. The red litmus is first in the depth, later till near the surface quite discoloured, to turn red again by shaking with air. The thickness of the red layer in the curdled milk admits an accurate measure of the intensity of the growth and of the reduction process. The thinner the red layer the more intensive both functions must be.

## 2. Factors of variability.

Many, perhaps all lactic acid ferments display a high degree of variability as well in physiological as in morphological properties. Nevertheless this variability in different stocks, coming from different isolations of the same species, is not always equal by far, which may give rise to trouble in the study of the specific properties. The circumstances causing the variability are but partly known; decidedly belongs to them an oxygen pressure, too far above or too far beneath the optimum for the vital functions, which may, especially for the bacterium of the long whey (*Lactococcus hollandiae*), be demonstrated with exceeding clearness.

This remarkable species is characterised by a vigorous slime formation when cultivated in milk or whey, but loses this power at temperatures above 20° C., as well at the ordinary pressure of the atmospheric oxygen, as at complete exclusion of it, if the changed influence is allowed to act during some time on the growing microbes. This is shown by cultivating the whey in a closed bottle; the upper layer, just beneath the stopper, where a little air can find access, becomes quite liquid and contains a hereditarily constant, common *Lactococcus*, forming little acid and no slime. Also by cultivating the long whey microbe in tubes of boiled milk with access of air, after one or two re-inoculations, a *Lactococcus* is produced, which forms no slime at all. If the material for the reinoculation is secured from the depth of the cultures grown in closed flasks, at places where the access of air is impossible, and the inoculation is repeated once or more in the same way, a *Lactococcus* is likewise obtained which displays no trace of slime production.

At some depth beneath the surface, however, is a zone in which unchanged, slime forming, hereditarily constant material is found.

What in this case can be very easily ascertained, proves, at accurate investigation, also to be true for the other species of lactic acid ferments, namely, that they only then continue to display constant specific characters, when they are continuously cultivated at

a certain pressure of the oxygen, else, these characters are seen to disappear, whilst in fact, or apparently, new ones originate. Hence, in some cases it may be proved, in others the probability is shown, that each species must occur in three varieties, joined by intermediate forms, i. e. the normal form, a "high pressure variant", and a "low pressure variant".

As in wholly different groups of bacteria corresponding facts may be observed, there is cause to assign a fundamental signification to them.

A decisive factor which may cause the production of variants is furthermore the temperature, for experience proves that a prolonged cultivation above the optimum temperature of growth, gives rise to the appearance of forms distinctly different from the original stock.

In other cases the cause of the variability is unknown; not seldom for example, we find at the very first culture of a species taken from nature, strongly varying colonies, which prove to belong to the same species only because many colonies by sector-variation display the genetic alliance of the variants to the wild stock.

But then, too, there is reason to admit that the new vital conditions, to which the microbes are subjected just by the change of oxygen pressure and temperature, are the chief factors of the variation process which is, as it were, seen in action. This observation is of so general a nature and is so closely related to the essence of life, that it must be considered as probable, that also in higher plants and animals, local changes in the access or exclusion of oxygen, in connexion with temperature, play an important part in the morphogenesis.

As the examination of other species of microbes shows that the absence of certain nutrient substances in the culture medium, at free aëration and during growth, may cause hereditary variation, for example in *Schizosaccharomyces octosporus*, which in old cultures changes into the spore-free variant, totally differing from the chief form, there is reason also to believe, that also the said factor must be considered to explain the great variability of the lactic acid ferments; but the observations there about are not yet fit for definite conclusions.

### 3. *Elective culture of the microbes of the slimy lactic acid fermentation.*

There is reason to assume that the slime producing lactic acid ferments are the normal forms and the non-slime formers, species or variants derived from them. Hence, the former deserve to be considered in the first place.

To the typical slime producing species belongs the microbe of the long whey (*Lactococcus hollandiae*), which particularly before the introduction of pure cultures in the dairy industries, played an important part in the fight against cheese defects in North-Holland, and is still here and there practically used to that end.

Further I have found that the popular food known in Norway as "tjaette molken", a sample of which I owe to the kindness of Mr. PENNINK of Rotterdam, consists of milk, in which the long whey microbe, or at least a nearly allied form, secretes acid and slime.

Other materials in which these and allied microbes occur, were till now unknown, evidently because of the uncertainty about culture conditions and the lack of a good accumulation method. Taking the idea "species" in the broad sense, I think there is no objection as to bringing the group of forms, found in the manner described below, to the species just mentioned.

Starting from the following properties, the most characteristic for the microbes of the slimy lactic acid fermentation:

1<sup>st</sup>. The optimum temperature for their growth is at 20° or lower,  
2<sup>nd</sup>. they can only compete in anaërobic cultures with the other microbes, and

3<sup>d</sup>. the medium must consist of substances containing peptones as nitrogen and carbonhydrates as carbon source, I succeeded in finding a method giving rise to their accumulation.

It is true that I only examined a single material in this way, the common baker's yeast, but the investigation of the soil of fermenting or fermented substances, in short of materials of most varying description may be done in a corresponding way.

The experiment is arranged as follows.

Into a 30 c.c. closed bottle, filled with maltextract, to which is added 1/2% of peptone siccum and which contains c.a. 10% extract, a little pressed yeast is introduced, for instance 1/2 gram. Placed at a temperature of 18' to 20° C. a quiet fermentation sets in, which is allowed to continue 24 to 72 hours, whereby, because of the absence of air the yeast hardly grows, but the various lactic acid ferments reproduce quickly. Other microbes do not develop. Not seldom in this first culture have the contents of the flask already become somewhat slimy.

Whether this be the case or not, a not too small quantity from it is transplanted into a bottle quite filled with boiled, air-free milk, for instance 1/3 c.c. into 30 c.c. of milk. At the same low or a somewhat higher temperature only a flora of lactic acid ferments can develop, and if the slime-forming species is present, it is the most

vigorous. We then see that after 2 or 3 days the milk become slimy and by inoculation into milk whey, a culture will start which sometimes differs so little from the ordinary long whey, that we may conclude to an identity of species.

Of course, I cannot foretell that such microbes occur in any yeast sample taken at random, hence I must add that for my experiments I used pressed yeast from the Yeast and Alcohol manufactory at Delft.

Such a culture in milk differs it is true in some respects from what is obtained by growing long whey from North Holland in milk, as in the former case short rods or oblong cocci are observed, and in the latter, shorter forms more reminding of the common micrococci.

I expect that by repeating this experiment various deviating varieties will be found, and by application of the method to other infection material perhaps new species of slime lactic acid ferments may be discovered.

#### 4. *Elective culture of the lactococci of cream souring.*

As the lactococci and lactobacilli, which both occur in spontaneously or otherwise soured milk, in cheese, and various other dairy products, seem to grow nowhere better than in milk,<sup>1)</sup> the culture experiments here considered, should be taken with milk.

In order out of the innumerable microbes of the crude milk practically to come to a pure culture of *Lactococcus*, the management is as follows.

The optimum of growth is at 30° C. or lower, and as all species of *Lactococcus* (like those of *Lactobacillus*) are strongly microaërophilous, sometimes even anaërobic (i. e. cannot grow at all at full atmospheric pressure on plates), it is best to cultivate in absence of air.

A stoppered bottle is quite filled with commercial milk and placed at 30 C. After 24 hours or somewhat later a *Lactococcus*-flora begins to replace the other microbes, while not seldom a feeble fermentation of *B. coli* or *B. aerogenes* has preceded.

After one or two re-inoculations under the same conditions, but

<sup>1)</sup> It is not impossible that there are "peptones" which, together with glucose or lactose, are still better food for the lactic acid ferments than milk itself. How very differently peptones of dissimilar origin act on microbes is easily observed in yeast species which in general grow better on "plant peptones" than on "animal peptones". The introduction of the word "bios" to denote those nitrogen compounds which are best fit as yeast food, is an attempt to circumscribe the peptoneproblem has been given. The relation between "peptones" and the lactic acid ferments is still closer than between these substances and the different yeasts; but it is here not the place to insist on this point.

into well boiled milk, which is done by transferring a trace of the first culture to the second bottle, quite filled with boiled, air-free milk, and so on, the lactococci free themselves completely from all foreign microbes and a material is obtained, which displays a high degree of purity and of practical usefulness. If the acidifying power of the microbes obtained by the experiment is lower than wished for, for example 5, whilst 8 to 10 c.c. of normal acid on 100 c.c. milk is desired, this must be attributed to the accidentally present stock. It is necessary then to begin a new experiment, following the same way as described, or it can be advisable to perform the first inoculation with some good butter-milk.

As buttermilk, however, very often contains lactose yeast, in the latter case a vigorous alcohol fermentation may at first be expected in the bottles. But it soon disappears by inoculation into milk rendered free from oxygen by boiling.

If in this way, thus in absence of air, the culture has been prolonged, a fairly constant acid amount is obtained at each renewed inoculation, which does not, however, rise above 10—12 c.c. normal in 100 c.c. of milk. On whey agar or whey gelatin plates the growth at the air of the thus obtained lactococci is different, as sometimes a great many aërobic colonies arise, which cause the same acidification as the cultures in the bottles, while in other cases nothing is seen to grow.

The first group corresponds with the usual commercial forms destined for the souring of cream, which commonly consist of cultures of the microbes dried on milk sugar or starch; moreover there are commercial aërobic pure cultures in milk or whey, which are sold in bottles.

The second group, that is the cultures non-growing at the air, may still better be used for the cream souring than the aërobic stocks, as the anaërobic forms of *Lactococcus* show more aptness to secrete the flavour desired in butter, than the more aërophilous bacteria.<sup>1)</sup>

As well for this reason as for the great purity of the cultures made after this "bottle method", there is reason to prefer them in dairy work to the commercial so-called pure cultures, which for the greater part are by no means pure, but mostly contain, besides lactococci, numerous contamination germs of the milk. In consequence of frequent investigations I can therefore advise interested persons to use the here described method. Best would be if these cultures were

<sup>1)</sup> Of late I have also met with such like anaërobic lactic acid bacteria in commercial preparations.

prepared in the creameries themselves, but also the sellers of pure cultures, by following the above prescriptions, will obtain a better product than by the more usual way of selection of aërobic colonies. Besides, the management is simpler and more scientific.

To my opinion there is no satisfying ground to class the aërobic and anaërobic forms of *Lactococcus*, which can be produced after the said method, in separate species. They are but variants of one and the same species, whose oxygen requirements are different, which also appears from the fact that in the course of time one and the same stock shows considerable differences with regard to the said relation. Moreover, by several isolations all transitions between the more or less aërobic stocks may be obtained.

Finally it should be borne in mind, that by applying the "bottle method" at low temperature, in rare cases instead of a culture of real *Lactococcus* a *Lactobacillus* is obtained, which may likewise be had by colony selection from cheese. Using this *Lactobacillus* I did not observe at all the pleasant flavour of the anaërobic lactococci, so that I do not recommend these bacilli for cream souring.

##### 5. *Elective culture of the lactic acid bacilli.*

If milk, soured spontaneously by *Lactococcus lactis*, or still better, buttermilk, is placed at exclusion of air in a thermostat of ca. 40° C., the original acid amount of 8 to 12 c.c. will in most cases rise after some days to about 18 or 20 c.c. per 100 c.c. of milk. For this experiment it is best to use a stoppered bottle of 250 to 300 c.c. capacity quite filled with milk. If for the first experiment a smaller quantity is used the result becomes uncertain, either by the disturbing influence of the air, or by the scarcity of the inferred bacteria.

The first change commonly observed in the sour milk is a moderately vigorous alcoholic fermentation, caused by the hardly ever lacking lactose yeast, and at the same time a complete separation of the caseine, which is driven to the surface of the liquid by the carbonic acid.

Microscopically we find that the lactococci present at first, are succeeded by more lengthened forms, truncated at the ends and united in chains, whereby the acid titer may considerably diminish, for instance in 12 hours from 8 c.c. to 6 c.c., which should be ascribed to the lactose yeast, for which the free lactic acid can serve as carbon food. By transference, at exclusion of air, the lactose yeast, as in the elective culture of lactococci, is rapidly dispelled by the then stronger lactic acid ferments.

Real lactobacilli mostly appear after 2 or 3 days and then the acid rises rapidly parallel to their multiplication to 20, even to 25 c.c. normal per 100 c.c. of milk. When this degree of souring is reached, there is usually no further increase observed, not even after several days, and whenever this does take place, there should be thought of aëration, by which the growth of vinegar bacteria and acetic acid formation from alcohol, have become possible.

The pure culture of lactobacilli is sometimes easy, in other cases, with more anaërobic stocks, it is more difficult. Always, however, it is troublesome with these pure cultures to obtain a considerable souring in milk and there is most chance of success (but even then the success is not quite certain) by souring lactobacilli together with *Lactococcus* which serves for the first souring to 8 c.c. If this amount of acid is reached, and the pressure of the oxygen sufficiently diminished, which in a stoppered bottle is likewise brought about by the presence of the lactococci, the lactobacilli can develop and cause further souring.

From the observation that by the described experiment more or less perfectly anaërobic lactobacilli are obtained, follows that here as in the case of *Lactococcus* different varieties may be expected. At a continued research the differences prove to extend over other characteristics also and may become so great, as well from a morphologic as from a physiologic point of view, that it seems necessary to create new species.

Especially the dimensions of the rods, the more or less branched state of the colonies on agar plates, the slime formation, the either or not originating of carbonic acid as fermentation gas beside the lactic acid, and the action or non action on different sugars give rise to this consideration. The deeper however we enter into these distinctions, the more troublesome it becomes to devise such descriptions as are wanted to present to other investigators an image of the results of our own researches; so numerous become the forms which nature, or better perhaps, which culture produces, and so slight are the differences by which these forms are distinguished, if we do not confine ourselves to the extremes of the groups.<sup>1)</sup>

If the latter is done, two distinct forms call attention, which on a former occasion I named<sup>2)</sup> *Lactobacillus caucasicus* and *L. longus*.

<sup>1)</sup> For further information see W. HENNEBERG, Zur Kenntniss der Milchsäurebakterien. Sonderabdruck aus Zeitschrift für Spiritusindustrie. No. 22--31, 1903. PAREY, Berlin.

<sup>2)</sup> Sur les ferments lactiques de l'industrie. Archives Néerlandaises. Sér. 2, T. 6, p. 212, 1901.

Without attributing a special value to this classification I yet wish to keep to it as I think that the facts to be mentioned are fairly well comprised thereby.

The longusgroup is characterised by its not acting on maltose, so that in maltextract no, or very little acid is formed, but it does decompose milksugar. In milk the forms of this group, if grown after a previous culture of *Lactococcus* which has produced 5 to 8 c.c. of lactic acid per 100 c.c. of milk, will once more produce a certain, even a like quantity of acid so that ca. 16 c.c. may be titrated, the latter amount being however an exception. Generally no evolution of carbonic acid is observed but sometimes it is, and then so much gas can arise that a milk beverage is acquired foaming like champagne.

By a series of transitions, the longus forms obtained at 40° C., are joined with lactobacilli which at a lower temperature find their optimal vital conditions, but which are rarer in milk.

The caucasicus group comprises those lactobacilli, which are able, independently of lactococci to produce in milk a very high acid formation. At 37 to 40° C. it is possible after three days of their action to titrate 20 to 25 c.c. of normal acid per 100 c.c. of milk. When that amount is reached further acid formation stops. In this case, too, there is a parallel form which, beside much lactic acid, also evolves carbonic acid. What by-product is then formed from the lactose molecule beside the carbonic acid is not yet clear; probably it is aethylalkohol. G. BERTRAND has proved that these ferments can produce succinic acid. They greatly owe their notoriety to their presence in kephir, which subject I have touched before<sup>1)</sup>. Later however I have come to the conclusion<sup>2)</sup> that their distribution is by no means restricted to kephir only, but that they also occur in our climate, sometimes in buttermilk, in cheese and even in common baker's yeast.

#### 6. *Yoghurt and maya.*

The use of soured milk as drink and food is so familiar to many Eastern countries, and dates from so remote an antiquity that there can be no doubt as to its favourable effect on health, and the establishment of various societies which try to popularise new preparations of that nature, seems to prove that the attention of the Western nations begins to be drawn towards it.

Both in the preparations of the Eastern nations and in those of

<sup>1)</sup> Sur le Kefyr. Archives Néerlandaises. T. 23, p. 428, 1891.

<sup>2)</sup> Ferments lactiques de l'industrie l. c.

industry are always found lactic acid ferments of the genus *Lactobacillus*, mostly of *Lactococcus* too. These lactic acid ferments alone determine the character of the "leben raib" of Egypt,<sup>1)</sup> of the "yoghurt" of Bulgaria,<sup>2)</sup> and probably also that of the "prostokwacha" and the "véranetz" of Russia, which METCHNIKOFF mentions. In the "kephir" of the Caucasus, the "koumys" of Central Asia,<sup>3)</sup> and the "mazun" of Armenia,<sup>4)</sup> occurs moreover, lactose yeast, which may, however, under certain circumstances be wanting, without the character of these beverages being lost. All other microbes, which are mentioned in literature as occurring in the said beverages or their ferments, such as *Oidium*, *Mucor*, other moulds, torula, red yeast, vinegar bacteria, butyric acid ferment, proteolytic bacteria, are only present by deficient preparation, so that it may be said that in all examined cases a pure lactic acid fermentation proves to be the wanted process, whilst eventually also an alcoholic fermentation is wished for or suffered<sup>5)</sup>.

Hence, in the commercial preparations which start from yoghurt, only lactic acid ferments are cultivated. I have in particular investigated the products of "Le Ferment", mentioned beneath, as also a substance, sold as "maya" or Bulgarian ferment,<sup>6)</sup> to which my attention was drawn by Dr. DE LINT at Scheveningen. Here I will shortly describe the latter preparation.

It consists in a yellowish strongly acid reacting powder, composed, after chemical, microscopical and bacteriological examination, of caseine lactic acid, lactose, fat and lactic acid bacteria; it is evidently nothing

<sup>1)</sup> Annales de l'Institut Pasteur. T. 16, p. 65, 1902.

<sup>2)</sup> MASSOL et GRIGOROFF, Revue médicale de la Suisse romande 1905 p. 716. BERTRAND et WEISWEILLER, Action du ferment Bulgare sur le lait. Ann. de l'Institut Pasteur, T. 20, p. 977, 1906.

<sup>3)</sup> For Kephir and Koumys see WEIGMANN in LAFAR Technische Mykologie. Bd. 2. p. 128. 1905.

<sup>4)</sup> Centralblatt für Bacteriologie, 2te Abt. Bd. 15, p. 577, 1906.

<sup>5)</sup> The study of literature leads at first view to a quite other result, as many microbiological descriptions are made by beginners, not sufficiently acquainted with the properties of lactic acid ferments, and who have attributed an exaggerated weight to the different kinds of infections named above.

<sup>6)</sup> On the bottle stands: Maya bulgare, Société de la maya bulgare, GARNIER & Co., Paris, 16 Rue Popincourt. The Société de Pury, Montreux, brings into commerce a ferment of the same nature under the name of "maya bacilline", and the Société HENNEBERG, Geneva, a liquid preparation as "lacticose". Besides there are to be had in Paris Lactobacilline de METCHNIKOFF in "Le Ferment", Fournisseur de l'Assistance publique, 77 Rue Denfert-Rochereau, who sells also, the "Biolactyle" of FOURNIER and the "Bacilline paralactique" of TISSIER (the preparations of this firm make a very good impression).

else but yoghurt evaporated at low temperature, perhaps in the vacuum. As to the preparation of the "yoghurt" itself by means of this ferment, it is done as follows and gives good results.

Milk is evaporated to half its volume, cooled to a (not nearer indicated) temperature, for which I took 40°, as 45° proved too high and 37° too low, and on a quantity of 250 c.c., so much ferment is strewn as can be put in a little spoon distributed with the flacon containing the maya. After 6 hours already the curdling of the milk becomes perceptible, after 24 hours I titrated 12 c.c. and after 3 × 24 hours 20 to 23 c.c. of normal lactic acid per 100 c.c. of the evaporated milk, which by that time is changed into yoghurt.

As a titer of 10 c.c. corresponds to 0.9% of lactic acid, the titer 20 corresponds to somewhat less than 2% of the vanished milk sugar. Supposing that the evaporated milk contains about 9.6% of milksugar it follows that 7% of milksugar has remained undecomposed. The caseine is of course curdled and the whole has changed into a solid but soft, sweet tasting mass.

The evaporation of the milk is not necessary, but when prepared from ordinary milk, the yoghurt remains more liquid, and as the acid formation is equally strong as in evaporated material, there remains about 2.5% of the original 4.8% milksugar, so that in this case the taste is much less sweet.

If in the said way yoghurt has been prepared in the presence of air and is re-inoculated into a new quantity of milk, then the result is yoghurt of the same acidity as the first time. But after 3 or 4 transferrings difficulties arise and only with great quantities of infection material further souring can be obtained. The experiment succeeded much better when the yoghurt was prepared in a quite filled stoppered bottle; the transferring can then be longer continued, but I do not know whether this will do in the long run. Evidently the difficulty here, too, is the right choice of oxygen pressure, whereby the inferred lactic acid bacteria preserve their properties unchanged; and this difficulty is still increased by the presence of two different forms, with unequal optima as to temperature, and probably as to oxygen pressure also.

One of these forms is again a *Lactococcus*, the other a *Lactobacillus*.

The former deviates somewhat from the common *Lactococcus*, in as much as it is more extended, reminding of short rods, and furthermore by possessing a higher optimum as to the temperature whereby the growth is quickest, which optimum proves nearer to 37° than to 30° C. Hence, this form is as it were a transition to a *Lactobacillus*. Isolation on milk agarplates was very easy, even at 30° C.

As to the second species, the *Lactobacillus* proper of yoghurt, it was troublesome to grow its colonies on milk agar plates, but on malt extract agar it was more easily obtained. In literature it has been named *Bacillus Mussol* by GRIGOROFF, but I think that name superfluous as the characters correspond fairly well with those of the kephir bacilli which also occur in our country; for instance, as has been observed before, in yeast and buttermilk. Sown in slightly soured milk this *Lactobacillus* can produce the strong acid mentioned above, without the help of other bacteria. Evolution of carbonic acid does not take place and the product has a very pure taste, although a beginning of fat cleavage seems inevitable at such a high amount of acid.

METCHNIKOFF ascribes a very favourable influence to the use of yoghurt, as it diminishes the phenomena of autointoxication starting from the intestinal canal, and he explains this effect by accepting that the *Lactobacillus*, after passing the stomach, continues active in the intestine, and checks<sup>1)</sup> the formation of the obnoxious products which derive from other bacteria species. I do not doubt but this may be brought about by the lactic acid, but I think it highly improbable that the presence of the lactic acid bacteria from the yoghurt themselves should be required in the intestine. I think this conclusion is necessary, first because, without the use of yoghurt or other soured milk preparations, there occur in the intestine lactic acid ferments of different species, and second, because the conditions for lactic acid formation by the active ferments are wanting or must at least be very unfavourable there.

As to the first point I refer to the following experiments.

If sterile milk is infected with faeces of different origin (man, cattle) and treated as described for the elective culture of *Lactococcus*, without access of air and repeatedly reinoculated at a temperature between 23° to 26° C., the said genus of microbes is indeed obtained by which as good cream souring can be obtained as with the pure cultures prepared in the before described way.

If sterile milk is infected in a corresponding way and exposed to the conditions wanted for *Lactobacillus*, that is, if cultivated in absence of air at 40 to 45° C., a fermentation of coli will first arise and later or simultaneously a butyric acid and no lactic acid ferment-

<sup>1)</sup> Quelques remarques sur le lait aigri. Rémy, Paris, 1907. In this paper METCHNIKOFF gives many assertions but no decisive experiments. Besides, his bacteriological elucidation, p. 26, is not clear. The elaborate and interesting work of Dr. A. COMBE, L'autointoxication intestinale, Paris 1907, is neither quite convincing from a microbiological point of view.

tation, which latter would inevitably arise if the lactic acid ferments were present in a rather considerable number. Only by repeated transferences *Lactobacillus* is produced, which after some inoculations forms 10 to 13 c.c. of normal acid.

Hence, there is no doubt as to the presence of *Lactobacillus* and *Lactococcus* in normal faeces. They are, however rare, and belong by no means to the intestinal flora proper, like *coli*, but to the accidental flora, which consists of all that is introduced and is able to pass the stomach and intestines alive, without multiplying. There seems to be no cause to attribute any important influence to this fact.

As to the second point, why in the intestinal canal the conditions for the growth of the active lactic acid ferments are wanting, it is that in the contents of the intestines an alcalic reaction exists, and that the sugars which are formed or introduced there, in as much as they are not absorbed by the intestinal wall, will surely be attacked by *coli*, which in these circumstances is the stronger and dispels all competitors.

Why *coli* (and *aerogenes*) so completely defeat the lactic acid ferments, should, to my opinion, be explained by the important fact, not sufficiently considered in literature, that the first mentioned species can quite well live on peptone only, and multiply at its expense, while the active lactic ferments completely lack this faculty and, beside peptone, require a carbohydrate for food.

If, moreover, it is borne in mind that *coli* in the presence of a carbohydrate can also feed on other sources of nitrogen than peptone, for example on amines and ammonium salts, whereas the active lactic acid ferments cannot, and decidedly want peptones for nitrogen food, it is clear that for the different forms of *coli* practically every where in the intestinal contents a good feeding material is present, and that in the few localities where it would also be sufficient for the lactic acid ferments, it will be seized upon by *coli*. Where only peptones occur, *coli* will moreover increase the already alcalic reaction of the contents and thus, not for itself but for the lactic acid ferments, render the conditions of life more unfavourable.

Hence it seems evident why in the intestinal canal a coliflora can exist but no lactic acid flora.

The yellow coloured faeces of babies during the lactation period may be alleged to support this view. They consist microscopically almost solely of bacteria, for far the greater part of common colibacteria<sup>1)</sup>, among which there occur real lactic acid ferments, but

<sup>1)</sup> For different children not always the same varieties; sometimes, for instance non-fermenting forms reminding of *Lactobacillus*, for which I before indeed took such bacteria.

as in the case described before in quite an inferior number. This fact acquires a special significance when we consider that ESCHERICH, the discoverer of the colibacillus, has proved that this condition exists directly behind the baby's stomach, where *coli* and *aërogenes* are predominant which, in reference to the preceding, necessitates the conclusion that even at those portions of the intestines where a lactic acid flora should first be looked for, it is evidently unable to sustain itself.

There is no doubt but here too, the strongly disinfecting action of the stomachal hydrochloric acid plays a part, as this acid, at a much lower titer than the lactic acid checks the growth of the lactic acid ferments, but hence can be neutralised by much less alkali, which is not indifferent to *coli*, which produces alkali.

In so far as the theory of METCHNIKOFF and COMBE is right, after which yoghurt or other sour milk preparations counteract the auto-intoxication from the intestinal canal, it seems certain that here should more be thought of the influence of a milk diet and the free acid taken up with the milk, than of a specific intestinal flora. But in how far the apparently proved decrease of indol and phenol, whose quantity is considered as determining the degree of auto-intoxication, deviates, at a nutrition with soured milk preparations instead of meat, from this decrease when non-soured milk is used, — to my opinion the real core of the question, — has not been considered by the said authors.

Admitting that the soured preparations really deserve to be preferred, I think that especially in Holland, it must be possible with good buttermilk in as simple a way to reach the wished for end, as with the various exotic ferments, whose descriptions give the impression that the preparators are but imperfectly acquainted with the general phenomena of the lactic acid fermentation in milk.

Although I see no fundamental difference between the use of buttermilk and yoghurt, it is certain that the latter may be prepared in a very simple way under medical control, and hence, to my meaning, deserves to be recommended in certain cases.

Summarising the preceding I come to the following conclusion.

In milk three chief forms of lactic acid fermentation, determined by temperature, are to be distinguished, namely at very low temperature, the slimy lactic acid fermentation; at a middle temperature the common lactic acid fermentation caused by *Lactococcus*; and at higher temperature the lactic acid fermentation by *Lactobacillus*.

The elective culture of the microbes of the slimy fermentation, succeeds by cultivating baker's yeast in absence of air between 15°

and 18° C. in malt extract and transferring to boiled milk or whey at a somewhat higher temperature. The acidity obtained remains low and amounts to 3 to 5 c.c. of normal acid per 100 c.c. of milk.

The elective culture of *Lactococcus* takes place by allowing milk to sour in a stoppered bottle at 20° to 25° C. and transfer it repeatedly to boiled milk at that temperature. The thereby obtained stocks of *Lactococcus lactis* are mostly anaërobic but specifically not to be distinguished from the more aërobic forms which may be produced by the same experiment. The acid mostly remains at about 8 c.c. of normal acid per 100 c.c. of milk, but may become 10 to 12 c.c.

The elective culture of *Lactobacillus* succeeds best by cultivating buttermilk in absence of air at 37° to 40° C. and inoculating it into boiled milk, at 30° C. and higher, the acidity can rise from 18 to 25 c.c. of normal acid per 100 c.c. of milk.

The active lactic acid ferments are very variable; as factors of hereditary constant variation are recognised cultivation at too high or too low oxygen pressure, and cultivation at a temperature above the optimum of growth.

Lactic acid ferments do not lack in the intestinal flora, but play there an inferior part.

A considerable difference between Eastern and Western lactic acid ferments does not exist.

Yoghurt and other such like sour milk preparations deserve the attention of hygienists.

**Chemistry.** — “*On the course of the plaitpoint line and of the spinodal lines, also for the case, that the mutual attraction of the molecules of one of the components of a binary mixture of normal substances is slight*”, by Mr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of April 26, 1907).

1. In the latest volume of These Proceedings <sup>1)</sup> Dr. KEESOM (also in conjunction with Prof. KAMERLINGH ONNES) stated some important results, inter alia concerning his investigation on the special case that one, e.g.  $a_1$ , of the two quantities  $a_1$  and  $a_2$  is very small; which is

<sup>1)</sup> KAMERLINGH ONNES and KEESOM, These Proc., Dec. 29, 1906, p. 501—508 [On the gas phase sinking in the liquid phase etc. (Comm. 96b)]; KEESOM, Ibid. p. 508—511 [On the conditions for the sinking etc. (Comm. 96c)]; KEESOM, Ibid. March 28, 1907, p. 660—664 (Comm. 96c continued); KAMERLINGH ONNES and KEESOM, Ibid. of April 25, 1907, p. 786—798 [The case that one component is a gas without cohesion etc. (Suppl. N<sup>o</sup>. 15)].

realised, among others, for mixtures of He ( $a_1$ ) and H<sub>2</sub> ( $a_2$ ). In these papers, particularly in the last, a particular kind of plaitpoint line has been repeatedly mentioned, viz. one passing from the critical temperature  $T_0$ , called "third" by me (KEESOM's  $T_{km}$ ), to the *highest* of the two critical temperatures  $T_2$  (KEESOM's  $T_{k_1}$ ).

Now the theoretical possibility of such a course of the plaitpoint line, i.e. of *one of its two branches*, has been first brought to light by me in a series of Discussions on this subject<sup>1)</sup>. Not only for the special case  $b_1 = b_2$ , for which among others, fig. 1 of June 21, 1905 holds, but for all possible cases (see specially TEYLER I and II). We found that such a course will always be found, when the ratio of the two critical temperatures  $\theta = \frac{T_2}{T_1}$  is *larger* than the value of this ratio, for which the plaitpoint line has a *double point*. This type was called type I by me. (see also fig. 1 of Oct. 25, 1906).

The case that a plait *starts* from  $C_0$  to  $C_2$ , or also at the same time from  $C_2$  to  $C_0$  (when there is a minimum temperature in the plaitpoint line) is not new (see K. O. and KEESOM, p. 788 below), but has been before described and calculated by me in all particulars.

The *double point* in the plaitpoint line, discovered by me in 1905 (June 21), did not only give the key to the possibility of such a course, which had already been ascertained for mixtures of water and ether, of ethane and methylalcohol<sup>2)</sup>; but also the *connection*

<sup>1)</sup> These Proc. May 25, 1905, p. 646—657; Ibid. June 21, 1905, p. 33—48; Ibid. Aug 17, 1905, p. 144—152 (Cf. also Arch. Néerl. 1905, p. 373—413); Ibid. Jan 25, 1906, p. 578—590 (Also Arch. Néerl. 1906, p. 224—238); Ibid. Oct. 25, 1906, p. 226—235. Further Arch. TEYLER (2) X, Première partie, p. 1—26 (1905); Ibid. Deuxième partie, p. 1—54 (1906). Henceforth I shall refer to papers in these Proceedings by mentioning the *date*, to papers in the Arch. TEYLER by putting TEYLER I or II.

<sup>2)</sup> I do not quite understand why in cases as for He + H<sub>2</sub> the plait considered is particularly called a "*gasplait*". With exactly the same right the two coexisting phases might be called *liquid* phases, especially at the higher pressures in the neighbourhood of the point  $C_0$ . With reference to water-ether, etc. we speak of a gas phase and a liquid phase before the three phase equilibrium is reached, i.e. at higher temperatures; and when at lower temperatures the equilibrium mentioned has established itself, of two liquid phases. The "gas phase" is then determined by the branch plait of the original transverse plait (which latter has now the peculiar shape directed towards  $C_0$  in the neighbourhood of the axis  $x=0$ ). But I acknowledge that this is perfectly arbitrary, it being difficult to indicate where the pressure is high enough on such a plait to justify us in speaking of liquid phases. Would it not be better to follow here VAN DER WAALS' terminology, and speak of *fluid* phases, and to call the two phases *liquid* phases at temperatures where the three phase equilibrium is found? Otherwise in this latter case — keeping to K. O. and KEESOM's terminology — we should have to speak of *three* coexisting *gas* phases, a rarefied one and two very dense ones, which latter, however, we should never refer to as gas phases in the *perfectly identical* case of water + ether.

of the different series of *hidden* plaitpoints, etc. etc., as has, inter alia, been indicated in Jan. 25, 1906 (cf. also TEYLER II). Dr. KEESOM does not mention that in his figure I (loc. cit. p. 794) besides the plaitpoint line from  $K_m$  to  $K_1$  drawn there, there *always* exists also a *second* branch, which runs along the  $v$ -axis in the neighbourhood of  $x=1$  from the point where  $v=b$  to  $K_2$  — and which gives rise to a *three phase equilibrium* at lower temperatures, as this has been explained by me. (also in Jan. 25, 1906 and TEYLER II).

The fact whether a plait extends in the way mentioned, depends therefore, as we said before, *in the first place* on the fact whether the values of  $\frac{b_2}{b_1}$  and  $\frac{a_2}{a_1}$  (so of  $\theta = \frac{T_2}{T_1}$  and  $\pi = \frac{p_2}{p_1}$ ) are such that  $\theta$  is larger than that value of  $\theta$  for which the plaitpoint line has a *double point* with given value of  $\pi$ . The knowledge of this double point, being therefore of so great importance for the distinction of the different types, I have carried out in TEYLER I the lengthy calculations required for this, and drawn up the results obtained in tables. [See also TEYLER II, where fig. 22 (p. 30) represents the results *graphically*].

Hence *not* the fact that  $T_{km} > T_{k_1}$  [with perfect justice KEESOM says in a footnote (loc. cit. p. 794) that  $T_{km}$  may also be  $< T_{k_1}$ ], but only the fact that  $\theta$  lies *above the double point value*, determines the considered course of the plaitpoint line. (See also Oct. 25, 1906, where I summed up most of the results obtained by me).<sup>1)</sup>

It is true that KEESOM mentions in a note (loc. cit. p. 786) that I have examined the plaitpoint line for the case  $a_1 = 0$ , but this statement is not quite complete, for I have not only examined such a plaitpoint line for this particular case  $a_1 = 0$ , which I cursorily mentioned in a note (June 21, 1905, p. 39), but for all cases. Qualitatively the plaitpoint line  $C_0 C_2$  for the case  $a_1 = 0$  is not distinguished in anything from that for the case  $a_1 > 0$  (provided it remain in the case of type I), hence there was no call for a special investigation of the form of the spinodal line and of the plait for  $a_1 = 0$ , this having already been done for the general case. Moreover KEESOM himself considers later on the case  $a_1$  *small*, and no longer  $a_1 = 0$ , which of course does not occur in practice.

Also the equation of the spinodal line (for molecular quantities):

$$RTv^3 = 2(1-x)(v\sqrt{a_1} - b_1\sqrt{a})^2 + 2x(v\sqrt{a_2} - b_2\sqrt{a})^2,$$

<sup>1)</sup> Prof. VAN DER WAALS says (These Proc., March 23, 1907, p. 621), "that as yet no one has succeeded in giving a satisfactory explanation of the different forms (of plaits)." I think I have done so to a certain degree in my papers of 1905-1906.

given by KEESOM, had already been drawn up by me (May 25, 1905, p. 652) in the identical form:

$$RTv^3 = 2 \left[ x(1-x)(\alpha v - \beta \sqrt{a})^2 + a(v-b)^2 \right],$$

where  $\alpha = \sqrt{a_2} - \sqrt{a_1}$  and  $\beta = b_2 - b_1$ .

2. The answer to the question whether the plait extends from  $C_0$  to  $C_2$  *with* or *without* double point in the *spinodal* curve, i. e. with or without *minimum* plaitpoint temperature, in other words the answer to the question whether the plait passes from  $C_0$  to  $C_2$  undivided, or whether two plaits extend on the  $\psi$ -surface, one starting from  $C_0$ , the other from  $C_2$ , which meet at the minimum temperature — depends on the value of  $\theta = \frac{T_2}{T_1}$  (on which also  $\frac{T_2}{T_0}$  depends)

for given value of  $\pi = \frac{p_2}{p_1}$ . The condition for this I derived in Aug. 17, 1905, p. 150, and Jan. 25, 1906, p. 581. In the summer of 1906 I calculated the place of the minimum itself (Cf. Oct. 25, 1906, 234, line 18—16 from the bottom), but seeing that the paper, which at that time had already been completed and sent to the editor of the Arch. Teyler, has not yet been published (it may be even some time before it is), I think it desirable to publish already now the calculation in question.

Like the calculations of KEESOM, VERSCHAFFELT and others, it starts from the supposition that  $a$  and  $b$  do not depend on  $v$  or  $T$ , and that these quantities may be represented by

$$a_x = [(1-x)\sqrt{a_1} + x\sqrt{a_2}]^2 ; \quad b_x = (1-x)b_1 + x b_2.$$

So in conformity with BERTHELOT and others we assume that  $a_{12} = \sqrt{a_1 a_2}$ . Some time ago Prof. VAN DER WAALS raised his voice against this supposition<sup>1)</sup>, and it seems to me that there is really much to be said in favour of  $a_{12}$  being *in general* not  $= \sqrt{a_1 a_2}$ . But as a first approximation the equation put may be accepted, the more so as also the variability of  $b$  with  $v$  and  $T$  is neglected. That in consequence of the assumption  $a_{12} = \sqrt{a_1 a_2}$  the left region, mentioned by VAN DER WAALS, would be compressed to an exceedingly small region, can hardly be adduced as an argument against this supposition; rather the fact that the attractions are *specific* quantities, and that therefore  $\epsilon_{12}$  need not be  $= \sqrt{\epsilon_1 \epsilon_2}$ .

For the calculation of the minimum we start from the equation of the spinodal curve, derived by us (loc. cit.):

<sup>1)</sup> These Proc., March 28, 1907, p. 630—631.

$$RT = \frac{2}{v^3} \left[ x(1-x)(av - \beta \sqrt{a})^2 + a(v-b)^2 \right], \dots (1)$$

or

$$RT = \frac{2\alpha^3}{v} \left[ x(1-x) \left( 1 - \frac{\beta \sqrt{a}}{v} \right)^2 + \frac{a}{\alpha^2} \left( 1 - \frac{b}{v} \right)^2 \right],$$

which with  $\frac{b_1}{v} = \omega$  ,  $\frac{\beta}{v} = n\omega$  ,  $\frac{\sqrt{a_1}}{\alpha} = \varphi$  passes into

$$RT = \frac{2\alpha^2}{\beta} n\omega \left[ x(1-x) \left( 1 - n\omega(\varphi+x) \right)^2 + (\varphi+x)^2 \left( 1 - (1+n\omega)\omega \right)^2 \right], (1a)$$

For  $\frac{\sqrt{a}}{\alpha} = \frac{\sqrt{a_1+x\alpha}}{\alpha} = \varphi+x$  and  $\frac{b}{v} = \frac{b_1+x\beta}{v} = \omega + n\omega = (1+n\omega)$ .

Now the spinodal curve must show a double point, in other words:

$$\frac{\partial f}{\partial x} = 0 \quad \text{and} \quad \frac{\partial f}{\partial \omega} = 0,$$

when  $f$  represents the second member of (1a). The first equation gives:

$$(1-2x)(1-z)^2 - 2x(1-x)(1-z)n\omega + 2(\varphi+x)(1-y)^2 - 2(\varphi+x)^2(1-y)n\omega = 0,$$

when for the sake of brevity  $n\omega(\varphi+x) = z$  and  $(1+n\omega)\omega = y$  is put. Bearing in mind that  $n\omega = \frac{z}{\varphi+x}$ , we get for the last equation:

$$(1-2x)(1-z)^2 - \frac{2x(1-x)}{\varphi+x} z(1-z) + 2(\varphi+x)(1-y)^2 - 2(\varphi+x)(1-y)z = 0. \quad (a)$$

The second equation yields, when in (1a) the factor  $\omega$  is brought within [ ]:

$$x(1-x) \left[ (1-z)^2 - 2\omega(1-z)n(\varphi+x) \right] + (\varphi+x)^2 \left[ (1-y)^2 - 2\omega(1-y)(1+n\omega) \right] = 0,$$

or

$$x(1-x) \left[ (1-z)^2 - 2z(1-z) \right] + (\varphi+x)^2 \left[ (1-y)^2 - 2y(1-y) \right] = 0,$$

i. e.

$$x(1-x)(1-z)(1-3z) + (\varphi+x)^2(1-y)(1-3y) = 0. \dots (b)$$

From (b) we solve:

$$x(1-x) = -(\varphi+x)^2 \frac{(1-y)(1-3y)}{(1-z)(1-3z)}. \dots (3)$$

Also from (a):

$$= \left[ -2(\varphi+x)(1-y)^2 + 2(\varphi+x)(1-y)z + \frac{2x(1-x)}{\varphi+x} z(1-z) \right] : (1-z)^2,$$

or

$$1-2x = \left[ -2(\varphi+x)(1-y)^2 + 2(\varphi+x)(1-y)z - \frac{2(\varphi+x)(1-y)(1-3y)z}{1-3z} \right] : (1-z)^2,$$

when for  $x(1-x)$  the value from  $\beta$  is substituted. Further reduction yields:

$$1-2x = \left[ -2(\varphi+x)(1-y)^2 + 2(\varphi+x)(1-y)z \left\{ 1 - \frac{1-3y}{1-3z} \right\} \right] : (1-z)^2,$$

or

$$1-2x = -\frac{2(\varphi+x)(1-y)}{(1-z)^2} \left[ (1-y-3z) \frac{y-z}{1-3z} \right],$$

or

$$1-2x = -\frac{2(\varphi+x)(1-y)(1-y-3z(1-z))}{(1-z)^2(1-3z)} \quad \dots \quad (\alpha)$$

From  $(\alpha)$  and  $(\beta)$  follows, as  $(1-2x)^2 = 1-4x(1-x)$ :

$$1+4(\varphi+x)^2 \frac{(1-y)(1-3y)}{(1-z)(1-3z)} = \frac{4(\varphi+x)^2(1-y)^2}{(1-z)^4} \cdot \frac{[(1-y)-3z(1-z)]^2}{(1-3z)^2},$$

i. e.

$$1 = \frac{4(\varphi+x)^2(1-y)}{(1-z)^4(1-3z)^2} \left[ (1-y) \left\{ (1-y)-3z(1-z) \right\}^2 - (1-3y)(1-z)^2(1-3z) \right].$$

Arrangement according to the powers of  $z$  yields for [ ]:

$$(3y^2-y^3) - 6z(y+y^2) + 3z^2(1+5y+2y^2) + z^3(-8-12y) + 6z^4,$$

or

$$y^2(3-y) - 6yz(1+y) + 3z^2(1+5y+2y^2) - 4z^3(2+3y) + 6z^4,$$

which may be reduced to

$$(y-z)^2(6z^2-8z+3-y),$$

so that we find:

$$1 = \frac{4(\varphi+x)^2(1-y)(y-z)^2(6z^2-8z+3-y)}{(1-z)^4(1-3z)^2},$$

from which may be solved:

$$(\varphi+x)_m^2 = \frac{(1-z)^4(1-3z)^2}{4(1-y)(y-z)^2(6z^2-8z+3-y)}, \quad \dots \quad (2)$$

through which  $\varphi+x$  is expressed in the two parameters  $y$  and  $z$ . In consequence of this  $(\beta)$  passes into

$$x_m(1-x_m) = -\frac{(1-z)^2(1-3z)(1-3y)}{4(y-z)^2(6z^2-8z+3-y)}, \quad \dots \quad (3)$$

from which  $x_m$  may be calculated with given values of  $y$  and  $z$ . Then  $\varphi_m$  is also known through (2), i.e. expressed in  $y$  and  $z$ .

Further we now find for  $RT_m$  according to (1a):

$$RT_m = \frac{2\alpha^2}{\beta} n\omega \left[ -\frac{(1-z)^3(1-3z)(1-3y)}{4(y-z)^2(6z^2-8z+3-y)} + \frac{(1-z)^4(1-3z)^2(1-y)}{4(y-z)^2(6z^2-8z+3-y)} \right],$$

as  $n\omega(\varphi+x) = z$  and  $(1+nx)\omega = y$ . Reduction yields:

$$RT_m = \frac{2\alpha^2}{\beta} n\omega \frac{(1-z)^4(1-3z)}{4(y-z)^2(6z^2-8z+3-y)} \left[ 1-3z)(1-y) - (1-z)(1-3y) \right].$$

The expression between [ ] is  $= 2(y-z)$ , hence,  $\frac{n}{\beta}$  being  $\frac{1}{b_1}$ , we get:

$$RT_m = \frac{\alpha^2 \omega \cdot (1-z)^4(1-3z)}{b_1 (y-z)(6z^2-8z+3-y)}.$$

Let us express this in  $T_1$ , the critical temperature of one component. ( $T_1 < T_2$ ). We find:

$$T_1 = \frac{8}{27} \frac{a_1}{b_1} = \frac{8}{27} \frac{\alpha^2 \varphi^2}{b_1},$$

as  $\frac{\sqrt{a_1}}{\alpha} = \varphi$  was put. At last we get:

$$\frac{T_m}{T_1} = \frac{27}{8} \frac{\omega}{\varphi^2} \frac{(1-z)^4(1-3z)}{(y-z)(6z^2-8z+3-y)} \dots \dots \dots (4)$$

Now

$$z = n\omega(\varphi+x) \quad ; \quad y = (1+nx)\omega,$$

from which we solve.

$$n\omega = \frac{z}{\varphi+x} \quad ; \quad y = \omega + \frac{xz}{\varphi+x},$$

hence:

$$\omega = y - \frac{xz}{\varphi+x} \quad ; \quad \frac{1}{n} = \frac{y}{z}(\varphi+x) - x \dots \dots \dots (5)$$

Now  $\omega$  and  $n$  have been expressed in  $y$  and  $z$ , as  $(\varphi+x)_m$  and  $x_m$  had already been expressed in  $y$  and  $z$  by (2) and (3).

As further:

$$1+n = 1 + \frac{\beta}{b_1} = \frac{b_2}{b_1} = \frac{\theta}{\pi},$$

and

$$1 + \frac{1}{\varphi} = 1 + \frac{\alpha}{\sqrt{a_1}} = \frac{\sqrt{a_2}}{\sqrt{a_1}} = \frac{\theta}{\sqrt{\pi}},$$

when  $\theta = T_2 : T_1 = \frac{a_2}{b_2} : \frac{a_1}{b_1}$  and  $\pi = p_2 : p_1 = \frac{a_2}{b_2^2} : \frac{a_1}{b_1^2}$ , we have also:

$$\theta = \frac{\left(1 + \frac{1}{\varphi}\right)^2}{1+n} \quad ; \quad \pi = \frac{\left(1 + \frac{1}{\varphi}\right)^2}{(1+n)^2}, \dots \dots \dots (6)$$

so that also  $\theta$  and  $\pi$  can be expressed in  $y$  and  $z$ .

Reversely we may now also think the corresponding values of  $\omega$ ,  $x$  and  $T_m$  to be solved for any given pair of values of  $\pi$  and  $\theta$ , though *explicitly* this is impossible, so that we shall have to be satisfied with the set of equations from (2) to (6).

The further discussion of these equations, particularly with regard to the branch  $C_0A$  of the plaitpoint line, in connection with the *longitudinal plait*, will be found in the paper, which will shortly appear in the Arch. Teyler. There the course of the *pressure* is also examined, which we no further discuss here. It is only desirable to calculate the data for the "third" critical temperature  $C_0$ , viz.  $x_0$  and  $T_0$  — not because these data are indispensable for the following considerations, but because KÆSOM includes them in his considerations, and it is profitable in any case to know something concerning the relation  $\frac{T_0}{T_1}$  or  $\frac{T_0}{T_2}$ .

As  $v = b$  for the point  $C_0$ , so  $y = \frac{b}{v} = 1$ , and the equation of the  $v, x$ -projection of the plaitpoint line (Aug. 17, 1905, p. 146; Teyler I and II), viz.

$$(1-z)^3(1-2x-3a(1-x)n\omega) + 3(\varphi+x)(1-y)^2(1-z)(1-2z) + \frac{(\varphi+x)^2(1-y)^3(1-3y)}{x(1-x)} = 0,$$

is reduced to

$$1-2x_0-3x_0(1-x_0)n\omega_0 = 0,$$

or as  $y = (1+nx)\omega$ , and hence  $\omega_0 = \frac{1}{1+nx_0}$ , to

$$(1-2x_0)(1+nx_0) - 3x_0(1-x_0)n = 0,$$

from which follows

$$x_0 = \frac{(n+1) - \sqrt{n^2+n+1}}{n} \dots \dots \dots (7)$$

From this is seen that the situation of  $C_0$  depends only on the value of  $n$  or  $1+n = \frac{b_2}{b_1}$ .

The corresponding value of  $T_0$  is found from (1a). For  $y = 1$  we find:

$$RT_0 = \frac{2\alpha^2\omega_0}{b_1} x_0(1-x_0)(1-z_0)^2,$$

in which  $\omega_0 = \frac{1}{1+nx_0}$  and  $z_0 = n\omega_0(\varphi+x_0)$ .

As  $T_1 = \frac{8}{27} \frac{\alpha^2\varphi^2}{b_1}$  (see above), we have:

( 42 )

$$\frac{T_0}{T_1} = \frac{27 \omega_3}{4 \varphi^2} x_0 (1 - x_0) (1 - z_0)^2 \dots \dots \dots (8)$$

Hence we can immediately calculate  $x_0$  and  $T_0$  from (7) and (8) for any given set of values of  $\theta$  and  $\pi$ , or  $\varphi$  and  $n$ .

3. For our case ( $a_1$  small) it is now important to know, when a minimum occurs in the plaitpoint line  $C_0 C_2$ , when not. For this purpose we shall derive the condition that the minimum is to appear exactly in the point  $C_2$ . Evidently this condition will then indicate the limit between the two cases that there occurs a minimum in the neighbourhood of  $C_2$  or not — in other words whether the line of the plaitpoint temperatures in  $C_2$  descends first and rises later on to  $T_0$  in  $C_0$ ; or whether there is an immediate rise from  $T_2$  to  $T_0$ . (We call to mind that with us  $T_2$  is always the *highest* of the two critical temperatures  $T_1$  and  $T_2$ ).

Now  $y = \frac{b}{v} = \frac{1}{3}$  in the point  $C_2$ , while  $x = 1$ . Hence equation (2) passes into

$$(\varphi + 1)^2 = \frac{(1-z)^4 (1-3z)^2}{4 \times \frac{2}{3} (\frac{1}{3} - z)^2 (6z^2 - 8z + \frac{2}{3})} = \frac{81 (1-z)^4}{16 (2-3z)^2},$$

from which follows:

$$\varphi + 1 = \frac{9 (1-z)^2}{4 (2-3z)},$$

hence

$$\frac{\sqrt{a_2}}{\sqrt{a_1}} = 1 + \frac{1}{\varphi} = 9 \frac{(1-z)^2}{(1-3z)^2} \dots \dots \dots (a)$$

From

$$z = n\omega (\varphi + x)$$

follows further, as  $\omega = \frac{b_1}{v} = \frac{b_2}{v} \times \frac{b_1}{b_2} = \frac{1}{3} \frac{1}{1+n}$  and  $x = 1$ :

$$z = \frac{1}{3} \frac{n}{1+n} (\varphi + 1) = \frac{3}{4} \frac{n}{1+n} \frac{(1-z)^2}{2-3z}.$$

This yields:

$$\frac{1+n}{n} = \frac{3 (1-z)^2}{4 z(2-3z)},$$

or

$$\frac{b_2}{b_1} = 1 + n = \frac{3 (1-z)^2}{(1-3z)(3-5z)} \dots \dots \dots (b)$$

When we put:

$$\sqrt{\frac{a_2}{a_1}} = \kappa \quad ; \quad \frac{b_2}{b_1} = \lambda,$$

the simple relation

$$\lambda \geq \frac{\kappa}{3 + 2\sqrt{\kappa}}, \dots \dots \dots (c)$$

follows from (a) and (b) after some reduction, in which the sign  $\geq$  refers to the existence of a minimum in the neighbourhood of  $C_2$ .

The condition (c) found by us is quite identical with that, which we derived before from the formula for  $\frac{1}{T_1} \left( \frac{dT_x}{dx} \right)_0$  found by us (Aug. 17, 1905, p. 150 and Jan. 25, 1906, p. 580). This condition was:

$$\theta < \frac{4\pi\sqrt{\pi}}{(3\sqrt{\pi}-1)^2}.$$

With this difference, however, that we then considered  $\frac{1}{T_1} \left( \frac{dT_x}{dx} \right)_0$  at  $C_1$ , whereas we have now examined the branch of the plaitpoint line which starts from  $C_2$ , so that we have to calculate  $\frac{1}{T_2} \left( \frac{dT_x}{dx} \right)_1$  and to derive the condition of the minimum from this. But it is immediately seen that it is obtained by substituting  $\frac{1}{\theta}$  for  $\theta$  and  $\frac{1}{\pi}$  for  $\pi$  in the above condition.

So we find:

$$\frac{1}{\theta} < \frac{\frac{4}{\pi\sqrt{\pi}}}{\left( \frac{3}{\sqrt{\pi}} - 1 \right)^2},$$

or

$$\theta > \frac{\sqrt{\pi}(3-\sqrt{\pi})^2}{4} \dots \dots \dots (c')$$

And it appears immediately that (c) is identical with (c'), when we substitute  $\frac{\theta^2}{\pi}$  for  $\kappa^2$  and  $\frac{\theta}{\pi}$  for  $\lambda$  in (c).

This furnishes a good test, both of the accuracy of the above derived formula (c), and of the condition (c'), derived by us before.

Let us now examine what values of  $\lambda$  and  $\kappa$  correspond according to the condition (c), so that the minimum still appears exactly in  $C_2$ . The corresponding values of  $z$  required for the calculation of  $T_0$ , may be found from (a), giving:

$$z = \frac{1}{3} \frac{\sqrt{\kappa}-3}{\sqrt{\kappa}-1}.$$

The subjoined table combines the calculated values. We call attention to the fact that the minimum in the neighbourhood of  $C_2$  can only belong to the branch  $C_2C_0$  for type I ( $\theta >$  the double point value), and never to the branch  $C_2C_1$  for type II or III ( $\theta <$  the double point value). For  $T_2 > T_1$  being put, the minimum on  $C_2C_1$  cannot possibly lie at  $C_2$ , but it can lie in the neighbourhood of  $C_1$ .

	$\kappa = \sqrt{\frac{a_2}{a_1}}$	$\lambda = \frac{b_2}{b_1}$	$\theta = \frac{r^2}{r}$	$\pi = \frac{r^3}{r^2}$	$x_1$	$\frac{T_0}{T_1}$	$\frac{T_0}{T_2} = \frac{T_0}{T_1} \times \frac{1}{\theta}$
$\kappa = 1/3$	$\infty$	$\infty$	$\infty$	$\infty$	0	$\infty$	1 (Case $a_1 = 0$ )
$1/6$	25	$1^{12}/_{13}$	325	169	0,279	364	1,12
$1/9$	16	$1^6/_{11}$	176	121	0,365	209	1,19
0	9	1	81	81	0,500	108	$1\frac{1}{3}$
$-1/3$	4	$4/7$	28	49	0,694	—	—
-1	$2^{1/4}$	$3/8$	$13^{1/2}$	36	0,800	$30^{3/8}$	$2^{3/4}$
$\mp \infty$	1	$1/5$	5	25	0,896	—	—
$5/3$	$1/4$	$1/16$	1	16	0,968	9,30	9,30

That is to say: for a gas *without cohesion* as one of the components of the mixture ( $a_1 = 0, \kappa = \infty$ )  $\lambda$  would have to be larger than the limiting value  $\infty$ , for a minimum to appear in the line  $C_2C_0$  in the neighbourhood of  $C_2$ . (Then  $T_0/T_2 < 1$  would be at the same time). For finite values of  $\lambda$  this cannot be satisfied, and the line  $C_0C_2$  proceeds with  $T_0 > T_2$  without a minimum.

For a gas with *feeble cohesion*, where e.g.  $\kappa = \sqrt{\frac{a_2}{a_1}} = 16$ ,  $\lambda = \frac{b_2}{b_1}$  must be  $> 1^5/_{11}$ , for a minimum to appear.  $T_0/T_2$  is then  $< 1,19$ .

For He—H<sub>2</sub>  $\frac{a_2}{a_1}$  is about 175, hence  $\kappa = 13,2$  according to an estimation of KEESOM (These Proc., March 28, 1907, p. 661; Ibid. April 25, 1907, p. 794). To this corresponds according to formula (c) the limiting value  $\lambda = 1,29$ . Now KEESOM estimated (loc. cit.) this value at about 2 for He—H<sub>2</sub>, and 2 being  $> 1,29$ , there is a minimum in the plaitpoint line in the case of He—H<sub>2</sub>. This minimum can be fully calculated by the aid of the formulae (2) to (8). The value of  $T_0/T_2$  is then smaller than about 1,25.

For  $\kappa = 2^{1/4}$ ,  $\lambda$  must be  $> 3/8$ , and then  $T_0/T_2 < 2^{1/4}$ . Etc., etc.

The larger therefore the value of  $a_1$  — the smaller in other words the value of  $\kappa$  — the smaller also the limiting value of  $\lambda$ , above which a minimum is to be expected, the sooner this will therefore appear, and at comparatively large corresponding values of  $T_0/T_2$ .

But as we already observed in § 1, all this refers only to the existence or non-existence of a *minimum* in the line  $C_0 C_2$ . That this line has the shape in question, depends on quite different circumstances — viz., as I already showed in June 21, 1905, p. 33—48 for  $b_1 = b_2$ , and further extended to the general case in later papers (particularly TEYLER I), it depends only on this, whether for the given value of  $\pi$  the value of  $\theta$  is found above that at which the *plaitpoint line* has a *double point* or not. And the criterion for this is fig. 1 of Oct. 25, 1906 (see also TEYLER II). If we are *above* the limiting line  $DBPAC'$ , we are in the region of type I, where one of the branches of the plaitpoint line runs from  $C_0$  to  $C_2$  (the other from  $A$  to  $C_1$  — see e.g. fig. 1 of Juni 21, 1905 and fig. 1 of Jan. 25, 1906). And *below* the limiting line we are in the region of type II (or III), where the branches of the plaitpoint line are  $C_1 C_2$  and  $AC_0$ . But for all this consult the papers cited.

April 1907.

APPENDIX. After I had written the above considerations, the Continuation of the last cited paper by K. ONNES and KEESOM appeared in These Proceedings, April 25, 1907, p. 795—798. There a condition is derived for the appearance of a minimum plaitpoint temperature, which is identical with that which I published Jan. 25, 1906 (formula (3), p. 581), at which result also VERSCHAFFELT (These Proc., April 24, 1906, p. 751) arrived a month later.

For on p. 796 K. O. and KEESOM give the condition (see formula (2)):

$$\sqrt[4]{\frac{\alpha_2}{\alpha_1}} = \frac{1}{3} \left[ -1 + \sqrt{1 + 3 \frac{b_2}{b_1}} \right].$$

Now in my notation  $a_2/a_1 = 1/2$  (see above; I denote viz. the component with the smallest value of  $a$  by the index 1; KEESOM does the reverse). Further  $b_2/b_1 = 1/2$ , so that the above formula passes into

$$\sqrt[4]{\frac{1}{2}} = \frac{1}{3} \left[ -1 + \sqrt{1 + 3/2} \right],$$

from which follows:

$$\lambda = \frac{x}{3 + 2\sqrt{x}},$$

being my above formula (c). And concerning this we have just proved that it is identical with my relation and that of VERSCHAFFELT (Jan. and April 1906), viz.

$$\theta = \frac{4\pi\sqrt{\pi}}{(3\sqrt{\pi}-1)^2},$$

which is of general application, irrespective whether the branch of the plaitpoint line starts from  $C_2$  towards  $C_1$  or towards  $C_0$ . As we already observed, this expression holds on the side of the component I, when  $\theta = T_2/T_1$  and  $\pi = p_2/p_1$ , so for the branch starting from what is point  $C_1$  with me. For  $C_2$  (KEESOM's  $K_1$ )  $\theta$  and  $\pi$  must simply be replaced by  $1/\theta$  and  $1/\pi$  (see above in § 3).

So in my opinion the footnote on p. 795 in the paper by K. O. and K. of April 25, 1907 is not accurate, for according to the above the conclusion of VERSCHAFFELT (and mine) does not require any qualification, because the formula<sup>1)</sup> given by us holds for any course of the plaitpoint line, irrespective of the fact whether the considered branch runs from  $C_2$  to  $C_1$  or to  $C_0$ . For the transition of the two types takes place gradually through the double point of the plaitpoint line, and hence the two types are analytically included in the same formula, so that only one expression exists for  $\frac{dT_x}{dx}$ ,

which holds equally for the two cases. And if any doubt should remain, this must be removed, when from the above the identity is seen between the relation derived last by K. O. and K., and the general one of VERSCHAFFELT and me.

It will be superfluous to observe that the so-called (homogeneous) "double *plaitpoint*" in the branch of the plaitpoint line  $C_0C_2$ , of which K. O. and K. speak, is identical with the fully discussed minimum and with the double point in the spinodal line, and should not be confounded with the "double *point*", found by me in the (whole) plaitpoint line, where the two branches of this line intersect, and which separates the two types I and II (or III), the data for which double point can be calculated for the general case only with great difficulty. (see Teyler I).

<sup>1)</sup> In the footnote on p. 795 it says maximum temperature; this must of course be minimum temperature.

**Astronomy.** — “*On periodic orbits of the type Hestia.* By Dr. W. DE SITTER. (Communicated by Prof. J. C. KAPTEYN).

The problem, of which some particular solutions will be treated here, is the following. Two material points  $S$  and  $J$ , having the masses 1 and  $\mu$ , move with uniform angular velocity  $n' = 1$  in circles in one and the same plane round their centre of gravity. The constant distance  $SJ$  is adopted as unit of length. Another material point  $P$ , with an infinitely small mass, moves in the same plane under the influence of the Newtonian attractions of  $S$  and  $J$ . This is the problem which has (for  $\mu = 0.1$ ) been so exhaustively treated by DARWIN in Vol. XXI of the *Acta Mathematica*. The particular solutions which are treated below are those in which the orbit of  $P$  is periodic and its limit for  $\text{Lim. } \mu = 0$  is an ellipse with a small excentricity, described round  $S$  as a focus with a mean motion not differing much from 3. If this limiting orbit (i.e. the undisturbed orbit) is a circle, then the solution is, in POINCARÉ's phraseology, of the first sort (*sorte*), and its period is  $T = \frac{2\pi}{n-1}$ . If the excentricity of the undisturbed orbit differs from zero, the solution is of the second sort, and the limiting value of the period for  $\text{Lim. } \mu = 0$  is  $\text{Lim. } T = 2\pi$ . These solutions of the second sort are at the same time of the second genus (*genre*) relatively to those of the first sort.

The solutions of the first sort are the orbits of DARWIN's “Planet A”. This family of orbits undergoes within the range here considered a transition from stability to instability, which has been discussed by POINCARÉ in an investigation contained in the articles 383 and 384 of his “*Méthodes Nouvelles*” (Vol. III, p. 355—361). The results there reached will be derived here by a different (and, as it seems to me, simpler) reasoning.

DARWIN's work also presents an example of an orbit of the second sort, viz. the orbit figured by him on page 281 and designated as  $\alpha_0 = - .337$ . Although POINCARÉ proves the existence of solutions of this kind, he seems to have overlooked the fact that DARWIN had actually computed one of them.

These solutions and their stability I wish to consider from the point of view of the general theory developed by POINCARÉ in the first and third volumes of the “*Méthodes Nouvelles*”. The following is a summary of those general theorems, proved by POINCARÉ, which will be used here. They are true for every problem capable of being reduced to two degrees of freedom, containing one variable parameter, and admitting for each value of this parameter a finite

number of periodic solutions. It need hardly be mentioned that their valency is restricted to a certain domain of the several variable quantities of the problem, of which it will however not be necessary to transgress the limits.

A periodic solution is completely determined by the values of the parameter and of one constant of integration or "element". The periodic solutions occur in families, the members of which are classified according to increasing or decreasing values of the parameter. These families may be graphically represented by curves  $\phi(\alpha, \beta) = 0$ , where  $\alpha$  is the parameter of the problem and  $\beta$  the determining element.

The stability or instability is determined by a certain quantity  $\alpha$ , which is by POINCARÉ called the characteristic exponent. If the period is  $T$ , then values of  $\alpha$  differing by a multiple of  $\frac{2\pi i}{T}$ , must be considered as identical. The following three cases are possible:

$\alpha T$  purely imaginary . . . . . the solution is *stable*  
 $\alpha T$  real . . . . . the solution is *evenly unstable*  
 $\alpha T$  complex, with imaginary part  $= \pi i$ : the solution is *unevenly unstable*<sup>1)</sup>.

A solution having the period  $T$  can as well be conceived to have the period  $T' = 2T$ . If it is unevenly unstable with reference to the period  $T$ , it is evenly unstable with reference to the period  $T'$ .

Within each family the exponent  $\alpha$  and the period  $T$  vary continuously with the parameter  $\alpha$ . The product  $\alpha T$  and the differential coefficient  $\frac{d\phi}{d\beta}$  become equal to zero for the same values of  $\alpha$ . The curve  $\phi = 0$  then either has a multiple point, or is tangent to a line  $\alpha = \text{const.}$  The family splits into two branches, or, which comes to the same thing, two families have one member in common. If  $(\alpha_0, \beta_0)$  is the point representing this common member, then we have the following rules.

The number of branches of the curve  $\phi = 0$  (i. e. the number of families of periodic solutions) for  $\alpha > \alpha_0$  differs by an even number from the number of branches for  $\alpha < \alpha_0$ .

The branches which part from the point  $(\alpha_0, \beta_0)$  towards the direction of increasing  $\alpha$  are alternately stable and evenly unstable<sup>2)</sup>. The

<sup>1)</sup> The names *even* and *uneven instability* have been introduced by DARWIN. POINCARÉ distinguishes them as instability of the first and second "classe". The relation of DARWIN'S quantity  $c$  to the exponent  $\alpha$  is given by the formula  $\alpha T = i\pi c$ .

<sup>2)</sup> To avoid circumlocution I speak of "stable and unstable branches", meaning branches whose points represent stable and unstable solutions respectively.

same thing is true of the branches on which  $x$  decreases. The two branches between which lies the part of the line  $x = x_0$  on which  $\beta < \beta_0$ , are either both stable, or both unstable, and similarly the two branches enclosing the other half of the line  $x = x_0$ . If  $T$  is the period of one of the branches and  $T'$  of another, and if  $T_0$  and  $T'_0$  are the values of these periods in the point  $(x_0, \beta_0)$ , then  $T_0$  and  $T'_0$  are mutually commensurable. If  $T''_0$  is their least common multiple, then  $\alpha_0 T''_0 = 0$ . If e. g.  $T'_0 = 2.T_0$ , then the instability is even with reference to the period  $T'$ .

As an illustration of these general rules I may be allowed to mention a few of the simplest cases.

1. The curve  $\phi = 0$  is tangent to the line  $x = x_0$ . There are two families, springing from a common member, which come into existence at this value of the parameter. One of them is stable, and the other is evenly unstable. An example of this is presented by DARWIN'S families  $B$  and  $C$  of satellites.

2. The curve has a double point. Two families are "crossing" each other, at the same time exchanging their stability.

3. The curve consists of one branch tangent to the line  $x = x_0$  and another branch intersecting the first in the point of contact. The two families which come into existence at this value of the parameter are both stable or both unstable. The third family, which exists both for  $x > x_0$  and for  $x < x_0$ , becomes stable if it was unstable and unstable if it was stable.

The cases 2 and 3 are the only ones occurring in the present investigation.

The proof of the above supposes that the problem can be reduced to the second order, so that there are only two characteristic exponents ( $+a$  and  $-a$ ). The choice of the parameter is determined by the way in which this reduction is effected, or is conceived to be effected. DARWIN uses the integral of JACOBI for this reduction. Consequently his parameter is the constant  $C$  to which this integral is equal. This constant  $C$  is a function of the two elements  $a$  and  $e$ . The first of these can be replaced by the mean motion  $n$ , or by the period  $T = \frac{2\pi}{n-1}$ . In consequence of the reduction of the problem by means of the integral of JACOBI one of these elements, say  $T$ , is eliminated. This therefore appears no longer as an arbitrary constant of integration, but is entirely determined by  $C$  and  $e$ . On the other hand  $C$  is entirely determined by  $T$  and  $e$ . Now DARWIN'S calculations show that  $T$  continually increases if  $C$  decreases. It is therefore irrelevant for our purpose whether we consider  $C$  or  $T$  as the

‡

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parameter of the problem. The parameter which I will use here is  $T' = 2T$ . This change from  $C$  to  $T'$  can also be conceived as no more than a simplification of language. Instead of saying: "the solution corresponding to the value of  $C$  for which the period of the solution of the first sort is  $\frac{1}{2} T'$ ", I say: "the solution corresponding to the value  $T'$ ".

In DARWIN'S work  $\mu$  has the constant value 0.1. If now we choose a convenient element  $\xi$ , we can conceive the curves  $\phi(T', \xi)$  to be drawn. Next imagine the same thing to be done for other values of  $\mu$ , and take  $\mu$ ,  $T'$  and  $\xi$  as rectangular coordinates. The curves  $\phi(T', \xi)$  belonging to the various values of  $\mu$  then produce a surface, every point of which represents a periodic solution.

If, on the other hand, we take for  $T'$  a fixed value  $T'_1$ , considering  $\mu$  as the variable parameter, then we have another problem, also admitting families of periodic solutions, which can be represented by curves  $\psi(\mu, \xi) = 0$ . If  $T'_1$  varies these curves describe again the same surface. The form of this surface will now be investigated. Its section by the plane  $\mu = 0.1$  then gives all periodic solutions of DARWIN'S problem.

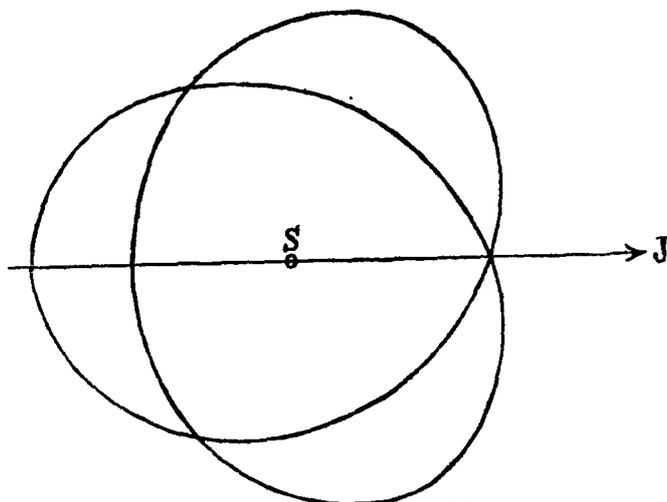
The element which I will use is  $\xi = e_0 \cos \tilde{\omega}_0$ , where  $e_0$  is the eccentricity and  $\tilde{\omega}_0$  the longitude of the perihelion of the undisturbed orbit, which is the limit of the orbit of  $P$  for  $\lim. \mu = 0$ . The longitude  $\tilde{\omega}_0$  is counted from a *fixed* axis which at the beginning of the period co-incides with  $SJ$ . The orbit of  $P$  is not periodic unless  $\tilde{\omega}_0$  has one of the two values 0 or  $\pi$ . Moreover at the beginning of the period  $P$  must be on the line  $SJ$ , i.e. there must be either opposition or conjunction.

Solutions of the first sort are characterised by  $\xi = 0$ . These solutions can have any period, therefore the whole plane  $\xi = 0$  is a part of our surface. The line  $\xi = 0$ ,  $\mu = 0.1$  represents DARWIN'S family  $A$ . For a value of  $T' = 2T$ , which lies between  $330^\circ$  and  $354^\circ$ , i.e. between  $1.83\pi$  and  $1.97\pi$ , this family loses its stability and becomes unevenly unstable. So there must be another family which at this point has a member in common with the family  $A$ . This new family must have the period  $T'$ , and is therefore of the second sort. If for the sake of argument we assume the change of stability to take place at the value  $T' = 1.9\pi$ , then we know of the branch of the curve  $\phi = 0$ , which represents this family, that for  $T' < 1.9\pi$  it is evenly unstable and for  $T' > 1.9\pi$  it is stable.

Now there are only four possible periodic solutions of the second sort, distinguished by the following positions of  $P$  at the beginning of the period:

- $\bar{B}$  :  $P$  in opposition in aphelion ( $\tilde{\omega}_0 = 0, \tilde{s} = +e_0$ )  
 $B'$  : ,, ,, ,, ,, perihelion ( $\tilde{\omega}_0 = \pi, \tilde{s} = -e_0$ )  
 $C$  : ,, ,, conjunction ,, perihelion ( $\tilde{\omega}_0 = 0, \tilde{s} = +e_0$ )  
 $C'$  : ,, ,, ,, ,, aphelion ( $\tilde{\omega}_0 = \pi, \tilde{s} = -e_0$ )

With reference to rotating axes, of which the axis of  $x$  co-incides with  $SJ$ , the orbits  $B$  and  $B'$  are identical, and similarly  $C$



Orbit of family  $B$  or  $B'$

Fig. 1.

and  $C'$ . The orbits  $B$  and  $B'$  are of the form represented in fig. 1. The orbits  $C$  and  $C'$  are of the same form, rotated through  $180^\circ$ , i.e. with the double point away from  $J$ .

The families  $B$  and  $B'$  are stable,  $C$  and  $C'$  are unstable. This is easily found by considering the equation which determines the exponent  $\alpha$ . This equation is (see POINCARÉ, Acta Math. XIII, p. 134):

$$n_1^2 \alpha^2 = \frac{d^2 \psi}{d\tilde{\omega}_2^2} (n_1^2 C_{22} - 2 n_1 n_2 C_{12} + n_2^2 C_{11})$$

Now using the variables employed by POINCARÉ l. c. pages 128 and 171, we find easily

$$n_1 = -1 \quad n_2 = 3 \quad C_{11} = C_{12} = 0 \quad C_{22} = -3 a_2^{-4}$$

If further in  $\psi$  (i. e. the average value of the perturbing function over one period) we neglect the terms which contain a higher power of  $e$  than the second, we find

$$\psi = \mu K e^2 \cos \varepsilon \quad \varepsilon = \tilde{\omega}_2 + 3 \tilde{\omega}_1$$

where  $\varepsilon$  is the mean longitude of  $P$  at the beginning of the period, and  $K$  is a positive constant.

We find thus

$$\alpha^2 = 3 \mu K e^2 x_2^{-4} \cos \varepsilon.$$

Thus, for positive values of  $\mu$ ,  $\alpha^2$  is negative, and therefore the orbit is stable, when there is opposition at the beginning of the period.

For positive values of  $\mu$  therefore  $BB'$  is stable and  $CC'$  is unstable, for negative values<sup>1)</sup> of  $\mu$   $BB'$  is unstable and  $CC'$  is stable. It is evident that, for  $\xi = 0$ ,  $B$  and  $B'$  co-incide, and similarly  $C$  and  $C'$ . The branch of  $\phi = 0$  which intersects  $\xi = 0$  in the point  $T' = 1.9 \pi$  therefore represents either the family  $BB'$  or the family  $CC'$ . In the first case it is stable, and therefore it must on both sides of the point of intersection bend round towards the right. In the other case it is unstable and encloses the stable part of the line  $\xi = 0$ .

Now DARWIN has, for  $C = 39.0$ , i. e.  $T' = 1.97 \pi$ , actually computed and drawn an orbit, which shows the form of fig. 1, viz.: the orbit  $x_0 = -.337$  which has already been quoted. This orbit thus belongs to the family  $B$ , but it also belongs to  $B'$ . It belongs to  $B$  if  $P$  is in aphelion at the beginning of the period and in perihelion in the middle of the period (being at both times in opposition to  $J$ ), and to  $B'$  in the opposite case. The branch of the curve  $\phi = 0$  which passes through the point  $T' = 1.9 \pi$  therefore represents the family  $BB'$ , and not  $CC'$ . Consequently it is stable, and that part of the section of our surface by the plane  $\mu = 0.1$ , which lies to the left of the line  $T' = 2 \pi$ , is thereby completely determined. This section is represented in Fig. 2. Stable families are there, and in the following figures, represented by heavy full lines, unevenly unstable families by broken lines, and evenly unstable ones by dotted lines.

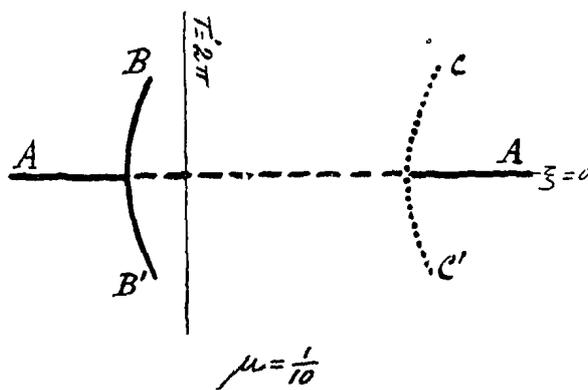


Fig. 2.

We next consider the section of our surface by the plane  $\mu = 0$ .

<sup>1)</sup> The meaning of a negative value of  $\mu$  is that the force emanating from  $J$  is repulsive, the force from  $S$  remaining attractive.

We know then that there are stable periodic solutions of the first sort with an arbitrary period, and of the second sort with the period  $T' = 2\pi$  and an arbitrary excentricity. The section therefore consists of the line  $\xi = 0$  and the part of the line  $T' = 2\pi$  between the points  $\xi = +1$  and  $\xi = -1$ . I wish, however, to confine myself to *small* values of  $\xi$ . This section is represented in Fig. 3.

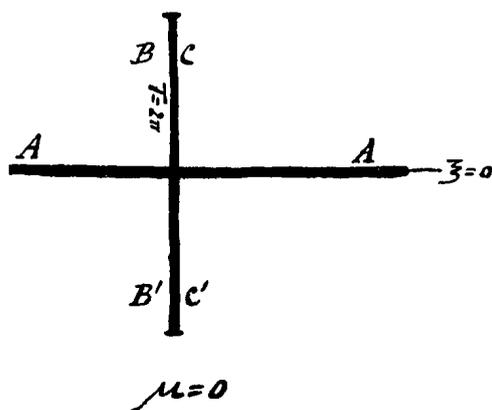


Fig. 3.

$BB'$ . This family being stable, that branch must on both sides of the point of intersection bend upwards, as is represented in fig. 4a.

Consider now the section of our surface by a plane parallel to, and at a very small distance from,  $\xi = 0$ . The orbits represented by the curves  $\chi(\mu, T')$  in this plane are all of the second sort. We can imagine these orbits to arise by a variation of  $\mu$  from the undisturbed periodic orbit of the second sort. They then appear as

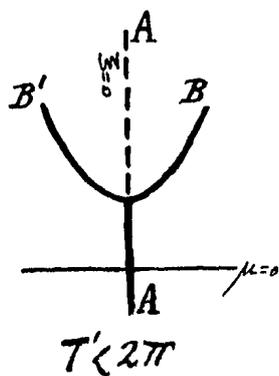


Fig. 4a.

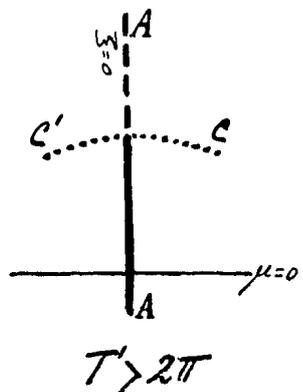


Fig. 4b.

solutions of a problem, in which the parameter is  $\mu$ ,  $\xi$  being kept constant, and thus  $T'$  (or  $C$ ) now is our element. These solutions have been studied by SCHWARZSCHILD (Astr. Nachr. 3506). For  $\mu = 0$  the period is  $2\pi$ . For small values of  $\mu$  there are (for each value of  $\xi$ ) two solutions, viz.  $B$  and  $C$  when  $\xi$  is positive,  $B'$  and  $C'$

when it is negative. The curve  $\chi = 0$  thus consists of two branches, both passing through the point  $\mu = 0, T' = 2\pi$ , and there exchanging their stability. Since now it has already been shown that the stable branch  $B$  is, for positive values of  $\mu$ , situated on the left side, the unstable branch  $C$  must be on the right side. The curves are represented in fig. 5.

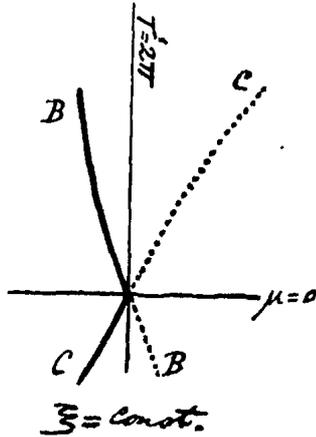


Fig. 5.

Our surface has thus been shown to consist of the plane  $\xi = 0$  and of two sheets, which pass through the line  $\mu = 0, T' = 2\pi$ , and then deviate to the left and to the right of the plane  $T' = 2\pi$ . The points of the left-hand sheet represent the stable family  $BB'$ , those of the right-hand sheet the unstable family  $CC'$ . This latter sheet therefore intersects the plane  $\mu = 0.1$  in a curve which on both sides of its point of intersection with the line  $\xi = 0$  bends off towards the right. In this same point of intersection the family  $A$  regains its stability, the stable part of the line  $\xi = 0$ , which represents this family, being enclosed between the two unstable branches of the section just considered. This state of things is rendered in the right-hand part of fig. 2. Also the form of the section of the surface by a plane  $T' = T'_2 > 2\pi$ , will need no further explanation. It is represented in fig. 4b. Whether this right hand sheet does reach up to the plane  $\mu = 0.1$ , so as to produce a real section, cannot be decided by this reasoning. If there is a point of intersection with the line  $\mu = 0.1, \xi = 0$ , this must correspond to a value of  $T'$  exceeding  $414.03 = 2.23\pi$ , since for this value the family  $A$  is still unevenly unstable, as is shown by DARWIN'S work. That the left-hand sheet does actually intersect the plane  $\mu = 0.1$  is shown by the existence of DARWIN'S orbit  $x_0 = -0.337$ , belonging to the family  $BB'$  (and also by the change of stability of the family  $A$ ).

Thus all results have been derived which have been found by POINCARÉ in the "Méthodes Nouvelles", already quoted. Naturally POINCARÉ also must leave the question, whether his results still hold for  $\mu = 0.1$ , unanswered.

It is not uninteresting to consider the solutions  $B$  and  $C$  from the point of view of the theory of perturbations. This can, of course, not teach us anything about their stability, but it will give information about the form of the curves  $\chi(\mu, T') = 0$  and  $\psi(\mu, \xi) = 0$  for small values of  $\mu$  and  $\xi$ . The period of the undisturbed solution is  $2\pi$ .

By the perturbing influence of  $J$  this is changed to  $T' = 2\pi + \tau$ . The conditions that the perturbed orbit shall be periodic are:

$$\int_0^{T'} \frac{d\tilde{u}}{dt} dt = \tau \qquad \int_0^{T'} \frac{d\lambda}{dt} dt = 6\pi + \tau,$$

where  $\lambda$  is the mean longitude of  $P$ . For the computation of the integrals we must use the mean motion affected by perturbations, i. e.  $n = 3 + \sigma$ . The left-hand members of these equations of condition are therefore functions of  $\tau$  and  $\sigma$ , and these two unknowns can be determined from them.

If in these equations of condition we neglect the square and higher powers of  $e$ , they become

$$\left. \begin{aligned} \tau &= \frac{na}{4} (2\pi + \tau) \mu [B^{(1)} \pm \{21 A^{(3)} + 10 A_1^{(3)} + 2 A_2^{(3)}\}] \\ 6\pi + \tau &= (3 + \sigma) (2\pi + \tau) - na (2\pi + \tau) \mu A_1^{(0)} \end{aligned} \right\} . \quad (1)$$

The upper sign in these equations must be used for the family  $CC'$ , the lower sign for  $BB'$ . The sum within the  $\{ \}$  being larger than  $B^{(1)}$ , we find that for the family  $BB'$   $\tau$  is negative, while for  $CC'$  it is positive, as has also been found above. Further the first equation shows that the numerical value of the differential coefficient  $\frac{d\tau}{d\mu}$  for the first family ( $BB'$ ) decreases if  $\mu$  increases, while for the other family it increases. Thus the left-hand branch of  $\chi(\mu, T') = 0$  has its concave side towards the line  $T' = 2\pi$ , and the right-hand branch its convex side, as is shown in fig. 5.

In the numerical computation we must not forget that the formulas (1) can only be considered as approximatively true. The solution of the equations is easily effected by means of the tables of RUNKLE, the argument for the determination of the different functions  $A_p^{(i)}$  being computed by

$$n = 3 + \sigma \qquad n^2 a^3 = f = \frac{10}{11}.$$

I find in this manner for the two families:

$$B: \quad \frac{\tau}{2\pi} = -0.085 \qquad T' = 1.83 \pi$$

$$C: \quad \frac{\tau}{2\pi} = +0.29 \qquad T' = 2.58 \pi$$

These are the periods of those orbits of the two families, which have  $\xi = 0$ , and which therefore co-incide with a member of the

family A, whose period is  $T = \frac{1}{2} T''$ . DARWIN'S computations show that the value of  $T''$  for which the families A and B co-incide must lie between  $1.836 \pi$  and  $1.97 \pi$ . The point of co-incidence of A and C is outside the region explored by DARWIN, the corresponding value of  $T''$  must therefore be larger than  $2.23 \pi$ .

If in the equations (1) we take account of the square of  $e$ , the right-hand member of the first must be multiplied by  $\sqrt{1-e^2}$ . In the second  $A_1^{(0)}$  must be replaced by

$$A_1^{(0)} + \frac{1}{4} e^2 \left( B_1^{(1)} \pm \{31 A_1^{(3)} + 24 A_2^{(3)} + 6 A_3^{(3)}\} \right)$$

and  $\frac{1}{2} e^2 \tau$  must be added to the second member. Now if we take  $T' = \text{const.}$  then  $\tau$  is constant and also  $\sigma$  can be taken to be constant. The second equation (1) then is of the form

$$\text{const.} = \mu (\tilde{P} + Qe^2) . . . . . (2)$$

Now we have  $\xi^2 = e^2$ , therefore (2) is approximately the equation  $\psi(\mu, \xi) = 0$ . For the family  $BB'P$  and  $Q$  are of opposite signs, for  $CC'$  they have the same sign. Thus the form of these curves as drawn in the figures 4a and 4b is confirmed. <sup>1)</sup>

**Physics.** — “*Contribution to the theory of binary mixtures. IV.*”

By Prof. J. D. VAN DER WAAALS.

Continued, see p. 849 vol. IX.

#### THE BINODAL CURVE.

We might think that for the determination of the binodal curve we could follow the following course. It is required for coexistence that besides the temperature three other quantities are equal, i. e.  $p$ ,  $q$  and  $M_1 \mu_1$ . If we now also trace the lines on which  $M_1 \mu_1$  is equal, we should have to seek in order to find a point of a binodal curve, the points satisfying the condition that the  $p$ ,  $q$  and  $M_1 \mu_1$  lines passing through this point intersect in still another point of the field. This search, however, being exceedingly difficult would give moreover no clear survey of the results. We shall, therefore not follow this course. Still I shall make some prefatory remarks on the course of this third group of lines. For it is by no means devoid of interest to know in which phases of a binary system the

<sup>1)</sup> This last paragraph has been added in the English translation.

molecular potential of one of the two components has the same value. We shall call this third group of lines "potential lines".

THE POTENTIAL LINES.

The value of  $M_1 \mu_1$  is equal to  $\psi - v \frac{d\psi}{dv} - x \frac{d\psi}{dx}$ ; by differentiation we find:

$$d M_1 \mu_1 = -v \frac{d^2 \psi}{dv^2} - x \frac{d^2 \psi}{dx^2}$$

or

$$d M_1 \mu_1 = v dp - x dq$$

If we want to know the shape of such a potential line, we must know  $\frac{dv}{dx}$  for such a line, which quantity we shall represent by

$\left(\frac{dv}{dx}\right)_{Pot}$ . For the value of this quantity we find then the expression:

$$\left(\frac{dv}{dx}\right)_{Pot} = - \frac{v \frac{d^2 \psi}{dx dv} + x \frac{d^2 \psi}{dx^2}}{v \frac{d^2 \psi}{dv^2} + x \frac{d^2 \psi}{dx dv}},$$

which may also be written:

$$\left(\frac{dv}{dx}\right)_{Pot} = \frac{v \frac{dv}{dx_q} - \frac{dv}{dx_p}}{\frac{dv}{dx_p} v - \frac{dv}{dx_p}}$$

So there is a locus in whose points  $\left(\frac{dv}{dx}\right)_{Pot} = \infty$ , and another in whose points  $\left(\frac{dv}{dx}\right)_{Pot} = 0$ . The former takes place when  $\frac{v}{x} = \frac{dv}{dx_p}$  i.e. this locus is the series of points in which lines drawn from the origin touch the  $p$ -lines. On the other hand  $\left(\frac{dv}{dx}\right)_{Pot} = 0$  if  $\frac{v}{x} = \frac{dv}{dx_q}$ ; for the points of the spinodal curve in which  $\frac{dv}{dx_p} = \frac{dv}{dx_q}$ , also  $\left(\frac{dv}{dx}\right)_{Pot}$  is equal to  $\frac{dv}{dx_p}$ .

The shape of the locus  $v = x \left(\frac{dv}{dx}\right)_p$  is different, according as the  $p$ -lines have the course as in the left region of the general  $p$ -figure, or as is the case in the middle region or in the right region. The

course of the  $p$ -lines being modified by the temperature, the value of  $T$  will also influence this shape.

Let us first put a left region at a value of  $T$  below  $T_{k_1}$  and also below  $T_{k_2}$ . Then tangents may be drawn to all  $p$ -lines from the origin. The points of contact on the side of the small volumes then form a continuous series of points which begins in the point in which the liquid branch of the curve  $\frac{dp}{dv} = 0$  intersects the 1<sup>st</sup> axis, and moves further and further away from this curve as it approaches the 2<sup>nd</sup> axis, remaining all the time at smaller volumes than those of the curve mentioned. The points of contact on the side of the large volumes also form a continuous series of point, which starts in the point in which the vapour branch of the curve  $\frac{dp}{dv} = 0$  intersects the 1<sup>st</sup> axis, and also moves further and further away from this curve as it draws near the 2<sup>nd</sup> axis. This series of points has always larger volume than the curve  $\frac{dp}{dv} = 0$ . So when a potential line passes through such a series of points it is directed parallel to the  $V$ -axis. The locus of the points in which a potential line runs parallel to the  $X$ -axis, and which is found by drawing tangents from the origin to the  $q$ -lines, is a curve consisting of one single branch, which at small volumes crosses the field from a certain point of the first axis to the point  $v = b$  and  $x = 1$ . But the shape of this curve is very different, dependent on the more or less complicated shape of the  $q$ -lines. Without entering into further details we shall only observe, that when  $q$ -lines run as is the case in the absence of  $\frac{d^2\psi}{dx^2} = 0$ , this curve will have no point in common with the preceding one; but if  $\frac{d^2\psi}{dx^2} = 0$  exists, and intersects  $\frac{d^2\psi}{dv^2} = 0$ , the curve on which  $\left(\frac{dv}{dx}\right)_{Pot} = 0$ , passes round  $\frac{d^2\psi}{dx^2} = 0$ , and twice intersects the line, on which  $\left(\frac{dv}{dx}\right)_{Pot} = \infty$ . These two points of intersection are again of importance for the shape of the potential lines. Then again a loop-potential line passes through one of these two points. In this case the double point is the point of intersection on the right, and the point of intersection lying on the left serves then again as isolated point, round which a series of potential lines run in closed figures. That in this case the point lying on the right is the double point, is in

connection with this that all potential lines terminate in the point  $v=b$  and  $x=1$ .  $M_1\mu_1$  is infinitely large on the line  $v=b$ , and on the second axis  $M_1\mu_1$  is negative infinite. In the point  $v=b$  and  $x=1$  the value of the potential for the first component must therefore be indefinite. When arriving at this point all potential lines touch the line  $v=b$ . In fig. 15 the course of the potential lines has been schematically represented for this case of non-miscibility in the liquid state. The first axis is cut or touched by the potential

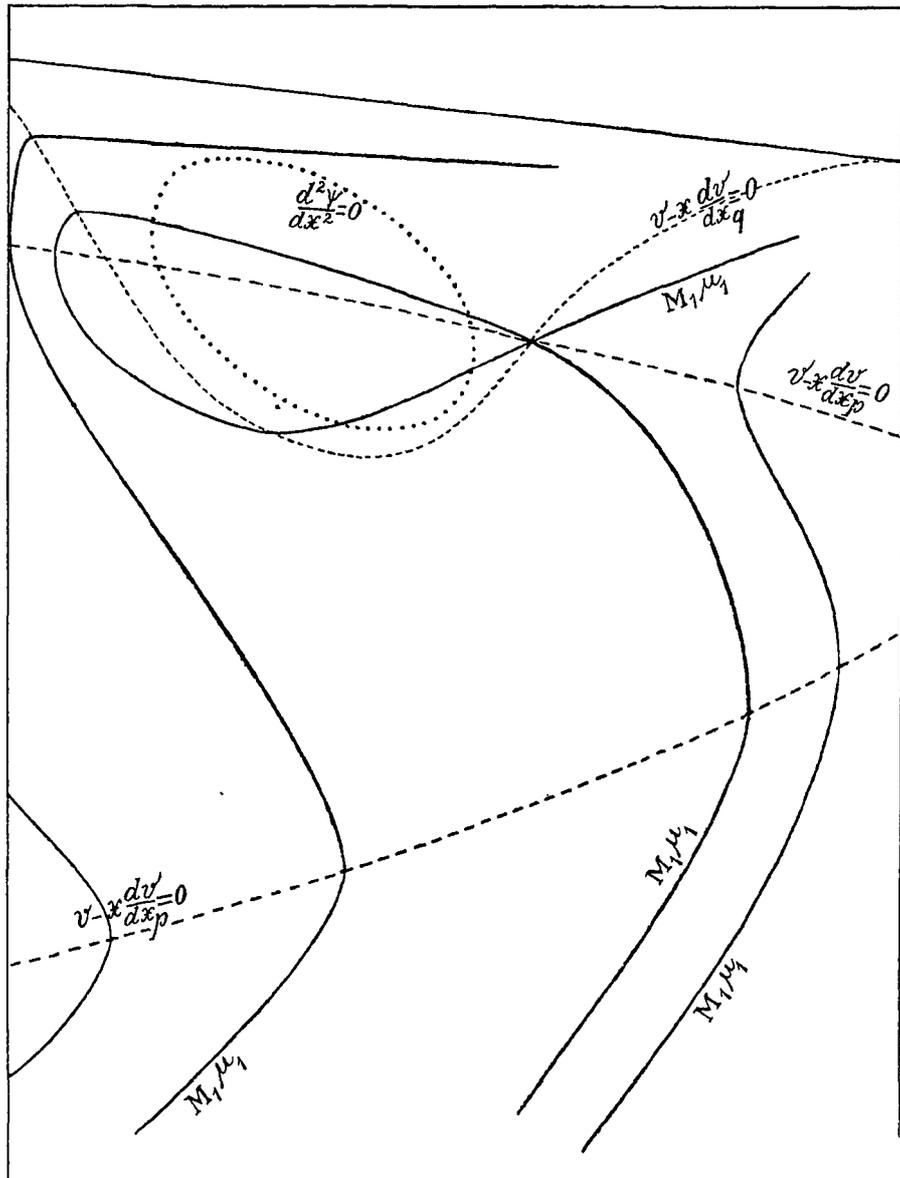


Fig. 15.

lines of every degree.  $M_1\mu_1 = -\infty$  for  $v = \infty$ . If  $v$  decreases,  $M_1\mu_1$  increases till the potential has reached a highest value in the point of maximum pressure  $\left(\frac{dp}{dv} = 0\right)$ . With further decrease of  $v$  the potential diminishes, till the final point of the unstable state is reached, where  $\frac{dp}{dv}$  is again equal to 0. There  $M_1\mu_1$  is minimum. If the point  $v = b$  is reached,  $M_1\mu_1 = \infty$ . With very large volume  $M_1\mu_1$  is approximately equal to  $MRT \log \frac{1-x}{v}$ , in which also a function of  $T$  is left out, which may generally be left out in the construction of the  $\psi$ -surface for definite value of  $T$ ; from this shape for  $M_1\mu_1$  it is seen that the portions of the potential lines which start from the 1<sup>st</sup> axis for large volume, may almost be considered as straight lines directed to the point  $x = 1$  and  $v = 0$ . If the potential line starts from the volume  $v_1$ , the equation of the initial portion is  $v = v_1(1-x)$ . If  $v_1$  should be  $= \infty$ , and so  $M_1\mu_1 = -\infty$ , the value of  $M_1\mu_1$  is negative infinite for every value of  $x$  for  $v = \infty$ , which it is also all along the second axis. The rule that for very large volumes the initial portions of the potential lines may be considered as straight lines already follows from the law of DALTON that each of the components in a mixture of gases behaves as if it alone was present in the volume. If  $v = v_1(1-x)$ , the density of the first component has the same value, and the quantities determined by the density, are the same; e. g. the pressure and the potential. If the circumstances are as assumed in fig. 15, there is of course also a locus where  $\left(\frac{d^2v}{dx^2}\right)_{M_1, v_1} = 0$ , which is again a loop-line passing through the double point of the potential lines. If the locus  $v - x \frac{dv}{dx_q} = 0$

does not intersect the other  $v - x \frac{dv}{dx_p}$ , all the potential lines have the simple shape which they have on the left side and on the right side in fig. 15.

If we suppose a left region at a value of  $T$  above  $T_{k_2}$ , the locus  $v - x \frac{dv}{dx_p} = 0$  is subjected to a modification. Then the two branches of  $\frac{dp}{dv} = 0$  have joined, and in the same way the two branches of this locus will join; but both lying outside  $\frac{dp}{dv} = 0$  the point of

junction will lie at larger  $x$  than the point of junction of the branches of  $\frac{dp}{dv} = 0$ . This junction must then take place in a point of inflection of a  $p$ -line, as is immediately seen when in a  $p$ -figure the tangents are drawn from the origin in the circumstances mentioned, in which it also appears that the point of contact then lies on a  $p$ -line of maximum value. So the point of junction mentioned is a point in which the tangent of a  $p$ -line in its point of inflection passes through the origin. From the differential equation of  $v - x \frac{dv}{dx_p} = 0$ , if  $v$  is taken as function of  $x$  and  $p$ , follows for this locus:

$$\frac{dp}{dx} = \frac{x \frac{d^2v}{dx^2_p}}{\frac{dv}{dp_x} - x \frac{d^2v}{dp dx}}$$

The potential lines of low degree have then lost the points in which they are directed vertically, and have then a very simple shape. With decreasing volume they no longer run back to smaller value of  $x$ .

In the second place let us choose a region in the middle, where the two points of intersection of  $\frac{dp}{dx} = 0$  and  $\frac{dp}{dv} = 0$  are found. Even though the two branches of  $\frac{dp}{dv} = 0$  remain entirely separated, this is not necessarily the case with the two branches of  $v - x \frac{dv}{dx_p} = 0$ . It is easy to see that the branch at the smaller volumes lies above  $\frac{dp}{dv} = 0$  only from  $x = 0$  to the double point of the  $p$ -lines. With higher value of  $x$  it lies below it. In the same way the branch of  $v - x \frac{dv}{dx_p} = 0$  at larger volumes lies below  $\frac{dp}{dv} = 0$  only from  $x = 0$  to  $x$  of the double point. This lower branch passes through the double point, and lies above  $\frac{dp}{dv} = 0$  with greater value of  $x$ . The two branches join as soon as there exists a  $p$ -line, for which the tangent in the point of inflection is directed to the origin. If at minimum critical temperature the line  $\frac{dp}{dv} = 0$  possesses a splitting point, the curve  $v - x \frac{dv}{dx_p} = 0$  is restricted to the left part, and is

closed for smaller value of  $x$  than that of the splitting point. If, however, the region extends far to the right, then also the right part of  $\frac{dp}{dv} = 0$  can again contain a closed part of  $v - x \frac{dv}{dx_p} = 0$ , with a top at a certain value of  $x$ , and the open side at  $x = 1$ . Also for regions lying entirely on the right side it remains of force that  $v - x \frac{dv}{dx_p} = 0$  lies within  $\frac{dp}{dv} = 0$ ; so that if  $\frac{dp}{dv} = 0$  no longer extends over the entire width,  $v - x \frac{dv}{dx_p}$  cannot extend any longer over the entire width either.

If also in such middle region, and at the same time in a right region we examine the course of the locus  $v - x \frac{dv}{dx_q}$ , where the potential lines are directed horizontally, we see when consulting figs. 5 and 6 that the locus mentioned remains restricted to smaller volumes than those of the line  $\frac{dp}{dx_v} = 0$  so long as the curve  $\frac{d^2\psi}{dx^2} = 0$  does not exist, or if it does, for all points outside this curve. If  $\frac{dp}{dx_v} = 0$  cuts the curve  $\frac{d^2\psi}{dx^2} = 0$ , the locus mentioned passes through these points of intersection. Within  $\frac{d^2\psi}{dx^2} = 0$  the line  $v - x \frac{dv}{dx_q}$  lies at larger volumes than those of  $\frac{dp}{dx_v} = 0$ . But then no intersection of  $v - x \frac{dv}{dx_q} = 0$  and  $v - x \frac{dv}{dx_p} = 0$  inter se is to be expected. Hence there is no question of a loop-potential line. The result would have been perfectly different, if we had also examined the course of  $M_2 \mu_2$ . But this may be considered superfluous, now that we know the course of the  $q$ -lines, so of  $M_2 \mu_2 - M_1 \mu_1$  and of  $M_1 \mu_1$ . This by no means exhausts the properties of the course of the potential lines, but as we are not going to avail ourselves of this third group of lines for the determination of the binodal line, I think that it will suffice to mention the above properties.

For the determination of the course of the binodal line we shall make use of the equation of p. 57, viz. :

$$d M_1 \mu_1 = v dp - x dq.$$

But first some preliminary remarks. Among all the lines to be discussed in a theory of mixtures the isobars and the binodal lines are to be

considered as the most important ones, because they can be the subject of experimental investigation. Though it is necessary for a clear insight that for a simple substance we know that below certain temperature the isotherm possesses unstable parts, and that we can indicate the limits of these unstable parts, yet the determination of the points of coexisting equilibrium is of the greatest importance for the experiment. In the same way it is, indeed necessary for a clear insight into a binary mixture that the existence of the unstable phases and their limits are known, so the spinodal curve; but the knowledge of the binodal line is of still more importance, and to determine the latter must be taken as the final end of all considerations, because it can constitute the subject of experimental investigation, and the results derived from our considerations can only be tested by experience in so far as they refer to the binodal line. If we are to admit an exception to this rule, this applies to the plaitpoints to whose existence could be concluded without an examination of the binodal curve being necessary. But moreover, it deserves attention that not even the whole of the binodal line can be realised by the experiment. The binodal line can possess portions lying in the unstable region, and others which are metastable. This has already been observed in the *Théorie Moléculaire* (Cont. p. 14), but appears in an ampler and more complete measure from the diagrams occurring in *These Proc.* March and June 1905. At the same time it appears there how very complicated the binodal line can be, when the spinodal curve hardly deviates from the usual shape. Hence if the more or less complexity of a plait is to be judged according to its spinodal curve or according to its binodal curve, a very different opinion will be arrived at.

Thus paying attention to the properties of the binodal curve I have been able to speak of a main plait and a branch plait in the last cited paper. In the same way, regarding only the binodal line and its nodal lines, we may speak of a transverse plait and a longitudinal plait, whereas, regarding only the spinodal curve, we shall have to consider these two as one single plait. However, to prevent confusion, it is desirable to follow one and the same terminology. At the moment it seems most desirable to me to consider particularly the spinodal curve when choosing the name, leaving that part out of account that may also sometimes exist, but which then encloses the concave-concave part of the  $\psi$ -surface. If no plait-point exists on the spinodal curve, or only one and then a realisable one, such a plait might be called a normal one. If besides there are a couple of heterogeneous plaitpoints found, we

might speak of an abnormal, or as I did in preceding pages of this communication, of a complex plait. If the spinodal curve has split up at certain value of  $T$ , which may take place in consequence of the curve  $\frac{dp}{dv} = 0$  having split up, there are two plaits, one of which might be called the right plait, and the other the left plait. If it has split up in consequence of a separation between the curves  $\frac{dp}{dv} = 0$  and  $\frac{d^2\psi}{dx^2} = 0$ , we might distinguish the two plaits by the names "transverse plait and longitudinal plait". Every time that the separation into two plaits takes place, two *homogeneous* plaitpoints make their appearance. With transition of a normal plait to a complex one a couple of *heterogeneous* plaitpoints appear. If then we wish to pay attention to properties of the binodal curve, other names might be thought desirable, but then it would be advisable to state distinctly that this is done to call attention to the special shape of the binodal line.

The equation  $dM_1\mu_1 = v dp - x dq$  simplifies for a simple substance to  $dM_1\mu_1 = v dp$ , and may be considered in this form to lead to the construction for the point of coexistence. This construction can be carried out directly if as axes a  $p$ -axis and a  $M_1\mu_1$ -axis is chosen, in which case we get a curve intersecting itself (Cont. II p. 4 fig. 1), or we can choose as axes a  $v$ -axis and a  $p$ -axis, and apply the law of MAXWELL. In the latter case we think  $dM_1\mu_1 = v dp$  written in the form:  $dM_1\mu_1 = d(pv) - p dv$ , the integral of which is

$(M_1\mu_1)_b - (M_1\mu_1)_a = (pv)_b - (pv)_a - \int_a^b p dv$ . For coexistence we must have  $(M_1\mu_1)_b = (M_1\mu_1)_a$ , and  $p_a = p_b = p_{Coex}$ , so that we get:

$$p_c(v_b - v_a) = \int_{v_a}^{v_b} p dv.$$

For a binary mixture we get for the determination of coexistence, so for the determination of the points of the binodal curve, the same simple equation:

$$dM_1\mu_1 = v dp,$$

when following the series of points for which  $dq = 0$  and so a  $q$ -line, in the execution of the construction.

Let us assume that we wish to apply MAXWELL'S law. Then following a  $q$ -line, we draw the value of  $p$  at every value of  $v$ , and

seek how many times a straight line may be drawn parallel to the  $v$ -axis, so that  $p(v_b - v_a) = \int_a^b p dv$ . If this can take place only once, the extremities of this straight line indicate the value of  $v$  of the phases coexisting with each other, and the distance of this straight line above the  $v$ -axis the value of the pressure for this pair of coexisting phases, and the chosen  $q$ -line cuts then no other branches of the binodal line. This may take place several times, when the chosen  $q$ -line passes 4 times through the binodal curve, or when there are 6 points of the binodal curve on the chosen  $q$ -line. To ascertain whether this can take place 0 times, or 1, 2 or more times, we have to pay attention in the first and foremost place whether or not the chosen  $q$ -line intersects the spinodal curve, and if it does, how many times. For every time when a  $q$ -line cuts the spinodal curve, there is either maximum pressure or minimum pressure for the points of this  $q$ -line. In the points of the spinodal curve a  $p$ -line touches the chosen  $q$ -line, and one and the same  $p$ -line, having either larger or smaller value than the  $p$ -line which touches, will pass through two points lying on either side of the spinodal line. Thus in fig. 7 (p. 738) there is maximum pressure in point 4 of the  $q_1$ -line, and minimum pressure in point 2, but for larger volume than that of point 4 the pressure is always smaller than in 4, and the smaller as  $v$  is larger, and in points of the same  $q$ -line in which  $v$  is smaller, the pressure is always larger than in 2, and the larger as we follow the  $q_1$ -line to its initial point, where  $p = \infty$ . If we now construe  $p$  as function of  $v$ , the  $p$ -line has a shape similar to that of an ordinary isotherm. For  $v = \infty$ ,  $\mu = 0$ , there is a maximum and a minimum pressure, and for  $v = b$ ,  $p = \infty$ . MAXWELL'S rule may then be applied, but only once.

So this  $q_1$ -line will possess two points of the binodal curve. In fig. 7 this will be the case for every  $q$ -line. For the line  $q = \infty$ , or for the first substance we find the coexisting phases of that substance, and for  $q = -\infty$  or for the second substance, the coexisting phases of the second substance. If starting from a certain point of the  $v, x$ -diagram we draw both the  $p$ -curves as function of  $v$ , viz. the  $p$ -curve when we follow the  $q$ -line which passes through the chosen point, and the  $p$ -curve when we remain at constant value of  $x$ , then the 2<sup>nd</sup> curve has always greater value of  $p$  than the first for all values of  $v$  smaller than that of the point chosen. Thus in fig. 7 the pressure in a point lying more to the left to which the  $q$ -line moves is smaller than is the case for constant value of  $x$  at the same value of  $v$ .

Now let the point from which we start be the point of the binodal curve lying on the vapour side. Then, if we apply MAXWELL'S rule to the two curves, it follows from the circumstance that  $p$  is always larger for the curve at constant  $x$ , in the first place that MAXWELL'S line for this  $p$ -curve lies higher than that for the  $p$ -curve when we follow the  $q$ -line, and in the second place that on the vapour side the binodal curve for given  $x$  always lies at larger volumes than the vapour volumes would be when every mixture was to be considered as homogeneous. In the same way on the liquid side at smaller volumes. Just as the binodal line lies outside the line  $\frac{dp}{dv} = 0$ , the binodal line lies outside the phases which would coexist if every mixture should behave as a simple substance. Properties which also immediately follow from the  $\psi$ -surface.

In fig. 7*b* only  $q$ -lines of lower degree intersect the spinodal curve. The  $q$ -line of the highest degree which still has points in common with the spinodal curve, which points are coinciding points is that passing through the plaitpoint. When we follow this  $q$ -line maximum and minimum pressure will have coincided, and drawing  $p$  as function of  $v$ , we get a line which has an horizontal tangent in the plaitpoint, and at the same time a point of inflection, just as an ordinary isotherm in the critical point. This is a remark which always holds for a plaitpoint, also for a hidden plaitpoint; but then the special point in the  $p$ -line where  $\left(\frac{dp}{dv}\right)_q$  and  $\left(\frac{d^2p}{dv^2}\right)_q$  is equal to 0, lies on the unstable branch. There is a third possibility for the situation of this special point, viz. that it lies on what we might call the liquid branch of the  $p$ -line, as will presently appear.

Let us now consider the case of fig. 8, and let us choose there a  $q$ -line which intersects the spinodal curve 4 times, as is the case with one of the  $q$ -lines drawn. If starting at large volume we follow this  $q$ -line, we meet, still at large volume, the spinodal line in a point where  $p$  has a maximum value; in the second point where the  $q$ -line leaves the unstable region for the first time, there is maximum pressure. In the third point where this  $q$ -line enters the unstable region again, there is again maximum pressure, and in the fourth point when the unstable region is finally left there is again minimum pressure. Now to draw  $p$  properly as function of  $v$ , we must know the value of  $\left(\frac{dp}{dv}\right)_q$ . Now:

$$\left(\frac{dp}{dv}\right)_q = \frac{dp}{d\alpha_1} \left(\frac{d\alpha_1}{dv}\right)_q + \frac{dp}{d\alpha_2}$$

which equation may be written in the following form:

$$\left(\frac{dp}{dv}\right)_q = -\frac{\frac{d^2\psi}{dv^2} \frac{d^2\psi}{dx^2} - \left(\frac{d^2\psi}{dx dv}\right)^2}{\frac{d^2\psi}{dx^2}}.$$

From this form we see that  $\left(\frac{dp}{dv}\right)_q$  is positive in the unstable region only when  $\frac{d^2\psi}{dx^2}$  is positive. If  $\frac{d^2\psi}{dx^2}$  is negative, then  $\left(\frac{dp}{dv}\right)_q$  is again negative in the unstable region, and when the  $q$ -line intersects the curve  $\frac{d^2\psi}{dx^2} = 0$ ,  $\left(\frac{dp}{dv}\right)_q = \infty$ . In fig. 16 the course of  $p$  as function of  $v$  when this  $q$ -line is followed, has been schematically represented.

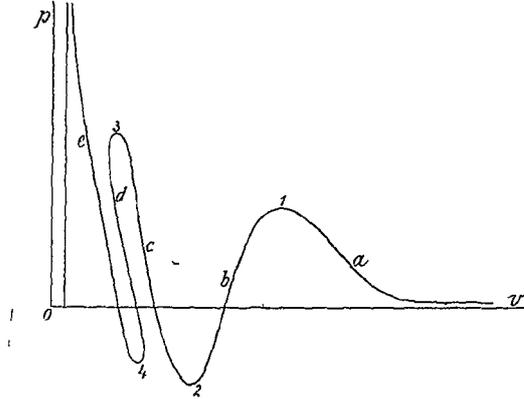


Fig. 16.

Now we have to examine how many points of the binodal line lie on this  $q$ -line. For this discussion I shall represent the branch right of point 1 by  $a$ ; the branch between 1 and 2 be then the  $b$ -branch etc. The number of times that MAXWELL'S rule can now be applied, is equal to the number of combinations in two of 4 quantities. Thus branch  $a$  could be combined, not with branch  $b$ , but with branches  $c$ ,  $d$  and  $e$ . The branch  $b$  may be found combined with  $d$  and  $e$ . And finally branch  $c$  with  $e$ . We do not mean to say that the application in those 6 cases is always actually feasible. This will be discussed presently when we discuss other  $q$ -lines. But for the  $q$ -line chosen here, it is really possible to trace those 6 MAXWELL lines. And then this  $q$ -line must cut the binodal curve 12 times. These 12 points of intersection are to be found in fig. 17: In this figure the  $q$ -line has the shape of fig. 8. It intersects the

spinodal curve, which has also been drawn in this figure, four times. It has a maximum and minimum volume. Between the points of largest and smallest volume the locus  $\frac{d^2\psi}{dx^2} = 0$  must be thought.

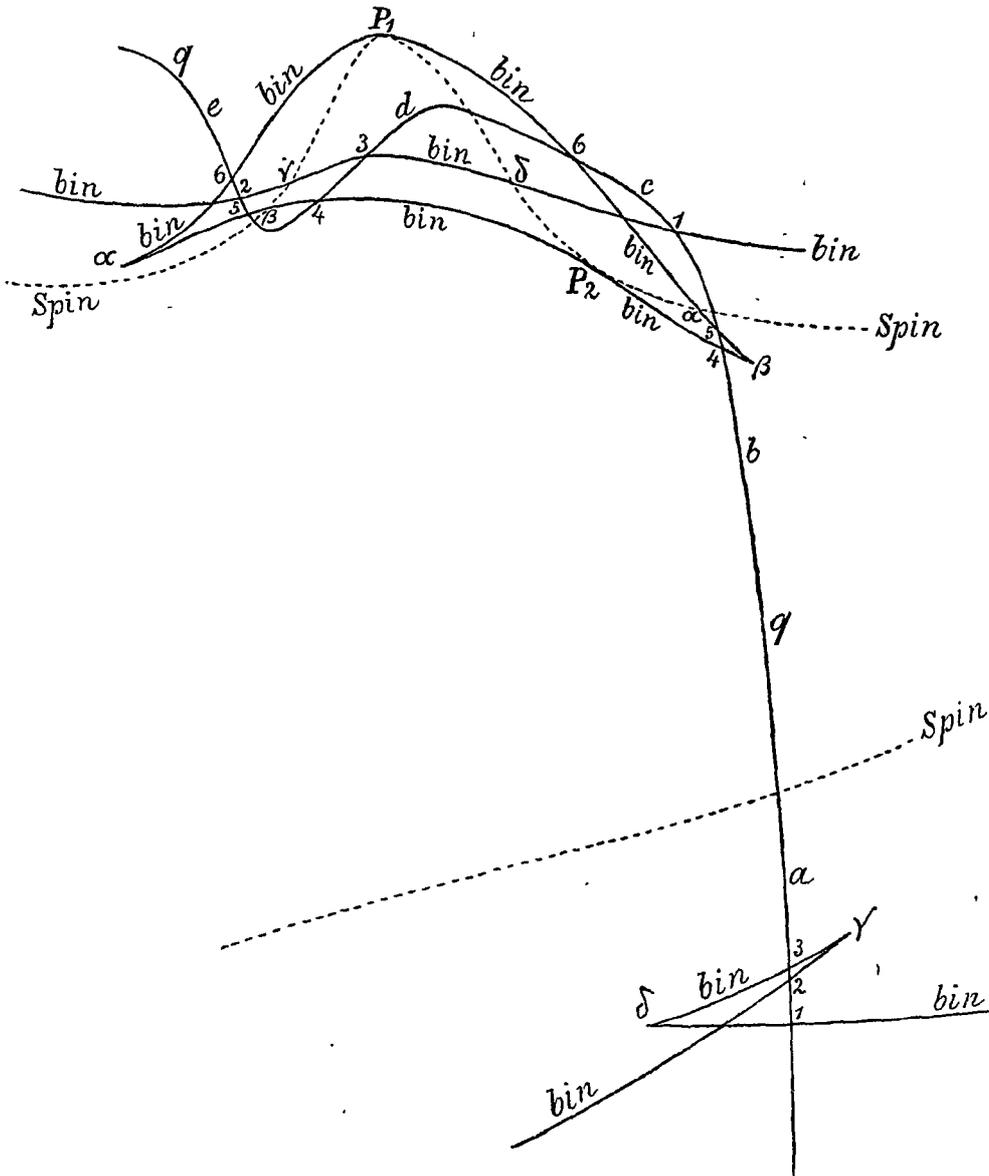


Fig. 17.

In this fig. 17 the binodal line has further been drawn, and on account of its intricate shape, it has been several times indicated by the sign *bin*. We may consider this binodal curve as consisting

of two separate parts. First that part that we might call vapour-liquid binodal curve. The liquid branch of this part has a regular course, but the vapour line branch has the well-known shape with two cusps. The nodal line belonging to the cusp  $\gamma$ , has its other extremity in the point  $\gamma$ , where the liquid branch of this binodal line passes through the spinodal curve. In the same way the two points indicated by  $\delta$  belong together as extremities of one same nodal line. The remaining part of the binodal curve forms a curve closed in itself. For this part of the binodal curve the two heterogeneous plaitpoints  $P_1$  and  $P_2$  are in the first place of importance. The points on the right and on the left of  $P_1$  lie in the stable region, the points on either side of  $P_2$  in the unstable region. If we continue the branch on the right of  $P_1$ , and pass through the spinodal curve in the point  $\alpha$ , then to this point as an extremity of a nodal line belongs another point  $\alpha$  as the other extremity of this nodal line, and there must again be a cusp for the binodal curve for this second point  $\alpha$ . In this second point  $\alpha$  the binodal curve returns again to higher value of  $w$ , and if it then meets the spinodal curve in the point indicated by  $\beta$ , another point  $\beta$  belongs to this, at which the right branch has a cusp. From this point the remaining part of the binodal curve has only points in the unstable region, and the points lying between the two points  $\beta$  are extremities of nodal lines which approach each other and coincide in  $P_2$ .

To find the 12 points in which this  $q$ -line cuts the binodal curve, let us apply MAXWELL'S rule to that portion of the  $p$ -figure with the branches  $a$ ,  $b$  and  $c$ , and determine the points denoted by 1. Let us also add the branch  $d$ , then the equality between the areas above and below the straight line would be disturbed, if the same straight line is retained, i. e. in this sense that the total amount of the areas above the straight line would be too large. From this follows that we must trace the straight line higher. For the points of the binodal curve which are determined by the combination of  $a$  with  $d$ , the pressure is, therefore, larger, while, as the figure shows, the volumes are both smaller than those of the corresponding points 1. The points determined by this combination have been indicated by 3. If we now also add the branch  $e$ , the pressure must again decrease. Then we determine the points denoted by 2. It will presently appear that the pressure in 2, though it is diminished, is still larger than in the points 1. By means of the combination of  $b$  with  $d$ , both branches in the unstable region, we determine the points 4; and after addition of the branch  $e$  the points 5, which must have lower pressure than the points 4. Finally the combination of  $c$  with  $e$  remains. Now

the situation of the  $q$ -line which we have chosen, is such, that the branch  $c$  remains on the right of the points of three-phase-pressure. From this ensues that if we have construed the  $p$ -line in fig. 16 correctly, the application of MAXWELL'S rule to the combination ( $c, e$ ) must yield a larger pressure for the points 6 than for the points 1; but it also follows from this that the pressure for the points 2 (combination of  $a, e$ ) lies between  $p_1$  and  $p_6$  — and so  $p_2 > p_1$ . But not all these 12 points are realisable. Every time an unstable branch occurs in the combination the nodes determined by this combination are not to be realised. So the points 3 (combination  $a, d$ ), the points 4 (combination  $b, d$ ), and the points 5 (combination  $b, e$ ) are not to be realised under any circumstances. Thus already 6 of the 12 points are excluded as belonging to unstable coexisting equilibria. Of the remaining 6 points 2 more are excluded, if metastable states are set aside. So summarising we determine the following points by means of the combination put by the side of it:

points	combination	
1 . . .	$a, c$ . . .	stable
2 . . .	$a, e$ . . .	metastable
3 . . .	$a, d$ . . .	unstable
4 . . .	$b, d$ . . .	unstable
5 . . .	$b, e$ . . .	unstable
6 . . .	$c, e$ . . .	stable

To construe all the points of the binodal curve we should have to treat all the  $q$ -lines in a similar way. For the first component ( $q = -\infty$ ) the  $p$ -line is the ordinary isotherm, in the same way for the second component ( $q = +\infty$ ) the isotherm for this component. So with increase of the value of  $q$  such a gradual change of the  $q$ -line must take place that it passes from the first shape to the second. With very large volume these extreme shapes may be considered to coincide. This is also the case with all intermediate forms. The modification remains chiefly restricted to the smaller volumes, and in the case of  $b_1 = b_2$  such a conclusion would be admissible also for the exceedingly small volumes. So long as the  $q$ -line (see fig. 4 and fig. 8) is still of so low a degree that it does not even pass through the lowest point of  $\frac{d^2\psi}{dx^2} = 0$ , the  $p$ -line has still the usual shape of an isotherm. Not before the  $q$ -line touches  $\frac{d^2\psi}{dx^2} = 0$ , does a special point make its appearance in the unstable branch. For this point of contact

$\left(\frac{dp}{dv}\right)_q = \infty$ , but  $\left(\frac{dp}{dv}\right)_q$  still remains positive on the left and on the right of that point. With somewhat higher degree of  $q$ ,  $\frac{d^2\psi}{dv^2} = 0$  is intersected twice, and two points may be pointed out in the  $p$ -line in the unstable branch where it is directed vertically. Between these 2 points  $\left(\frac{dp}{dv}\right)_q$  is negative. But then too the  $p$ -line has but 3 branches, and so MAXWELL'S rule can only be applied once; then we find only two points of the binodal curve, viz. a point indicating a liquid volume lying in the left side of the figure, and a point indicating a vapour volume, lying much more to the right side, but still remaining sufficiently on the left of the double point of the vapour binodal curve. Then the  $q$ -line cuts the binodal curve in no other points on the vapour side. If the value of  $q$  rises higher, a third special point appears again on the unstable branch of the  $p$ -line, i. e. when the  $q$ -line begins to have 4 points of intersection in common with the spinodal curve. This will be the case when it passes through the hidden plaitpoint  $P_2$  (see fig. 17). Then it touches the spinodal curve, but in such a way that  $\left(\frac{d^2v}{dx^2}\right)_q$  has the reversed sign of  $\left(\frac{d^2v}{dx^2}\right)_{spin}$ . The rule that in a plaitpoint the  $p$ -line and the  $q$ -line envelop the plait is, accordingly, restricted to the realisable plaitpoints. It must run exactly the other way about for hidden plaitpoints. So there  $\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)$  has the reversed sign of  $\left(\frac{d^2v}{dx^2}\right)_{spin}$  and of  $\left(\frac{d^2v}{dx^2}\right)_{bin}$ . In this third special point of the unstable branch of the  $p$ -curve

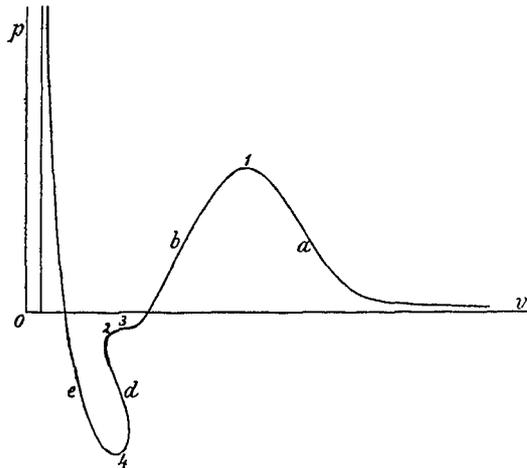


Fig. 18.

$\left(\frac{dp}{dv}\right)_q = 0$ , and also  $\left(\frac{d^2p}{dv^2}\right)_q = 0$ , and then the  $p$ -curve has the shape of fig. 18.

For  $q$  above this value the spinodal curve is cut in 4 points. The two new points of intersection lie then on the left and on the right of  $P_2$ , and at the beginning in the neighbourhood of this point. Then a portion lying in the stable region has been added to the  $q$ -line, from which we derive that  $p$  is smaller in the point of intersection lying on the right than that lying on the left. Not until now has the  $p$ -line the shape of fig. 16, but the branch  $c$  is still very small then, and the pressure of point 3 of this figure only little higher than of point 2. From this moment there could be question of the application of MAXWELL'S rule to the 5 branches  $a$ ,  $b$ ,  $c$ ,  $d$  and  $e$ , and so of the determination of the 12 points of the binodal curve. But at the beginning not all these 12 points are real. The application for the combination of the first and the last branch is certainly feasible, and it yields a couple of realisable points for the binodal curve, and in contradiction with our result when we treated this combination for the  $q$ -line in fig. 17, the points defined in this way are not metastable but stable. No less is the application possible for the combination  $(b, d)$ , and the two points determined then lie in the unstable region, and can be represented by the points 4 of fig. 17, provided they are shifted nearer the point  $P_2$ . The rule cannot be applied to the remaining 4 combinations. For the possibility of the application to the combinations  $(a, c)$  it is required that the length of branch  $c$  be such that the pressure of point 3 (fig. 19) be at least

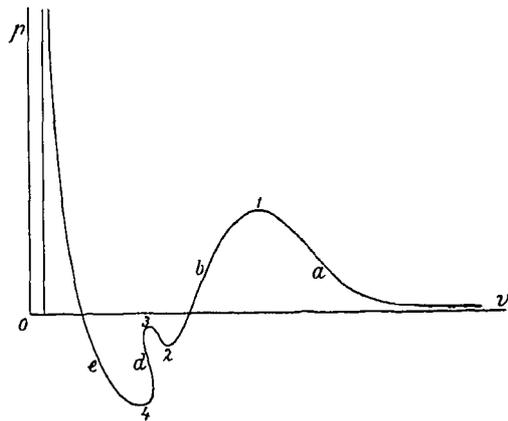


Fig. 19.

positive; and even this is not sufficient. If, namely, we have from point 3 a line //  $v$ -axis, and if then the area between the branches

$b$  and  $c$  and this line parallel to the  $v$ -axis is smaller than the area between the branches  $a$  and  $b$  above this parallel line, MAXWELL'S line would have to lie higher, and hence is not possible. A fortiori the combination  $(a, d)$ , which would require a still higher value of the pressure of MAXWELL'S line, will be excluded. For similar reasons the combinations  $(b, e)$  and  $(c, e)$  must be rejected. From this follows that the  $q$ -line which is of somewhat higher degree than that passing through  $P_2$ , must remain on the left side before the point  $a$  of fig. 1, and on the right side of the ridge of the vapour branch of the binodal line. If we continue to raise the value of  $q$ , the possibility of the combinations  $(a, c)$  and  $(a, d)$ , begin simultaneously, i. e. when the pressure of the point 3, which may be considered as the top of  $c$  and  $d$ , has risen so high that the MAXWELL line for the combination  $(a, c)$  would just go through point 3. In the same way the possibility for the combinations  $(b, e)$  and  $(c, e)$  begins at the same time, i. e. when the pressure of point 2, which is the lowest point of the branches  $b$  and  $c$ , has descended so low, that the MAXWELL line for the branches  $c$  and  $e$  would just pass through point 2. If all these possibilities exist, the twelve points can be pointed out on the  $q$ -line.

Which of these two simultaneously beginning possibilities presents itself first on rise of the degree of the  $q$ -line, will probably not be bound to a general rule. If we now follow such a  $q$ -line, beginning at small volume on the left side of fig. 17, we first meet point 2 on the binodal curve, which proceeds regularly from left to right on the liquid side; then 6 and 5 follow before we pass through the spinodal curve. When the  $q$ -line rises again, we meet 4 and 3, which have then to lie more to the right than on the  $q$ -line, for which fig. 17 has been drawn. When the  $q$ -line again descends we first meet point 1, then 6, afterwards 5 and 4, and at last on the vapour side the points 3, 1 and 2 in this succession. But of all these points only the points 2 are stable. The points 1 and 6 are metastable. The others are unstable. And on further rise of  $q$  we reach that special  $q$ -line which is to be considered as the principal one for the phenomena of coexistence, and which, with three-phase-equilibrium, passes through the three coexisting phases. This coexistence of three phases is met with when (see fig. 16) the MAXWELL line for the combination  $(a, c)$  is the continuation of the line for the combination  $(c, e)$ . At the same time this line is also the MAXWELL line for the combination  $(a, e)$ . Then the points 1 and 2 or 2 and 1 coincide on the vapour side. On the liquid side on the left the points 2 and 6 or 6 and 2 coincide, on the right on the liquid side the points 1 and 6 or 6 and 1. The points 3, 4 and 5 have remained; of them

3 and 4 are unstable coexisting equilibrium, and 5 is metastable. In this case of three phase pressure the second component occurs in the vapour in a greater measure than in the two liquids, in connection with the circumstances which give rise to this figure, viz. that the second component has higher value of  $b$  and lower  $T_k$  than the first. In fig. 3 Cont. II, p. 11 the course of the pressure is represented for the vapour-liquid binodal curve for this case.

With continued rise of the degree of  $q$  the  $p$ -curve, which entirely deviates from the shape of a simple isotherm for the last chosen values of  $q$ , must return to such a simple shape without abrupt changes. Thus the existence of 5 branches ceases when the  $q$ -line passes through  $P_1$ . The branches  $c$ ,  $d$  and  $e$  have then decreasing pressure with increasing volume. Only there is then a point where  $\frac{dp}{dv_q}$  and  $\frac{d^2p}{dv_q^2}$  is equal to 0 on this descending branch. But with still higher value of  $q$  also this particularity has vanished, and we approach to the usual shape of an isotherm. Already beforehand the  $q$ -line which above touches  $\frac{d^2\psi}{dx^2} = 0$ , was not found to run back to larger volumes in the unstable branch  $d^1$ .

If we increase the temperature to  $T_{k_2}$  a new plaitpoint  $P_3$  makes its appearance at  $x = 1$  and  $v = (v_k)_2$ . With further increase of the temperature the characters of the two realisable plaitpoints  $P_1$  and  $P_3$  begin to approach to each other. In fig. 17 the closed binodal curve belongs to  $P_1$ . Above a certain temperature, which I called transformation temperature (These Proc. March 1905), this closed binodal curve passes to  $P_3$ . At this transformation temperature the pairs of points  $\beta$  and  $\gamma$  have coincided on the spinodal curve in fig. 17, and two branches of the binodal curve touch, and  $\frac{d^2v}{dx^2}$  is the same for these two branches. But for further particulars I refer to the already frequently cited communication. We must only bear in mind that in the case treated here  $T_{k_2} < T_{k_1}$ , whereas in the figure which I gave before for this transformation it was assumed that  $T_{k_2} > T_{k_1}$ . Regarding the properties of the binodal curve we may then speak of a principal plait and of a branch plait. At much higher  $T$ ,  $P_3$  and  $P_2$  have coincided, and the binodal curve has become a normal simple line. (To be continued).

1) Strictly speaking the change of the  $p$ -line with increasing value of  $q$  is not a moving away from and then a return to the shape of an isotherm. It must be regarded as a progressive development, which proceeds in the same sense. To the last  $q$ -line belongs then also the infinitely large pressure along the line  $v = b$ . This portion is however, not necessary for the description of the binodal curve, at least when the plaitpoint  $P_1$  exists.

(June 21, 1907).

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

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PROCEEDINGS OF THE MEETING  
of Saturday June 29, 1907.

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(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundigé  
Afdeling van Zaterdag 29 Juni 1907, Dl. XVI).

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**Geology.** — “*On ore veins in the province of Limburg*”. By Prof. A. WICHMANN.

(Communicated in the meeting of March 30, 1907.)

In the spring of 1856 the ex-colonel of the Dutch East-Indian Army P. VAN SWIETEN, at the Hague, founded a “Mining Society for the Netherlands”<sup>1)</sup>, which obtained the concession for the mining field “Marie” in the southernmost part of the province of Limburg<sup>2)</sup>, in order to search for coal. After the first borings at Epen and Simpelveld had remained unsuccessful, the hamlet of Bommerig<sup>3)</sup>, community of Wittem, was taken, where on Oct. 11, 1856, a lode of ore was discovered of 0,80 meter thickness, at a depth of 56,20 M. and consisting chiefly of quartz and galena. Although it was suspected at once that this lode communicated with the one worked at Bleiberg in Belgium, situated to the SSE., yet the working of this lode was not taken in hand because of the great expense, involved in sinking a shaft. After this the Society continued its investigations in other parts of the mining field with insufficient results until it was dissolved after the available funds had been exhausted.

It has been known for a long time that the devonian and carboniferous strata in the environs of Aachen (Aix-la-Chapelle), extending mainly from the North-east to the South-west, are cleaved by faults directed almost perpendicularly to them and which appeared to be of great importance for the formation of ores<sup>4)</sup>. These masses of ores were found sparingly in the devonian system, mostly in those, belonging to the carboniferous limestone and only once — it was thought — in those of the coal-measures, namely at Bleiberg.

1) Nieuwe Rotterdamsche Courant, Thursday, May 22, 1856, N<sup>o</sup>. 140. The foundation act dates from June 11, 1856 (Dutch State Gazette, Thursday, July 10, 1856 N<sup>o</sup>. 162).

2) Situated a little over a kilometer to the North-east of Epen and  $\frac{1}{2}$  kilometers south of Mechelen.

3) Nieuwe Rotterdamsche Courant, Thursday, October 16, 1856; N<sup>o</sup>. 286. P. VAN SWIETEN. Rapport sur les opérations de la Société de l'union minérale pour la Néerlande de 1856 à 1857. Annales des Travaux publ. de Belgique XVI. Bruxelles 1857—58 p. 266—267 Pl. V.

4) C. DANTZ. Der Kohlenkalk in der Umgebung von Aachen. Zeitschr. d. D. geolog. Gesellsch. XLV. 1893 p. 599—683, Taf. 26. W. SCHULZ. Führer des Berg- und Hütten-Ingenieurs durch die Umgegend von Aachen. Aachen 1886, p. 37—41 m. Karte. G. D. UYLENBROCK. Le sud-est du Limbourg néerlandais. Annales de la Soc. géolog. de Belgique XXXII. Liège 1904—05. M. pag. 151—104., Pl. V.

G. DEWALQUE. Essai de carte tectonique l. c. Pl. IV.

On the most important fault — called by UJLENBROEK the “Geul Valley fault” — lie the mines Fossey, near Hergenraed (Rhenish Prussia), Moresnet (neutral territory) and Bleiberg (Belgium). Excepting the contact seams, containing calamine, the ores are galena, being the oldest formation as usual, zinc-blende and pyrites. The vein, found at Bommerig more than 50 years ago in the lowest stratum of the productive carbon, shows that from the south-east to the north-west the ores seek more and more the younger strata<sup>1)</sup> and that the direction of the Geul valley fault begins to deviate more towards the north-north-west after Bleiberg.

For years numerous borings were made in a more northern part of Limburg, which led to the sinking and working of some coal-pits. In December 1905 Mr. L. RUTTEN at Utrecht found on the dump of the mine “Carl”<sup>2)</sup> some pieces of ore which he presented to the Mineralogical-Geological Institute at Utrecht. Further investigations, undertaken by him, showed that these ores originated from a vein, met when sinking the shaft, at a depth of 278 metres, but of which the dip and direction had not been determined. He succeeded in securing a number of pieces, belonging to private people. The vein has only a thickness of 0.20 M. On the clay-containing salband pyrites has deposited, while the vein mass proper consists of calcite, developed in the cavities in the form of crystals, on which sometimes also crystals of pyrites are found. Beside this vein ores were also found, likewise on joints of the sandstone of the mine “Carl”, namely pyrites, but also zinc-blende, copper, pyrites, and galena. Moreover crystals of calcite are always found and generally dolomite.

In the mine Oranje-Nassau, near Heerlen, similar formations seem to occur, at any rate crystals of calcite, covered with pyrites, are found here on joints. Peculiar is here the regular coalescence, caused by the small cubes of pyrites accumulating at the poles, then continuing themselves on the obtuse edges of the scalenohedra and here gradually disappearing.

We finally point out that while in the Stolberg district the veins of galena, pyrites, zinc-blende, and calcite are still mostly bound to the carboniferous limestone these minerals occur in the more western Worm district on joints of the carboniferous sandstone, which is a more recent horizon, a phenomenon which repeats itself at Heerlen.

<sup>1)</sup> At Eupen they still occur in the devonian system.

<sup>2)</sup> Situated at 1½ kilometers east of Heerlen.

**Physiology.** — “*Nerve influence on the action of the heart. First communication. Genesis of the alternating pulse.*” By Dr. L. J. J. MUSKENS. (Communicated by Prof. H. ZWAARDEMAKER).

(Communicated in the meeting of April 26, 1907).

Whereas in 1897<sup>1)</sup> the writer has shown, that in the “pulsus regulariter intermittens” of the frog we have to see a result of slowed conduction between sinus and auricle<sup>2)</sup>, or between auricle and ventricle, which was later accepted by WENCKEBACH<sup>3)</sup> and recently proved by MACKENZIE<sup>4)</sup> for man, the problem of the pulsus alternans did not profit by the application of physiology on the diseased heart. It is true, that already years ago Traube directed the attention on those types of P. A. in which the period between the weak beat, and the next stronger one is smaller than between the larger and the smaller contraction, where i. o. w. the greater contraction commences too early. But until now only OEHRWALL<sup>5)</sup>, W. STRAUB<sup>6)</sup> and TRENDELENBURG<sup>7)</sup> have gone into the analysis of allied heart-curves of the frog, following up the way which had led to the elucidation of the intermittent pulse.

It is clear, that for this analysis we must not join those observers, who think that the explanation of the P. A. by inotropic influence amounts to something more than a simple periphrase of the fact, that every other pulse is weaker. For this misconception brings with it the additional drawback, that it cuts off the way for all further analysis.

In the alternating contraction of the ventricle we have to do not with a simple pathological phenomenon but rather with a general physiological function that makes its appearance in many circumstances, which tends to appear as well in vertebrate as invertebrate animals under uncommon conditions. We have here to deal with a capacity of the cardiac muscle which enables the ventricle to go on with rhythmical contractions even under those abnormal conditions.

Digitalis dyalisata, injected subcutaneously in the frog, brings about after some time peculiar changes in the heart-beat, after a

1) Geneesk. Bladen. 1897. 4e Reeks. Bo. 4. p. 77.

2) American Journal of Physiology. Vol. I. 1898 p. 509.

3) WENCKEBACH. Nederl. Tijdschr. v. Geneesk. 1899. I. Blz. 666.

4) MACKENZIE. British. Medical Journal. 24 October 1906.

5) OEHRWALL. Skandinavisches Arch. f. Physiologie. Bd. 8. 1898.

6) STRAUB. Arch. f. experimentelle Pathologie u. Pharmakologie. B. 45.

7) TRENDELENBURG. Arch. f. Physiologie. (Anal. u. Physiol.) 1903. p. 284.

certain period of normal contractions. In the transition of the normal period into the period of slow contractions, regularly curves are recorded, which together with curves formerly published of the living frog-heart (loc. cit.) throw light, on one of the, at least four varieties of P. A. which in my opinion must be distinguished, at least in the physio-pathology of the frog-heart. As to the three other types of P. A. I think, that the way may become clear to explain them equally.

*First form of P. A. with equal intervals.*

The ventricle beats in regular rhythmus alternately stronger and weaker, the beginning of the weak contraction is separated by the same length of time from the preceding and following contraction (fig. 1). This variety was described by ENGELMANN<sup>1)</sup> and ascribed to momentarily diminished conductivity. F. B. HOFMANN<sup>2)</sup> has shown, that this form of P. A. is often dependent on slight changes of the frequency of the heart-beat. STRAUB proved, that this P. A. under influence of antiarine easily gives way to "Puls-halbirung", which I often saw under influence of digitalis dyalisata.

*Second form of P. A. with retarded small contraction.*

In a former publication<sup>3)</sup> I described an example of P. A. observed in the dying frog-heart, where the interval between the greater and smaller  $V_s$  was longer than between the smaller and larger contraction. There it appeared, that the auricle continued to beat regularly. By comparing the intervals  $A-V$ , preceding the greater and smaller contractions, we concluded then, that the contraction-wave in the  $A-V$  bundle, eventually in the ventricle itself, might be slowed, which was the cause that the  $V_s$  not only came too late, but was also weaker.

The supposition, that this P. A. in certain cases might depend on changes of conductivity within the ventricle, had right of discussion, although this could not be strictly proved, as is remarked by WENCKEBACH. For one can never with certainty conclude to a change of conductivity within a heart cavity (e. g. within V) if the interval between the contractions of two cavities (e. g.  $A-V$ ) remained equal. But with the same certainty this meritorious observer is mistaken, when he, from the few curves (10a and 10b) of ENGELMANN generalises to the contrary i. e. to the exclusion of a similar relation in other

<sup>1)</sup> ENGELMANN, Arch. f. d. ges. Physiologie. Bd. 62. 1896. p. 556 seq.

<sup>2)</sup> HOFMANN. Arch. f. d. ges. Physiologie. Bd. 84. 1900. p. 165.

<sup>3)</sup> L. J. J. MUSKENS. Nederl. Tijdschr. v. Geneeskunde. 1902. No. II. Blz. 591.

cases. These curves cannot be looked upon as deciding in this point, because not there as in my cases, the auricle beats regularly, and therefore entirely different factors must be present, which has been overlooked by the writer. He appears to disregard, that in different lower animals, it was proved, that under influence of the vagus-nerve, at the same time the conductivity in one cavity can be improved, in others can be inhibited, which was confirmed by ENGELMANN, when he observed, how on the three bridges, veins-sinus, sinus-auricle, auricle-ventricle, independently of each other, conductivity might be changed; sufficient to show, that only very direct proofs could force us to admit, that under pathological circumstances this independence of conductivity in various parts should be lost. As well here, as also there, where WENCKEBACH explains the early smaller contraction by the quicker course of the weaker pulse-wave in the vessels, WENCKEBACH's conclusions appear to be much exposed to discussion. Also his conclusion, that there is no principal difference between P. A. with too early and retarded small contraction wave does not appear to be warranted by any well-known fact, certainly not by WENCKEBACH's suppositions. Sufficient facts can be adduced now, that here in different ways the same result can be arrived at.

To my former curves of P. A. brought about by poor nutrition, I now can add similar curves of P. A. brought about by injection of digitalis dyalisata (fig. 2).

In this case the interval  $S_i - V_s$  can easily be determined. This amounts to 20.6; 22.3; 20.9. In every case this interval is lengthened where it precedes a smaller contraction; i.e. the contraction-wave, which culminates in a smaller  $V_s$ , found more resistance on its way from the sinus to the ventricle and there was an undoubtable slowing of the conduction.

Looking carefully at the curve, one finds that the sinus contraction preceding a weak  $V_s$  shows a flattened top. By measuring the intervals of  $S_i$ , it becomes equally clear, that the sinus does not contract regularly and that it is the sinus contraction that comes too early, that is followed by a smaller  $V_s$ . Also the  $A_s$  preceding the weak  $V_s$  appears to be diminished in size.

Although it is not the place here, to go into detail about the new fact, that there exists a relation between the force of the sinus and auricular contraction and the force of the ultimate  $V_s$ , I will only remark, that in many similar experiments this relation was found. The question arises indeed, if in fact different parts of the three principal heart-cavities do maintain a special relationship in such a

way, that a completer sinus and auricular contraction tends to give rise to a completer ventricular contraction. If so, the next problem appears to be, whether this relation is kept up by special muscular arrangements or else whether nervous and ganglionic influence may play a rôle in it.

*Third Form of P.A. with retarded smaller contraction.*

Figure 3 is an example, where we find moreover reappearance of normal pulsation. Simple inspection of the pulsating heart made already the impression, that we had to deal with an antiperistaltic contraction; that the contraction-wave reaching the ventricle from the auricle, returned again to the auricle. BRANDENBURG<sup>1)</sup>, also PAN<sup>2)</sup>, HERING<sup>3)</sup>, VOLHARD<sup>4)</sup>, and SCHMOLL<sup>5)</sup> have observed antiperistaltic contraction, after the writer had long ago shown<sup>6)</sup>, that antiperistaltic contractions are a very constant phenomenon in the sinus of the turtle-heart.

In this case of fig. 3 we have to deal for the interpretation with 2 possibilities, 1. we may have to do with a real extra-contraction of auricle and ventricle, which results only in a very small elevation of the lever, because of its appearing in the beginning of the diastole, the ventricle being in the refractory period; or secondly we have to do with an antiperistaltic contraction wave, which on account of insufficient restoration of conduction in the  $A-V$  bundle and the ventricular musculature, can only give rise to a weak  $V_s$ .

Indeed, the first supposition could not be discarded if it were to be admitted that spontaneously under similar conditions in the frog such an extra- $A_s$ , followed by a very weak  $V_s$  could occur; an extra-contraction, which moreover was followed by an uncomplete compensatory pause. This conception is however hardly acceptable, if we take note of the systematical mode, in which this P. A., so to say, is prepared by the two abnormal contractions, which precede the very small  $V_s$ . Because these changes in the two ventricular contractions occur regularly at least in so far, as in my curves I come across similar cases, I think, that the other interpretation gains considerably in probable correctness. This supposition is therefore as follows: Under influence of the drug the conducting power within the ventricle is

1) K. BRANDENBURG. Arch. f. Anat. u. Physiol. Abt. 1904. Supp. p. 216.

2) O. PAN. Deutsche Zeitschr. f. klin. Medizin. Bd. 78. 1903. p. 128.

3) HERING. PFLÜGER'S Arch. Bd. 82. p. 1.

4) VOLHARD. Zeitschr. f. klin. Medizin. 1904. Bd. 53. p. 574.

5) SCHMOLL. Arch. f. klin. Medizin. 1907. p. 507.

6) Ned. Tijdschr. v. Geneesk. 1898. Deel II. Blz. 568 and Americ. Jnl. of Physiology; Vol. I. 1898. p. 504.

sensibly reduced. In the first only slightly weakened  $V_s$  only a part of the ventricular musculature could contract as a result of this disturbance of conduction. In the following contraction of the ventricle the wave spreads, however more slowly than in the normal cases (hence the stretched form of  $V_s$ ) over the entire ventricular musculature. As the conduction of the contraction wave can take place after the modern doctrine of GASKELL and ENGELMANN in all directions, the contraction wave in this case winds its way through this lengthened  $V_s$  to arrive antiperistaltically again at the auricle. After this only a part of the ventricular musculature has regained its conducting power sufficiently and a weakened  $V_s$  will join the antiperistaltic  $A_s$ . It is clear, that on account of the antiperistaltic contraction the wave from  $A$  to  $V$ , to  $A$  again; from  $A$  returning to another limited part of  $V$ ; then again to  $A$ , etc. will give rise to a pulsus alternans, in this case temporarily, whereby the interval between the commencement of the great contraction and that of the smaller one, is smaller than that between the small contraction and the greater contraction. One can among the dialysata-experiments recognise these cases there, where after a maximal toxic dose the frequency first became considerably slower, but finally quicker again. Whereas in the vena cava curve previously the pulsations of the sinus were easily visible, one does not find any indication of sinus contraction after the premortal pulse acceleration has set in.

We find therefore here a form of cardiac activity, which shows the same particularities as the P. A. formerly described by the writer for the poorly nourished frog-heart (Loc. cit. 1902) of which however the mode of origin was quite a different one.

The only objection, which can be adduced against this interpretation, is a theoretical one. Until now, it was looked upon as a dogma, that the unimpaired ventricular musculature under no circumstances shows the phenomena of dissociation. This dissociation between the different heart cavities and in every one separately, was explicitly described by the writer in several publications<sup>1)</sup>, especially regarding the sinus; its significance for our understanding of nerve influence on the heart, was more than once urged. Although in these experiments and those of ENGELMANN the occurrence of similar dissociations also of the unimpaired ventricle had to be acknowledged, the direct proof of its existence as far as I know, has never been

<sup>1)</sup> Geneesk. bladen 1897. p. 75. Proceedings of the American Academy of Arts and Sciences 1898. Vol. XXXIII. No. 71. p. 188. Americ. Jnl. of Physiol. 1898. p. 503 seq. Ned. Tijdschr. v. Geneesk. 1898. Deel II. Blz. 572 and 1902 Deel II. Blz. 583.

proved. Where under influence of digitalis dyalisata the tendency of the cardiac muscle to dissociation, as we saw above, is accentuated, there we could expect that if we combine this influence with the equally dissociating vagus influence, the evidence of dissociation also in the ventricle might come out. Indeed, during the influence of the vagus nerve on such an intoxicated heart, I found a curve which is apt to illustrate this dissociation. We have here to deal with the transition of an alternating pulse into a normal one, after a direct vagus stimulation and shortly after the inundation of the entire heart by a physiological salt solution (In the ventricular curve this is visible).

In my mind there is no doubt, that the small elevation after the reduced ventricular contraction cannot be interpreted, either as an auricular contraction (because nowhere in this or other tracings an  $A_s$  of this considerable height was observed) nor as an ordinary extra-systole of the ventricle. In the latter case it could not be explained not only why here an extra systole arose, nor why the preceding ventricular contraction coming at the right time, was so exceedingly diminished in size. We have here undoubtedly to do with a dissociation in time of two parts of the ventricular musculature (eventually also of the "Reizleitungssystem") and only when *after the pulsus alternans* a not completely synchronic contraction of these parts has taken place, and the entire musculature comes again at the same time in the refractory period, normal contractions can follow. According to this interpretation the difference between the great and the small contractions of the preceding P. A. is to be ascribed to the fact, that only in the great contractions a particular part of the muscular mass is reached by the contraction wave; whereas this part of the muscle is excluded from the contraction in the small  $V_s$ .

*Fourth form of P. A. with retarded great contraction.*

Of this type of P. A. I cannot adduce any curve met with in lower animals. The only specimen I have come across, is registered from a case of Basedow, who suffered from an exceedingly rapid and at the same time irregular heartbeat. It appears to me that here we have to deal with an automatically beating ventricle or better with a ventricle, in whom two divisions are beating independently, only every other  $V_s$  (the greater one) causing an antiperistaltic contraction reaching the auricle. Comparable curves have been published by MACKENSIE <sup>1)</sup> and WENCKEBACH <sup>2)</sup>, so that its occurrence in men can

<sup>1)</sup> MACKENSIE, British medical Journal, 1905, III. Comp. fig. 12 perhaps also fig. 5.

<sup>2)</sup> WENCKEBACH, Arrhythmie. 1903. P. 107.

be doubtlessly stated. In the latter curves no registration of the jugular vein was added to the ventricular curve, so that I am not in the situation to suppose or deny for these curves the same origin as in my curve.

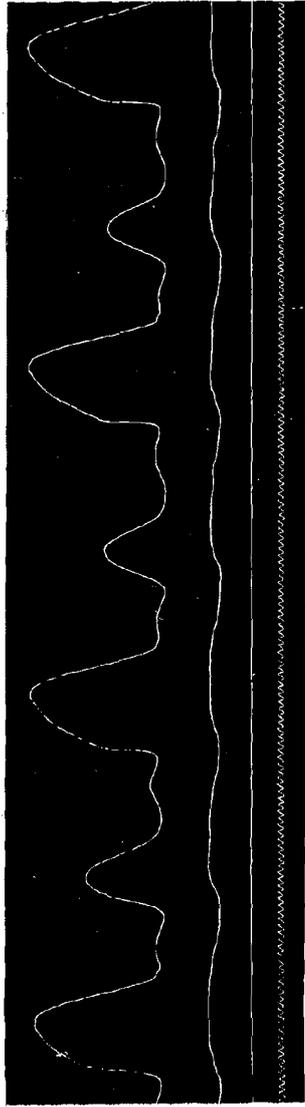
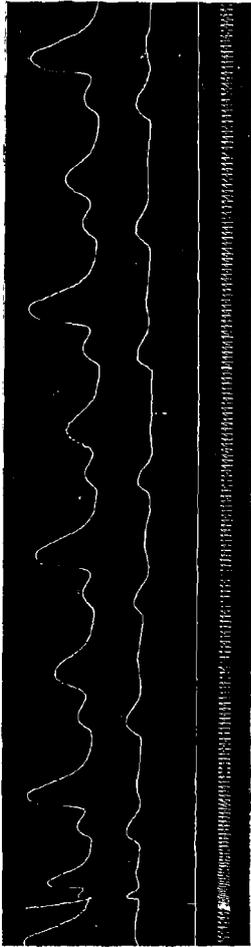
All in all it seems to me, that in these curves and their analysis we have important arguments, which tend to prove, that from the physiological side more special research is needed regarding the conduction within the individual divisions of the heart. For the first of the four described types of P. A. we have shown, that from physiological side the cause has to be sought in changed conductivity by which in the weak contractions, the contraction wave is limited to a part of V. For the second type of P. A. we thought we were able to bring direct proofs, while it became probable for the third type of P. A., that they are results of the conduction between the sinus and the ventricle becoming slower; and for the third form of P. A. it appeared probable that the P. A. is the result of the antiperistaltic contraction wave, so that we had here not a quantitative, but a qualitative change in the conductivity. Regarding the fact which TRENDLENBURG stated, that by stimulating the ventricle artificially the frequency of the ventricular rhythm may become much greater if slowly the stimulation is quickened, before "Halbierung" of the heart-beat makes appearance, then if within a short period a great frequency is attained, it is equally to be interpreted as follows: that by slowly increasing frequency the conductivity is enabled to adapt itself to the great demands; so that the moment is delayed where necessarily only partial contractions of the ventricle arise. Regarding the pathology, it appears to me that it is of importance for the knowledge of the pulsus trigeminus, discussed by WENCKEBACH, that from physiological side the importance of dissociation of the ventricle under certain circumstances as also the importance of the antiperistaltic contraction wave has been proved. With the statement that partial contractions do occur, it appears to me, that the necessity becomes evident, that the law of Bowditch has to be limited, in so far, that certainly every ventricular muscle fibre which contracts, does so with maximum force; but on the other hand, we have not to accept that necessarily in every ventricular contraction all muscular bundles contract equally.

Where we have to interpret curves like those of Tschirjew<sup>1)</sup> (cited by WENCKEBACH) of O. PAN<sup>2)</sup>, R. FINKELNBURG<sup>3)</sup> and HAY

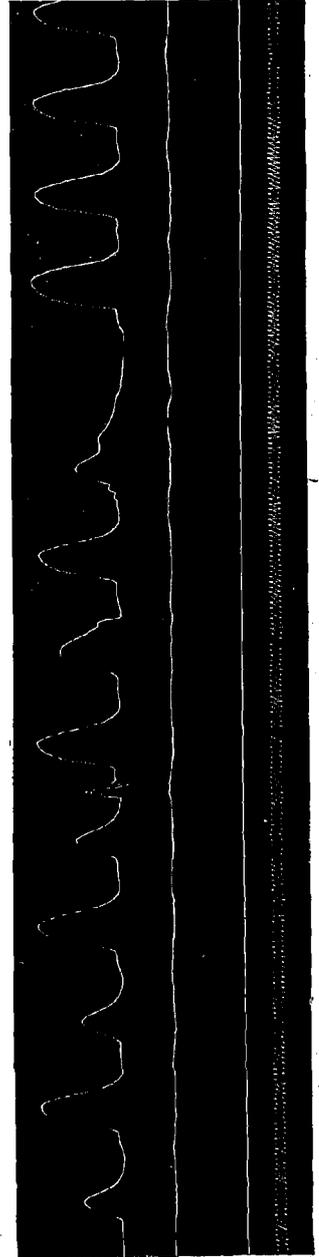
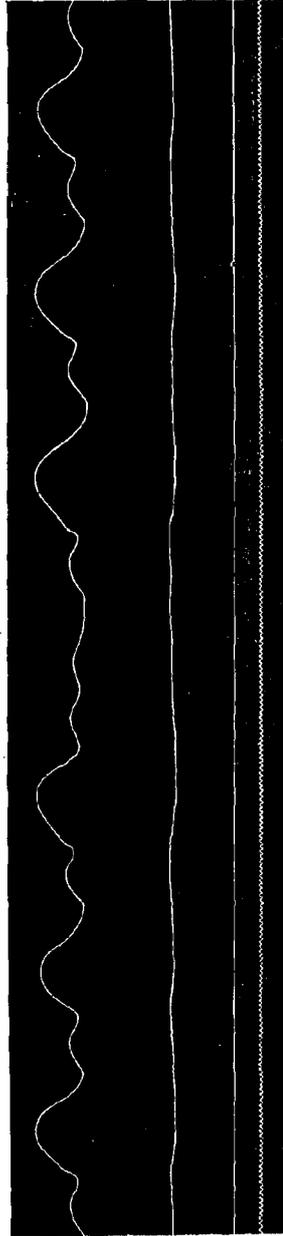
<sup>1)</sup> Tschirjew. Archiv für Physiologie. 1877.

<sup>2)</sup> O. PAN. Deutsche Zeitschrift. f. klin. Medizin. Bd. 78. 1905. p. 128.

<sup>3)</sup> R. FINKELNBURG. Cited by WENCKEBACH. 1905. Heft 1 and 2. p. 586.



Ventricles and  
Auricle.  
Vena cava int



and MOORE<sup>1)</sup> we should not neglect the value of these phenomena. For the absence of the compensatory pause (WENCKEBACH) finds in the above interpretation its complete explication. At the same time we can now regard HERING's opinion, that all pulsus bigemini should always depend on extra systoles as definitively rejected.

With FUNKE I agree finally in this that a further discussion about the question, whether apart from the pulsus alternans also the existence of a pulsus bigeminus must be acknowledged, is completely superfluous. On the other hand it might be desirable, if the experimental results of KNOLL and those of HERING in warmblooded animals about hemisystolia and heart-trigemini, should be taken up again, also in regard to the recent anatomical data.

Regarding these questions three recent researches must be regarded as important, firstly the observations of W. EINTHOVEN<sup>2)</sup>, whose accurate illustrations also of partial contractions, appear to promise a good deal for further analysis. Moreover the important researches of TAWARA<sup>3)</sup> in ASCHHOFF's Laboratory, which has shown, how far the division of functions in the ventricle of the warm- and perhaps also of the cold-blooded animals has gone.

Finally the observations of MACKENZIE<sup>4)</sup> who has shown us the possibility, to get information also in man about the movement of the auricle under pathological circumstances, so that we may expect also this field of work becoming fertile for scientific analysis.

The next thing should be, to bring also the sinus of man under the scope of the graphical method. WENCKEBACH<sup>5)</sup> thinks to have reason to believe, that dissociation of the sinus described by me in lower animals<sup>6)</sup> might be observed equally in men.

To physiology the task to examine what influences are able to dissociate the two principal bundles of the "Reizleitung" system and to get information about nerve influence as well regarding that system itself as upon the muscular mass of the ventricle.

<sup>1)</sup> HAY and MOORE. Lancet 1906. p. 1274.

<sup>2)</sup> EINTHOVEN. Tijdschr. v. Geneesk. II. No. 22.

<sup>3)</sup> TAWARA. Das Herzleitungssystem. 1906.

<sup>4)</sup> MACKENZIE. British medical Jnl. 1902. Nov. p. 1411.

<sup>5)</sup> WENCKEBACH. Arch. f. Physiologie. 1906. p. 361.

<sup>6)</sup> American Journal of Physiology. Vol. I. 1898. No. IV. p. 503.

**Zoology.** — “*On the structure of the nerve-cells in the central nervous system of Branchiostoma lanceolatum.*” (First comm.)  
By Dr. J. BOWKE. (Communicated by Prof. G. C. J. VOSMAER).

(Communicated in the meeting of April 26, 1907).

The methods of staining the elements of the nervous system, published in recent years by RAMON Y CAJAL, DONAGGIO, and especially by BIELSCHOWSKY, have enabled us to study the minute structure of the ganglion-cells not only of the lower animals but also of the vertebrates with more success than before. After having published in These Proceedings, some years ago<sup>1)</sup>, the results of my former investigations on the structure of the nerve-cells of Branchiostoma, then studied by means of the goldmethod of APATHY, it seemed advisable to describe here too the results of my recent investigations on the same subject by means of the methods mentioned above, because they extend and complete my former results in several directions.

Contradictory to the results of EDINGER<sup>2)</sup>, the only author who studied the central nervous system of amphioxus by means of the method of BIELSCHOWSKY, viz. that the method gave only scanty results for the neurofibrillae in the cells, in my preparations, stained after the method of BIELSCHOWSKY—POLLACK, in a great number of nerve-cells of several specimens of Branchiostoma a very clear and distinct picture was obtained of the neurofibrillae, not only in the nerve-fibres, but also in the body of the nerve-cells.

Preparations of material preserved in a mixture of platinum chloride-osmic acid-acetic acid and corrosive sublimate<sup>3)</sup>, and stained in thin sections with iron-haematoxylin after HEIDENHAIN, were used as control and for the study of the protoplasmic structures between the neurofibrillae.

The different cell-forms of the central nervous system gave there, where they were satisfactorily stained, as a rule the same mode of arrangement of the neurofibrillae in the cell-body; therefore I will restrict myself to describe here only some cell-forms at length and only refer briefly to the structure of other cells. At another place I hope soon to give more and fuller details.

<sup>1)</sup> Proceedings Roy. Akad. of Sc. Amsterdam, of the meeting of Oct. 25, 1902.

<sup>2)</sup> Anat. Anzeiger, Bd. 28, No. 17, 18, 24 April 1905.

\* <sup>3)</sup> According to Dr. LÉROS the best method for the preservation of the nervous system of Branchiostoma. I can fully agree with him in this statement. This mixture gives better results than all the others I tried.

1. As is well known, the very large nerve-cells ("Kolossalzellen") lying at about equal distances from each other in the axis of the spinal cord, possess a thick axonic fibre, that after leaving the cell-body describes a characteristic curve and passes into one of the colossal nerve-fibres that run in a longitudinal direction through the spinal cord, and a number of dendrites, springing from the cell-body at different points.

Sections of these cells, stained after the method of BIELSCHOWSKY, give a very clear picture of the neurofibrillar structure. In a section in which only some of the dendrites are to be seen, and not the axonic fibre with its "cône d'entrance" (of which more later on) these cells show an arrangement of the neurofibrillae as shown in fig. 1.

The cell is surrounded by a glious capsule, composed of fine interwoven fibrillae. The preservation of the nervous system in formol, necessary for the BIELSCHOWSKY-reaction, causes the cells to shrink a little, so that the pericellular cavity is larger than it is in normal life and in well-preserved specimens. Within the cell-body the neurofibrillae form a very distinct and regular network. Everywhere they anastomose with each other, nowhere I could discover free running fibres. The meshes are regular, round or many-sided, and nearly all of about the same size. A subperipheral zone is formed, where the meshes are somewhat smaller and the composing neurofibrillae a little coarser. From this zone a few coarse neurofibrillae may be followed in the network radiating to the central zone around the nucleus. The nucleus itself is not coloured in these preparations, but is only to be seen as a clear round or oval spot in the midst of the darkly stained network of the neurofibrillae. There where a dendrite leaves the cell-body, the meshes of the network are elongated in the direction of the processus (fig. 1, 4*b*, 6). In the dendrites themselves, at least in the coarser ones, the anastomosing of the neurofibrillae is to be seen still at some distance from the cell-body. In fig. 1 is drawn a section of 7  $\mu$  thick. In three of the following sections, passing through the dendrites, whose origin is shown in fig. 1, I could still see the anastomosing of the composing neurofibrillae. In fig. 2 is drawn one of the large dendrites of a similar colossal cell there where it branches into two. The network of the neurofibrillae, several coarser (and more darkly stained) fibrillae, and the continuity of the network in both branches is clearly to be seen. In the finer dendrites the neurofibrillae seem to become isolated sooner after having left the cell-body (fig. 1 at *b*). The same is to be seen in the smaller nerve-cells of the spinal cord (figs. 4*b*, 6).

The axon of the colossal nerve-cells has a somewhat different structure. As I described in my former paper <sup>1)</sup>, the colossal nerve-fibres contain a great number of closely set exceedingly fine separate fibrillae, which in well-preserved preparations are distributed regularly through the whole extent of the fibre. There where the axon enters the cell, this bundle of neurofibrillae may be followed some way into the cell-body; we see the fibres describe a curve or vortex around the nucleus, and then the thin fibres melt into the somewhat coarser network of the neurofibrillae described above.

The smaller, mediumsized and smallest nerve-cells of Branchiostoma, such as those that are drawn in figg. 4, 5 and 6, at the same scale as the cell figured in fig. 1, show the same arrangement of the neurofibrillae as the colossal nerve-cells, viz. a regular network, the meshes elongated there where a dendrite or axon leaves the cell, more or less rounded in the centre of the cell-body. The subperipheral zone with finer meshes and coarser fibrillae I could not find here; the network seemed everywhere to be regular throughout the cell-body. In fig. 4*a* and 4*b* two sections through the same mediumsized nerve-cell are drawn. In fig. 4*a* the nucleus is to be seen, and on it a very regular network of neurofibrillae, with only one layer of meshes, and therefore giving a very clear idea of the regularity of the network. This section passes through the centre of the cell-body. Fig. 4*b* shows the peripheral part of the same cell. The meshes are here more elongated in the direction of the processus, and in the network some fibrillae are coarser and more darkly stained; all of these run in the direction of the dendrite and leave the cell-body there; inside the cell they form part of the general network; in the dendrite they run more or less parallel to each other and do not anastomose any more (see page 2). The same features are to be seen very clearly in fig. 6, showing the neurofibrillar structure of another mediumsized nerve-cell lying somewhat more cephalad in the spinal cord.

In fig. 5 is drawn a very small ganglion cell (magnified to the same scale as the foregoing figures). Here too the network of the neurofibrillae is easily to be seen and the meshes are of about the same size as in the mediumsized nerve-cells described above, though smaller than in the colossal ganglion cells.

Fusiform cells, in which the neurofibrillae simply pass through the cell-body from one processus to the other without interruption, as I described them in my former paper, I was not able to find in

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<sup>1)</sup> These proceedings. Meeting of Oct. 25, 1902.

the preparations stained after BIELSCHOWSKY. Where the neurofibrillae were visible, they formed a network. In my preparations stained with chloride of gold after APATHY, which I looked over for these cells I however found them again. The uninterrupted course of the neurofibrillae was clearly to be seen. They are however only very rarely met with.

So we find in nearly all the cells a network of neurofibrillae with regular meshes. In full-grown animals the meshes in different cells are of about the same size. But when we examine the same kind of cells (for example the colossal ganglion cells) in very small animals, we find a neurofibrillar network of the same regularity but with much smaller meshes. So when we compare fig. 1, a colossal ganglion cell of a fullgrown Branchiostoma of 48 m.m. in length, with fig. 3, an analogue cell of an animal of 6 m.m. in length, we find a much smaller-meshed network. Those small animals have finished their metamorphosis already, and present nearly the same organisation as the adult animal. The nerve-cells therefore seem to have assumed already the definite arrangement of their neurofibrillar structure, but the meshes are much smaller. During the following growth of the nerve-cells the reticulum grows, but the structure remains the same. In different adult specimens the size of the meshes seemed always to be of the same order, and only to present the slight differences mentioned above.

When we compare this with the neurofibrillar structure, described for the ganglion cells of other animals, I will here especially call attention to the description of APATHY for Hirudineae and Vermes, of BOCHENEK for Helix, of DONAGGIO, CAJAL, MICHOTTE, LEGENDRE and the many authors, who have studied the ganglioncells of the higher vertebrates by means of the new elective histological methods. Among the descriptions by these authors of the neurofibrillar structure in the nerve-cells of the representatives of different classes of the animal kingdom, that of Branchiostoma takes just the place, we generally give to that animal in the animal series. In fig. 7 is drawn a sensory cell of a Pontobdella, with the neurofibrillar structure stained after APATHY. We see a very coarse network around the nucleus, with fibrillae radiating to the periphery and forming there a second network. The ganglion cells of Helix give according to BOCHENEK<sup>1)</sup> a much finer network. The meshes of this network are still much larger than those of the nerve-cells of Branchiostoma; these in their turn are larger and the fibrillae coarser than the neurofibrillar struc-

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<sup>1)</sup> Le Nevraze, Vol. III, Fasc. 1. 1901. page 85.

ture, as it presents itself in well-stained preparations of the nerve-cells of the higher vertebrates (as for example in the splendid figures of DONAGGIO). It seems that the higher is the organisation of the animal, and in consequence that of the nerve-cells, the finer and more regular is the network of the neurofibrillae in the nerve-cells. (cf. BOCHENEK).

The network of the neurofibrillae has no definite connection with the protoplasma-reticulum. In preparations, preserved in a mixture of HERMANN'S fluid and corrosive sublimate, and stained with iron-haematoxylin, the protoplasma has a very fine granular or fibrillar structure, and in the centre of many cells are shown curious diversely-shaped differentiations that remind us of the pseudochromosomes described by HEIDENHAIN, and of the rings, described in the ganglion cells of vertebrates (Teleostei, Rana). But it would take us too far, to describe these details here at some length.

2. An entirely different type of cells we find in the nerve-cells which form the large group of ganglion cells lying dorsally in the foremost part of the spinal cord just behind the brain ventricle, the so-called oblongata, extending from the niveau of the infundibular organ till beyond the first pigmented eye-cells. It is characteristic of the peculiar difficulties, with which the investigation of the histology of the nervous system of Branchiostoma is encumbered, that of the large number of authors, who have studied the subject, only JOSEPH<sup>1)</sup> two years ago gave a nearly accurate account of the structure of these cells. Even HEYMANS and VAN DER STRICHT in their very elaborate study of the histology of the nervous system of Branchiostoma, published in 1898, do not say a word about it, and only in one of the many beautiful drawings, with which their paper is illustrated, in two cells a slight indication of it is to be seen. JOSEPH says of these cells, that they present at the surface a finely striated border of minute rods, only at the side of the cell turned towards the surface of the animal, and underneath this striated border a coarsely granular darkly staining protoplasm. The same structure JOSEPH described in the cells lying close to the central canal in the spinal cord, covered by a pigment-cap, and being supposed to be light-perceiving cells. On these grounds JOSEPH put forward the suggestion, that the dorsal group of cells too consists of eye-cells, light-perceiving cells, differing only from the cells of HESSE by the absence of a pigmented cap-shaped cell.

This far-reaching suggestion is, I think, not proved, nor even made probable, by the facts. Even in the most carefully prepared sections

<sup>1)</sup> H. JOSEPH: Ueber einige Zellstructuren im Zentralnervensystem von Amphioxus. Verh. d. Anatom. Gesellschaft. Jena 1904. p. 16—26.

in which the structure of both cells was very clearly to be seen, the two types still present some marked differences, both in the nuclei and in the structure of the protoplasm and the differentiations on the surface of the cells. According to JOSEPH the nuclei of the dorsal cells and of the ventral eye-cells possessed a similar granular structure, differing from that of the other nerve-cells. In some cases this is true, but in other cases the same structure is found in the nuclei of other cells, and, when we examine a number of preparations, the structure of the nuclei both of the dorsal cells, of the ventral light-perceiving cells and of the other nerve-cells presents so many differences and varieties, that there cannot be drawn any conclusion out of that. But the capital difference between the two cell-forms lies in the absence of a pigmented cap-cell in the dorsal cells and the totally different form and structure of the two types.

The light-perceiving cells of the spinal cord possess a border of short minute rods, lying close against the cap-shaped pigment cell. The processus of the dorsal cells are much longer, and not rods, but exactly shaped like hairs, or cilia. These hairs (fig. 8-11) are rather long, slender and thickly set and their course is often more or less wavy. On the same cell they seem to be all of about the same length; the hairs on different cells do not vary much in length.

The ventral light-perceiving cells are all of the same regular form. The dorsal cells however present the most different forms.<sup>1)</sup> Some are rather regular (fig. 8), some are long and slender (fig. 9), some are of a very irregular shape, but in most cases these cells, when we reconstruct them from the thin sections, appear to have a very typical cup-shape. In fig. 10 I have drawn the median section through one of these cups, in which the central hole in the cell is figured, in fig. 11 such a cup-shaped cell is cut vertically to the axis of the cup.

These cells are surrounded by a glious basket of closely interwoven fibres (in the figures this network is represented by a dark colour) and the cells seem to fill up the room left by this basket so that between the surface of the cell and the inside of the basket there remains an open space, in which the hair-like processes of the cell-surface are seen. In well-preserved sections this space has the same width on all sides of the cell, where the surface carries the hair-like structures. The hairs reach from the surface of the cell nearly to

<sup>1)</sup> Only such cells are described here, which seemed to be perfectly preserved. All those cells, of which the irregular form seemed to be caused by bad preservation, are left out of the discussion.

the inside of the basket, as may be seen in the figures. There where no hairs are developed, the glious fibres lie close against the surface of the cell-protoplasm (fig. 8, 10, 11).

Where JOSEPH considers the hair-like processes to be only present at that side of the cell which is turned towards the surface of the animal, I cannot agree with him. When we compare horizontal and transverse sections carefully with each other, we must draw the conclusion, that the hairs may be developed on all sides of the cell, except there where the cell-body sends a dendritical process through the glious basket. Even there where the cell is shaped like a cup or calix, at both sides of the cup the cilia may be present (figg. 10, 11). The cilia at the inside of the cup are separated from each other by an ingrowth of the fibres of the glious basket (fig. 10). When the cell is cut at right angles to the axis of the calix, this may lead to the appearance of a ring of protoplasm, at both sides covered with the hairs, and surrounding a mass of coiled-up fibres, the ingrowing fibres of the glious basket (fig. 11).

The protoplasm of these cells shows a regular network of neurofibrillae, which differs from the network of the other cells of the spinal cord by its much larger meshes (compare figg. 8—10 with figg. 1—6); only at the periphery of the cell, under the hair-like processes, a finer network of neurofibrillae is to be seen (fig. 8). The hairs themselves seem to be implanted on a layer of small darkly staining granules or small rods, of which the definite structure is difficult to be seen. In many cases it is only represented by a somewhat more coarsely granular layer of protoplasm there where the cell-body is covered with the hairs.

All these things seem to point to the conclusion that these cells do not possess a light-perceiving function, as suggested by JOSEPH. The shape of the cells and the peculiar structure at least are not favourable to the hypothesis. But it is sure, that this group of cells, all presenting the same peculiar structure, has a distinct and peculiar function. The structure of the cells reminds us in the first place of a static organ, and especially cells as drawn in fig. 9 and fig. 11, seem to suggest such a function. The peculiar baskets of fibres surrounding the cells remind us of the cells of PURKINJE of the brain of the craniotes, but bearing in mind the very little we know about these cells and about the cells just described, it is more advisable to stop at these general suggestions and not to try to go more into details. The suggestion of JOSEPH at all events seems to me to be untenable.

A third type of cells differing from those which I described here, is that of the cells of the so-called infundibular organ in the ventral



wall of the brain-vesicle. These cells I mean to describe in my second paper.

*Leiden, 25 April '07.*

DESCRIPTION OF FIGURES ON THE PLATE.

All the figures are magnified 1600 times, and are drawn with a camera lucida of ABBE directly after the preparations. Apochrom. oil-immersion lens of ZEISS and compens-ocular No. 8.

- Fig. 1. Colossal nerve-cell with neurofibrillar network, of a Branchiostoma of 4.8 cM. in length (BIELSCHOWSKY—POLLACK's method).  
" 2. Dendrites of a similar cell of an animal of 5 cM. in length (same method).  
" 3. Neurofibrillar network of a colossal nerve-cell of a Branchiostoma of 6 mM. in length.  
" 4 *a* and *b*: Sections of a medium-sized nerve-cell of the same spinal cord as fig. 2.  
" 5. Section of a very small nerve-cell, with neurofibrillar network.  
" 6. The same as in fig. 4.  
" 7. Section of a sensory cell of *Pontobdella*, of 10 $\mu$ , treated after the gold-method of APATHY.  
" 8—11. Sections through different cells of the dorsal group of cells lying behind the brain-vesicle, taken from preparations of several adult specimens of Branchiostoma. In fig. 8 some of the adjoining cells are drawn, to demonstrate the similarity of structure of the nuclei in the two cell types.

In fig. 10 and fig. 11 are drawn two typical sections through cup-shaped cells of the dorsal group of cells. The body contained in the centre of the cell of fig. 11 is the prolongation of the glious basket surrounding the cell. Compare fig. 10.

**Physiology.** — "*On a third heart sound*". By W. EINTHOVEN, in collaboration with Messrs. J. H. WIJERINGA and E. P. SNIJDERS, assistants at the physiological laboratory at Leydèn.

When continuing the investigation of the heart sounds by means of the string galvanometer<sup>1)</sup>, we noticed that in some cardiophonograms, especially with the apex sounds of *W* i, recorded in February last, shortly after the vibrations of the second sound still another vibration was present; which admitted of no other interpretation than by regarding it as a third heart sound.

We could not at once explain how this third sound was produced, and we put off the closer investigation of this phenomenon, however

<sup>1)</sup> See: Die Registrierung der menschlichen Herztöne mittels des Saitengalvanometers. PFLÜGER's Arch. f. d. gesammte Physiol. Vol. 117, p. 461, 1907.

interesting it seemed to us, since for the present our time was taken up by other work.

A couple of months afterwards Dr. A. G. GIBSON of Oxford — to whom our former publications on the recording of heart sounds were known, but who could not be acquainted with our later observations — asked whether in our collection of cardiophonograms of normal persons there were any in which an extra sound was visible in the diastolic phase. GIBSON occupied himself with an investigation of the venous pulse<sup>1)</sup> and had noticed that with some persons, without a morbid affection of the heart, a low pitched sound could be heard at the apex during the cardiac pause, something like a distant 2<sup>nd</sup> sound, but feebler and much lower in pitch. The sound is clear and nothing like a murmur. This particular sound is of varying intensity being louder during the interval between the end of an expiration and the beginning of the subsequent inspiration.

We hope elsewhere to publish in a more extensive paper the cardiophonograms we obtained; here we shall only deal briefly with them. When we try to predict from the shape and dimensions of the curves what impression the third heart sound must make on the ear of the observer, we cannot describe it otherwise than GIBSON did: a distant diastolic sound of low pitch and clear tone, varying in intensity, but always feeble.

There can be no doubt that the sound, heard by GIBSON at Oxford, is the same sound we recorded at Leyden.

The measurements made with some cardiophonograms, show that with  $W_i$  the beginning of the third sound falls on the average 0.13 sec. (varying between 0.11 and 0.15 sec.) after the beginning of the second sound and on the average 0.32 sec. before the beginning of the following first sound. In the same curves the duration of the first sound is about 0.08 sec., of the second about 0.05 sec., of the third 0.02 to 0.03 sec. The first two sounds are murmurs, composed of tones of irregular pitch. The mutual distance of some tops in the curves shows that we have here tones of more than a hundred double vibrations per second, whereas the third sound seems to be built up of but one double vibration, the period of which amounts to about 0.02 sec.

The intensity of the third sound varies. While in some cardiac beats it is entirely absent, the amplitude of its vibrations reaches in other beats  $1/7$  of that of the first and second sounds. Putting the

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<sup>1)</sup> GIBSON'S investigation will shortly be published in "The Lancet" under the title: "The significance of a hitherto undescribed wave in the jugular pulse".

ratio of the amplitudes of the first or second sound to that of the third  $a = 7$ , and the ratio of the frequencies  $b = 2$ , the ratio of the intensities is  $a^2 b^2 = 196$ . Hence the third sound is at its maximum still about 200 times feebler than the first or second.

While the above given figures refer to the objective intensities, a comparison of the intensities of perception is still much less in favour of the third sound, since a tone of frequency 50 per second has objectively to be a little over a hundred times stronger <sup>1)</sup> than a tone of 100 vibrations a second, in order to produce an equally strong auditory impression. Consequently, if the third sound attains such an intensity that it is just audible still, the first and second sounds may be 20.000 times weakened, before also the auditory impression they produce, vanishes.

This explains the difficulty of the investigation by the method of auscultation. GIBSON <sup>2)</sup> emphasises this particularly and says that in order to hear the sound, accidental sounds must be excluded as much as possible, while one has to strain one's attention during the interval in which the sound occurs. Although the cardiophonograms leave no doubt as to the existence of the third heart sound with *Wi*, we have been unable to hear it by means of a stethoscope.

Regarding the explanation of the third sound we refer to the above mentioned more extensive paper which will shortly be published elsewhere. Here we will only state our conclusion that the sound cannot be put on a line with a prae-systolic murmur of the mitral valve, nor with a duplication of the second sound by non-simultaneous action of the aortal and pulmonal valves, but that it is probably caused by a second vibration of the valvulae semilunares aortae and must be regarded as a phenomenon of pretty common occurrence.

**Astronomy.** — "*On some points in the theory of Jupiter's satellites.*"

By Dr. W. DE SITTER. (Communicated by Dr. E. F. VAN DE SANDE BAKHUYZEN).

The following pages contain a short account of some investigations, which will soon be published, together with other results, in N<sup>o</sup>. 17 of the publications of the astronomical laboratory at Groningen.

A few words are necessary in explanation of the notations em-

<sup>1)</sup> Calculated according to MAX WIEN, PFLÜGER's Arch. f. d. gesammte Physiol. Bd. 97. p. 1. 1903. H. ZWAARDEMAKER and F. H. QUIX give in ENGELMANN's Arch. f. Physiol. p. 25. 1904, differences in the same sense, but of a different order of magnitude.

<sup>2)</sup> l. c.

ployed. The notations used by different writers on the theory of the satellites are discordant in a most regrettable manner. The tables, both those of DAMOISEAU and of DELAMBRE, distinguish the four satellites by the numbers 1, 2, 3, 4. This example is followed by MARTH, and I have also in all my previous work on the satellites used this notation, as is also done by Mr. COOKSON in the discussion of his observations. The theoretical writers, on the other hand, LAPLACE, TISSERAND, SOULLART use the suffixes 0, 1, 2, 3 or a corresponding number of accents. Another fundamental difference is in the designation of the perijoves. The letter  $\tilde{\omega}$  in the writings of DAMOISEAU, MARTH, COOKSON and myself represents the "own" perijove; SOULLART and TISSERAND use it for the osculating perijove. There are many more differences of this kind, which need not be enumerated here. Though thoroughly convinced of the great importance of a consistent notation, I am, reluctantly, compelled in this communication to depart from the notations employed by me elsewhere. In the first article of the present communication, which treats of a theoretical point, I have, to avoid the writing out at length of many well known formulas and results, closely followed TISSERAND's very clear argument in the fourth volume of his *Traité de Mécanique Céleste*. Accordingly in this first article, I will adopt TISSERAND's notation, with one exception. In the further articles I will return to the notation employed in my previous work.

1. *Theory of the libration.* As has been explained, the notations employed are TISSERAND's excepting the mean longitudes, which I denote by  $l_1, l_2, l_3$  instead of by  $l, l', l''$ . In addition to the quantities  $F, F', G, G'$  defined by (19) page 11 <sup>1)</sup> I wish to introduce

$$G_1 = \frac{4a}{a'} - 3a' A^{(1)} - a a' \frac{\partial A^{(1)}}{\partial a}$$

$$G_1' = \frac{4a'}{a''} - 3a'' A^{(1)} - a' a'' \frac{\partial A^{(1)}}{\partial a'}$$

TISSERAND assumes  $G_1 = G$  and  $G_1' = G'$ , which is only approximately true. If it is not desired to introduce this approximation, then on page 11, formula (20) we must in  $R_1$  replace  $G$  by  $G_1$  and similarly in  $R_1'$   $G'$  by  $G_1'$ .

The only further difference from TISSERAND's notation is in the definition of the libration. I put

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<sup>1)</sup> The references of pages and formulas are to those of TISSERAND, volume IV.

$$\vartheta = l_1 - 3l_2 + 2l_3 + 180^\circ, \dots [1]$$

TISSERAND, however, has

$$\vartheta = l - 3l' + 2l''.$$

The angle  $\vartheta$ , as defined by [1] is the angle to which the name *libration* was first applied by LAPLACE, and which is by him called  $\tilde{\omega}$ . (*Mécanique Céleste*, Livre VIII, art. 15, *Oeuvres*, tome IV pages 75 and 79 of the edition of 1845).

The differential equation determining the libration is

$$\frac{d^2\vartheta}{dt^2} = -\beta^2 \sin \vartheta \dots [2]$$

This equation is derived by the combination of the three equations

$$\left. \begin{aligned} \frac{d^2l_1}{dt^2} &= -Q_1 \sin \vartheta \\ \frac{d^2l_2}{dt^2} &= -Q_2 \sin \vartheta \\ \frac{d^2l_3}{dt^2} &= -Q_3 \sin \vartheta \end{aligned} \right\} \dots [3]$$

We have thus

$$\beta^2 = Q_1 - 3Q_2 + 2Q_3 \dots [4]$$

From these equations the whole theory of the libration is derived in the well known manner, on which, however, I will not dwell, my sole object being at present the determination of the quantities  $Q_1$ ,  $Q_2$  and  $Q_3$ .

For that purpose we start from the formulas given by TISSERAND at the top of page 20, which must however be completed as follows:

$$\frac{d^2Q}{dt^2} = -\frac{3}{a^2} \left( \frac{\partial R_1}{\partial \varepsilon} + \frac{\partial R_4}{\partial \varepsilon} \right) \dots [5]$$

and two similar equations for  $Q'$  and  $Q''$ .

Introducing the same auxiliary angles  $u$  and  $u'$  that are used by TISSERAND (formula (12) page 20), we get instead of TISSERAND's equations (B):

..

$$\begin{aligned} \frac{d^2 Q}{dt^2} = & \frac{3}{2} m'n^2 \left[ F(k \sin u - h \cos u) + \frac{a}{a'} G_1(k' \sin u - h' \cos u) \right] \\ & - 3n \left[ a_{0,1} \left( \{k^2 - h^2\} \sin 2u - 2kh \cos 2u \right) \right. \\ & \quad \left. + \frac{m'\sqrt{a'}}{m\sqrt{a}} a_{1,0} \left( \{k'^2 - h'^2\} \sin 2u - 2h'k' \cos 2u \right) \right. \\ & \quad \left. - 2b_{0,1} \left( \{kk' - hh'\} \sin 2u - \{kh' + hk'\} \cos 2u \right) \right]. \end{aligned}$$

$$\begin{aligned} \frac{d^2 Q'}{dt^2} = & - 3mn'^2 \left[ G(k' \sin u - h' \cos u) + \frac{a'}{a} F(k \sin u - h \cos u) \right] \\ & + \frac{3}{2} m''n'^2 \left[ F'(k' \sin u' - h' \cos u') + \frac{a'}{a''} G'_1(k'' \sin u' - h'' \cos u') \right] \\ & + 6n' \left[ a_{1,0} \left( \{k'^2 - h'^2\} \sin 2u - 2k'h' \cos 2u \right) \right. \\ & \quad \left. + \frac{m'\sqrt{a}}{m''\sqrt{a'}} a_{0,1} \left( \{k^2 - h^2\} \sin 2u - 2kh \cos 2u \right) \right. \\ & \quad \left. - 2b_{1,0} \left( \{kk' - hh'\} \sin 2u - \{kh' + hk'\} \cos 2u \right) \right] \\ & - 3n' \left[ a_{1,2} \left( \{k'^2 - h'^2\} \sin 2u' - 2k'h' \cos 2u' \right) \right. \\ & \quad \left. + \frac{m''\sqrt{a''}}{m'\sqrt{a'}} a_{2,1} \left( \{k''^2 - h''^2\} \sin 2u' - 2k''h'' \cos 2u' \right) \right. \\ & \quad \left. - 2b_{1,2} \left( \{k'h'' - h'h''\} \sin 2u' - \{k'h'' + h'k''\} \cos 2u' \right) \right]. \end{aligned} \tag{6}$$

$$\begin{aligned} \frac{d^2 Q''}{dt^2} = & - 3m'n''^2 \left[ G'(k'' \sin u' - h'' \cos u') + \frac{a''}{a'} F'(k' \sin u' - h' \cos u') \right] \\ & + 6n'' \left[ a_{2,1} \left( \{k''^2 - h''^2\} \sin 2u' - 2k''h'' \cos 2u' \right) \right. \\ & \quad \left. + \frac{m'\sqrt{a'}}{m''\sqrt{a''}} a_{1,2} \left( \{k'^2 - h'^2\} \sin 2u' - 2k'h' \cos 2u' \right) \right. \\ & \quad \left. - 2b_{2,1} \left( \{k'h'' - h'h''\} \sin 2u' - \{k'h'' + h'k''\} \cos 2u' \right) \right]. \end{aligned}$$

To derive from these the formulas [3] we must for  $h, k, h' \dots$  substitute the values

$$\begin{aligned} h &= B \sin u + B_1 \sin u' \\ k &= B \cos u + B_1 \cos u', \end{aligned} \quad \text{etc. . . . . [7]}$$

which are given by TISSERAND at the bottom of page 21. In the

result we then reject all terms which do not contain the argument

$$u' - u = \vartheta + 180^\circ,$$

or its multiples. We thus find easily

$$\left. \begin{aligned} \frac{d^2 \varrho}{dt^2} &= \frac{3}{2} m' n^2 \left[ F B_1 + \frac{a}{a'} G_1 B_1' \right] \sin(u-u') \\ &\quad - 3n \left[ a_{0,1} B_1^2 + \frac{m' \sqrt{a'}}{m \sqrt{a}} a_{1,0} B_1'^2 - 2b_{0,1} B_1 B_1' \right] \sin 2(u-u') \\ &\quad - 6n \left[ a_{0,1} B B_1 + \frac{m' \sqrt{a'}}{m \sqrt{a}} a_{1,0} B' B_1' - b_{0,1} (B B_1' + B_1 B') \right] \sin(u-u') \\ \frac{d^2 \varrho'}{dt^2} &= -3m n'^2 \left[ G B_1' + \frac{a'}{a} F B_1 \right] \sin(u-u') \\ &\quad + \frac{3}{2} m'' n'^2 \left[ F' B' + \frac{a'}{a''} G_1' B'' \right] \sin(u'-u) \\ &\quad + 6n' \left[ a_{1,0} B_1'^2 + \frac{m \sqrt{a}}{m' \sqrt{a'}} a_{0,1} B_1^2 - 2b_{1,0} B_1 B_1' \right] \sin 2(u-u') \\ &\quad + 12n' \left[ a_{1,0} B' B_1' + \frac{m \sqrt{a}}{m' \sqrt{a'}} a_{0,1} B B_1 - b_{1,0} (B B_1' + B_1 B') \right] \sin(u-u') \\ &\quad - 3n' \left[ a_{1,2} B^2 + \frac{m'' \sqrt{a''}}{m' \sqrt{a'}} a_{2,1} B''^2 - 2b_{1,2} B' B'' \right] \sin 2(u'-u) \\ &\quad - 6n' \left[ a_{1,2} B' B_1'' + \frac{m'' \sqrt{a''}}{m' \sqrt{a'}} a_{2,1} B'' B_1'' - b_{1,2} (B' B_1'' + B_1' B'') \right] \sin(u'-u) \\ \frac{d^2 \varrho''}{dt^2} &= -3m' n''^2 \left[ G' B'' + \frac{a''}{a'} F' B' \right] \sin(u'-u) \\ &\quad + 6n'' \left[ a_{2,1} B''^2 + \frac{m' \sqrt{a'}}{m'' \sqrt{a''}} a_{1,2} B^2 - 2b_{2,1} B' B'' \right] \sin 2(u'-u) \\ &\quad + 12n'' \left[ a_{2,1} B'' B_1'' + \frac{m' \sqrt{a'}}{m'' \sqrt{a''}} a_{1,2} B' B_1'' - b_{2,1} (B' B_1'' + B_1' B'') \right] \sin(u'-u) \end{aligned} \right\} [8]$$

We now put

$$\sin(u-u') = \sin \vartheta$$

$$\sin 2(u-u') = -2 \sin \vartheta,$$

Further we introduce the approximate values of  $B, B' \dots$  which TISSERAND gives in the middle of page 22, viz.:

$$B = m CG \quad B_1' = m'' CF' \quad B_1 = B'' = 0, \dots [9]$$

where  $C$  is a constant, the value of which is indifferent to our argument, and can easily be derived by comparison with TISSERAND.

We then neglect the squares and products of  $B$ ,  $B'$  . . . , and also the difference of  $G_1$  and  $G$ , and we put

$$n^2 a^3 = n'^2 a'^3 = n''^2 a''^3 = f, \quad . . . . . [10]$$

which also is only approximately true, and

$$-\frac{3}{2} \frac{f}{a'} C F G = K,$$

Introducing all these simplifications we find the equations (22) of TISSERAND, viz.:

$$\begin{aligned} \frac{d^2 l_1}{dt^2} &= - \frac{m' m''}{a^2} K \sin \vartheta \\ \frac{d^2 l_2}{dt^2} &= 3 \frac{m m''}{a'^2} K \sin \vartheta \\ \frac{d^2 l_3}{dt^2} &= - 2 \frac{m m'}{a''^2} K \sin \vartheta, \end{aligned}$$

In comparing these with TISSERAND it must not be forgotten that our  $\vartheta$  differs  $180^\circ$  from TISSERAND's. We have thus, if all the above mentioned approximations are introduced

$$Q_1 = \frac{m' m''}{a^2} K, \quad Q_2 = - 3 \frac{m m''}{a'^2} K, \quad Q_3 = 2 \frac{m m'}{a''^2} K. \quad [11]$$

The values [9], however, are only approximately true; they contain only the perturbations of the first order in the masses. Nevertheless the deviations of the values of  $Q_i$  from the truth caused by the adoption of these approximate values, and similarly by [10] and by the neglect of difference of  $G$  and  $G_1$ , are not of a serious nature. The neglect of the terms of the second degree in  $B$ ,  $B'$  . . . on the other hand, is very serious.

Now discarding all these simplifications, with the exception of  $B_1 = B_1'' = 0$ , which we continue to adopt, we find for the complete values of  $Q_1, Q_2, Q_3$ :

$$\left. \begin{aligned} Q_1 &= - \frac{3}{2} m' n^2 \frac{a}{a'} G_1 B_1' - 6n \left[ \frac{m' \sqrt{a'}}{m \sqrt{a}} a_{1,0} (B_1'^2 - B' B_1') + b_{0,1} B B_1' \right] \\ Q_2 &= + 3 m n'^2 G B_1' + \frac{3}{2} m' n'^2 F' B' + \\ &\quad + 12n' [a_{1,0} (B_1'^2 - B' B_1') + b_{1,0} B B_1'] + \\ &\quad + 6n' [a_{1,2} (B'^2 - B' B_1') + b_{1,2} B' B_1''] \\ Q_3 &= - 3 m' n''^2 \frac{a''}{a'} F' B' - 12n'' \left[ \frac{m' \sqrt{a'}}{m'' \sqrt{a''}} a_{1,2} (B'^2 - B' B_1') + b_{2,1} B' B_1'' \right] \end{aligned} \right\} [12]$$

Using the numerical data adopted by SOUILLART, and putting

$$m_1 = 10000 m, \quad m_2 = 10000 m', \quad m_3 = 10000 m''.$$

we find from formula [11]

$$Q_1 = + 0.03201 m_2 m_3$$

$$Q_2 = - 0.03794 m_1 m_3$$

$$Q_3 = + 0.00994 m_1 m_2,$$

From the formulas [12], on the other hand, we have:

$$Q_1 = \{ + 0.03009 - 0.00460 m_1 - 0.01156 m_2 - 0.00958 m_3 \} m_2 m_3 = \\ = + 0.01815 m_2 m_3$$

$$Q_2 = \{ - 0.03436 + 0.00389 m_1 + 0.00933 m_2 + 0.00809 m_3 \} m_1 m_3 = \\ = - 0.02438 m_1 m_3$$

$$Q_3 = \{ + 0.00794 - 0.00020 m_1 - 0.00016 m_2 - 0.00042 m_3 \} m_1 m_2 = \\ = + 0.00751 m_1 m_2.$$

The numerical coefficients depend almost exclusively on the ratios of the major axes, i.e. on the mean motions, and they can be taken as correct to the last figure given.

The corresponding periods, computed by the formula

$$T = \frac{2\pi}{\beta},$$

are, expressed in years:

from formula [11] . . . . .  $T = 6.318$

from formula [12] . . . . .  $T = 7.985,$

The difference is considerable.

The question naturally arises: why have these important terms of the second degree been overlooked by LAPLACE and SOUILLART? For LAPLACE, the answer is very simple: he has neglected the part  $R_4$  of the perturbing function throughout. For SOUILLART it is different. It is one of SOUILLART's great merits to have discovered the importance of this same part of the perturbing function, especially for the determination of the quantities  $B, B' \dots$ . The corrections which have been added by SOUILLART on this account to these coefficients, amount to a considerable part of the whole. Also SOUILLART evidently intended to find the expression for the period of the libration as completely as possible. On the pages 46 and 47 (Memoirs of the Royal Astronomical Society, Vol. XLV) he considers the different parts of the perturbing function, which can in the differential coefficients of the mean longitudes introduce the argument  $l_1 - 3l_2 + 2l_3$ . He, however, rejects them all, as giving negligible coefficients, and retains only the terms which had already been discovered by LAPLACE. Among the rejected terms are also the new terms treated above, which are discarded by SOUILLART on the ground that they are of the second degree in the excentricities (page 47, bottom). He here overlooks

that in these terms, for the same reason as in those of the first degree, the excentricities must be replaced by their perturbations with the arguments  $u$  and  $u'$ , in order to find the terms determining the libration. These terms thus are of the second degree, not in the excentricities, but in the quantities  $B, B' \dots$  and of *these* the squares are not negligible, as we have seen.

The question further arises: do not the terms of the third degree in the excentricities, i. e. those of the types

$$\begin{aligned} P e^3 \cos(2l' - l - \tilde{\omega}), & \quad Q e^3 e' \cos(2l' - l - 2\tilde{\omega} + \tilde{\omega}'), \\ R e^3 \cos(6l' - 3l - 3\tilde{\omega}), & \quad S e^3 \cos(4l' - l - 3\tilde{\omega}), \text{ etc.} \end{aligned}$$

also contribute appreciably towards the coefficients  $Q_i$ ? To find the answer to this question I have computed all the terms of this kind in  $Q_1$ . These terms of the third degree, which are of the fourth order in the masses, are:

$$\delta Q_1 = \{ + .00012 m_1^2 + .00079 m_2^2 + .00034 m_3^2 + .00061 m_1 m_2 + \\ + .00050 m_1 m_3 + .00124 m_1 m_3 \} m_2 m_3 = + .00071 m_2 m_3.$$

They are thus not wholly negligible. I have, however, not carried out the computation — which is rather complicated — for  $Q_2$  and  $Q_3$ , nor have I computed the terms of the fourth degree (i. e. of the fifth order in the masses). The development of the period  $T$  in powers of the masses evidently converges very slowly, and the period computed by the formulas [12] may very well be erroneous by a few tenths of a year.

2. *The equations of the centre.* The large inequalities, which in the integration by the method of variation of elements appear as perturbations of the excentricities and perijoves (formula [7] above), are in practice added to the longitudes and radii-vectores, and the excentricities and perijoves are conceived to be affected by their secular, but *not* by their periodic perturbations. I now return to the notations used in all my other work on the satellites, and I denote the excentricities and perijoves, defined in this way, by  $E_i$  and  $\Omega_i$ . We have then<sup>1)</sup>

$$\left. \begin{aligned} h_i &= 2 E_i \sin \Omega_i = 2 \sum_j \tau_{ij} e_j \sin \tilde{\omega}_j \\ k_i &= 2 E_i \cos \Omega_i = 2 \sum_j \tau_{ij} e_j \cos \tilde{\omega}_j \end{aligned} \right\} \dots \dots [13]$$

The sums extend over the values of  $j$  from 1 to 4;  $e_i$  and  $\tilde{\omega}_i$  are the "own" excentricities and perijoves of LAPLACE, the values of  $e_i$  are constant and  $\tilde{\omega}_i$  are linear functions of the time. Further

<sup>1)</sup> These  $h_i$  and  $k_i$  are thus *not* the same quantities as those denoted by  $h, k, h' \dots$  by TISSERAND.

$r_{ii} = 1$ , the other ratios  $r_{ij}$ , and the motions  $\frac{d\tilde{\omega}_i}{dt}$  depending on the masses. Thus if certain values of the masses are adopted, the ratios  $r_{ij}$  are thereby determined. If then  $h_i$  and  $k_i$  of the four satellites are known from the observations, then from the eight linear equations [13] (consisting of two sets of four each, with the same coefficients) we can determine the eight unknowns  $e_i \sin \tilde{\omega}_i$  and  $e_i \cos \tilde{\omega}_i$ , and from these again  $e_i$  and  $\tilde{\omega}_i$ . The method is exactly the same as the one used by me for the determination of the inclinations and nodes (see these Proceedings, 1906 March, pages 767—780). The values of  $h_i$  and  $k_i$  have been determined from the heliometer-observations made at the Cape Observatory, in 1891 by Sir DAVID GILL, and in 1901 and 1902 by Mr. BRYAN COOKSON. The results from these observations have been treated by the method just delineated, in two different suppositions regarding the masses, i. e. regarding the ratios

Satellite	Epoch	$e$			$\tilde{\omega}$			$\tilde{\omega}_{1900.0}$	
		System I	System II	$p.e.$	System I	System II	$p.e.$	System I	System II
I	1891.75	0°036	0°036	± 009	158°	157°	± 15°	248°	235°
	1901.61	.055	.055	± 22	136	136	± 36	48	50
	1902.60	.022	.021	± 17	262	270	± 27	120	131
II	1891.75	0 018	0 020	± 006	169	166	± 16.	300	274
	1901.61	.020	.019	± 14	318	315	± 37	292	294
	1902.60	.026	.026	± 9	302	301	± 24	261	267
	Mean	0.021	0.022					284	278
III	1891.75	0.086	0.086	± 003	179.7	179.6	± 2 0	201.4	200.4
	1901.61	.100	.101	± 9	198.2	198.1	± 5.6	193.9	193.8
	1902.60	.080	.080	± 6	219.0	218.8	± 4.0	212.2	212.3
	Mean	0.089	0.089					202.5	202.2
IV	1891.75	0.4284	0.4280	± 0015	142.28	142.29	± 0.20	148.19	147.83
	1901.61	.4228	.4216	± 30	148.92	149.05	± .40	147.76	147.96
	1902.60	.4261	.4262	± 25	149.06	149.03	± .34	147.20	147.28
	Mean	0.4258	0.4253					147.72	147.69

$\tau_{ij}$  and the motions  $\frac{d\tilde{\omega}_i}{dt}$ . The results are collected in the following table. The values of  $\tilde{\omega}_i$  for 1900.0, given in the last two columns, have been derived from those for the individual epochs for each system separately by means of the motions  $\frac{d\tilde{\omega}_i}{dt}$  corresponding to the assumed masses. The perijoves are counted from the assumed vernal equinox of Jupiter, whose longitude in 1900.0 is  $135^\circ.45$ .

The values of these elements, on which SOUILLART's theory is based, are:

(1900.0)	
$e_1 = 0.001$	$\tilde{\omega}_1 = 305^\circ$
$e_2 = 0.006$	$\tilde{\omega}_2 = 177$
$e_3 = 0.064$	$\tilde{\omega}_3 = 206.1$
$e_4 = 0.4160$	$\tilde{\omega}_4 = 152.69$

The results from the two systems are practically identical. The corrections to SOUILLART's values for the satellites II, III and IV, are considerable, and on the whole much larger than the deviations of the three epochs *inter se*. These corrections are thus undoubtedly real. The most remarkable of them is certainly the large own excentricity of II. The value of this element, assumed by DELAMBRE and DAMOISEAU is zero. The value used by SOUILLART in his theory is a pure arithmetical result, and has no weight whatever as a determination of the element. DAMOISEAU, however, has suspected the existence of an excentricity of practically the same amount as is found here. This is shown by the following quotation from his unpublished memoir, written in explanation of the construction of his tables, which I quote after SOUILLART<sup>1)</sup>. DAMOISEAU says there: "Nous avons des motifs de soupçonner dans l'orbite du second satellite une équation du centre propre de  $32^s$  en temps synodique (ce qui correspondrait à une excentricité propre de 0.00032738), mais notre incertitude sur la position du périjove, dont le mouvement est encore à calculer par la théorie, nous a fait remettre cette recherche à un autre temps." This excentricity, expressed in arc is  $0^\circ.0188$ , and it is therefore practically the same as the value found by me. The reason adduced by DAMOISEAU for not using it in his tables sounds somewhat strange: as a matter of fact the motion of the perijove had been determined long ago by LAPLACE.

With regard to Satellite I it is clear that the apparent equations

<sup>1)</sup> *Mémoires des Savants étrangers*, tome XXX, page 28.

of the centre derived from the observations — which moreover are only little larger than their probable errors — do not represent a true excentricity. It is not impossible that they are produced by the existence of surface markings on the disc of the satellite, causing the centre of light, which is observed by the heliometer, to be displaced relatively to the centre of gravity, the displacement being different at different epochs. Any attempt to explain the observed  $h_i$  and  $k_i$  on this hypothesis would, however, necessarily involve so many undeterminate quantities, that its success would be no proof of its representing a true fact of nature.

### 3. *Determination of the libration from the observations.*

In a communication made by me in 1905 to the "Nederlandsch Natuur- en Geneeskundig Congres",<sup>1)</sup> I have shown :

that the libration probably has an appreciable coefficient,

that the determination from the observations, not only of the phase and amplitude, but also of the period of the libration, is of the highest importance for the derivation of the masses, especially of the mass of Satellite I,

that this determination is possible from the observations made at the observatories at the Cape, Helsingfors and Pulkowa,

that most probably the period differs considerably from the value adopted by LAPLACE and SOUILLART, and

that this determination is intricately connected with an investigation of the long-periodic inequalities in the longitudes of the satellites, and that consequently the whole problem can only be solved by successive approximations.

In number 17 of the Publications of the Astronomical Laboratory at Groningen, which will soon be published, all these conclusions are confirmed and the successive approximations are carried out. In this communication I cannot dwell upon the details of this investigation, nor upon the difficulties which were encountered. I must confine myself to a brief statement of the results.

The observations used are the heliometer-observations of the Cape Observatory already quoted above, and further photographic plates taken at Helsingfors in the years 1892—93, 1893—94, 1894—95, 1895—96 and 1897, at Pulkowa in 1895—96, 1897 and 1898, and at the Cape in 1904. I thus had at my disposition ten oppositions

<sup>1)</sup> "Over de libratie der drie binnenste groote satellieten van Jupiter en eene nieuwe methode ter bepaling van de massa van Satelliet I." Handelingen van het 10de Congres, pages 125—128.

in all. For each of these corrections  $\Delta l_i$  to the assumed longitudes of the satellites were derived. These direct results from the observations can, however, not be used as they stand. There are, as has been mentioned above, in the longitude of each satellite four inequalities, whose periods are between 400 and 500 days, and whose coefficients are of the same order of magnitude as the libration. These inequalities therefore, during the few months over which each of the ten series of observations extends, are practically constant, and the correction  $\Delta l_i$  derived from the observations consequently contains, in addition to the correction  $\Delta \varepsilon_i$  to the mean longitude, and the libration, also the correction to the assumed values of these inequalities.

Now the coefficients of these inequalities are proportional to the excentricities and depend on the masses, and are therefore incertain to the same extent as these, i.e. to a very large extent. The periods of the four inequalities are so nearly equal, that they cannot be separated from each other. Further the period of the most important of them — important both by its magnitude and by its uncertainty — differs just so much from the average interval of one opposition to the next that, when we consider only the values at the epochs of opposition, the inequality presents itself as one having approximately the period of the libration, and can therefore not be separated from the libration itself. For all these reasons it was impossible to determine the libration *and* the long-periodic inequalities from these observations alone.

For the determination of the masses, leaving for the moment the mass of IV out of consideration, we have the following data:

1. the large inequalities in the longitudes of the satellites I, II and III,
2. the motion of the perijove of satellite IV,
3. the period of the libration.

The motion of the perijove of IV also depends on the compression of the planet, which must thus also be investigated, and is determined by

4. the motion of the node of satellite II.

The data mentioned under 1, 2 and 4 are those used by LAPLACE, 3 has for the first time been pointed out by me in the communication to the "Nederlandsch Natuur- en Geneeskundig Congres", quoted above.

The method by which the approximations have been conducted is the following. Certain values of the masses, approximately verifying the conditions 1, 2, and 4, are assumed, and the corresponding

values of the long-periodic inequalities are computed. Let these be  $\delta l_i'$ , and let  $\delta l_i^0$  be the values used in computing the tabular places which were compared with the observations. Then evidently the correction to the mean longitude corresponding to the assumed masses (and equations of the centre) is

$$\Delta l_i' = \Delta l_i - (\delta l_i' - \delta l_i^0).$$

From these  $\Delta l_i'$  we then determine the amplitude, the phase and the period of the libration. If this period co-incides with the one computed from the assumed masses, then the approximation is sufficient, if not, then the whole process is repeated with different masses.

The communication of the different approximations and of the residuals remaining after the substitution of the finally adopted values, would exceed the limits set to this paper. The formula finally derived for the libration is

$$\vartheta = 0^\circ.158 \sin \frac{t - 1895.09}{7.0}.$$

The adopted masses are

$$m_1 = 0.0000 \ 256$$

$$m_2 = 0.0000 \ 231$$

$$m_3 = 0.0000 \ 820$$

and the corresponding ratio of the distribution of the libration over the longitudes of the three satellites is given by

$$\frac{\vartheta_1}{\vartheta} = + 0.175 \quad \frac{\vartheta_2}{\vartheta} = - 0.260 \quad \frac{\vartheta_3}{\vartheta} = + 0.022^s$$

The mean longitudes (excluding libration) on 1900 January 0, Greenwich mean noon, are (counted from the point Aries)

$$l_1 = 142^\circ.604$$

$$l_2 = 99 \ .534$$

$$l_3 = 167 \ .999$$

$$l_4 = 234 \ .372,$$

By a comparison of these with the values at the epoch 1750.0 the following sidereal mean daily motions<sup>1)</sup> were derived

$$n_1 = 203^\circ.4889 \ 5652$$

$$n_2 = 101 \ .3747 \ 2411$$

$$n_3 = 50 \ .3176 \ 0790^s$$

$$n_4 = 21 \ .5710 \ 7132.$$

I have added no probable errors, which in the absence of the details of the observational material can only have a subjective value.

<sup>1)</sup> i.e. sidereal mean motions in a mean solar day.

**Geology.** — *“Considerations on the Starvingian “Zanddiluvium””*.

By P. TESCH. (Communicated by Prof. K. MARTIN).

The sandy areas form a great part of the Dutch land. When from the so-called diluvial half of our country the gravelous diluvium with the boulder-clay, the alluvial moors and river deposits and the regions where the wind has influenced the bottom, are subtracted, the districts are resting where the surface consists of sand without or with little gravel and which are gathered by STARING under the collective name of “zanddiluvium”. These districts have in the different parts of our country a different appearance and a different fertility. Therefore the neutral name of “zanddiluvium” has been chosen by STARING for a very good reason, in which name the origin rests undecided by this name. Yet he speaks on the pages 114 to 121 of the second volume of his “Bodem van Nederland” about the origin of these sand deposits as follows:

“Evidently it has been formed in the last part of the diluvial period or in the very first part of the alluvial period; for everywhere where it is found, it rests upon the gravelous diluvium and is covered by the alluvial beds.”

“This form (the horizontal position of the composing strata) connected with its position upon the gravelous diluvium and at the foot of the hills formed by this, permits to decide, with great probability, about the presumptive origin of the “zanddiluvium”. The sand with boulders and gravel being transported to the places where it is found now and having taken its present form, still a long time must have passed, before the surface was fastened by the vegetation and the currents were streaming in their present beds. During this period frost and rain will have had a stronger influence on these accumulations of sand and boulders than afterwards when their surface was protected by a thick crust of humus. The rocks which are capable of disintegration, many granites, mica slates, sand-stones and grits, have been converted into gravel, sand and clay, and the rain water has transported it for a great part to the valleys. These valleys were filled up and at the same time the hills became lower and took a more rounded form than was originally the case. That this sand represents the detritus of the gravelous diluvium and has been formed during the transition-time to the alluvial period, is also to be concluded from the reflection that such a formation must exist and that this formation cannot be pointed out in another than in this sand.”

STARING was however not ignorant of the fact that still other factors have contributed to the formation and the distribution of this sand.

This may be sure when we see, how on his geological map on some places along the great rivers alluvial sand-banks are placed on the "zanddiluvium", isolated from the present river-bed and how on the index of the colours "zanddiluvium" and "rivages diluviens" are marked with different character Z and Z' and yet this difference has not been sustained on the map. Here the same colour and the same character Z signifies "zanddiluvium" as well as "diluvial sand-banks" (map 19) and "river banks" (map 20). Apparently STARING would not decide, though he was convinced that those formations are not equivalent. He may not have said it clearly, yet the honour of having first recognized the problem is due to him.

So STARING's point of view in the matter was as follows:

The "zanddiluvium" includes all sanddeposits which have been formed after the glacial period and which are not surely alluvial. It has been washed away by rain water from the gravel-hills in the neighbourhood; yet on many places the possibility of another origin may be taken into consideration.

After STARING only three geologists, as far as is learned by the literature I can dispose of, have been engaged in the study of the postglacial "zanddiluvium".

At the 7<sup>th</sup> Physical and Medical Congress in 1899 (Transactions page 450) Dr. H. VAN CAPPELLE spoke on "de oorsprong van het heide- of hellingzand".

In the STARINGIAN "zanddiluvium" formations of a different age must be represented. The orator observed on many places (West-Drenthe, Gaasterland, Amersfoort etc.) between the sand which may be considered with great probability as the product of the washing from the gravel-hills, old surfaces which he connects with the interglacial period by the following reasoning:

"the younger diluvial currents which have formed the level sand of the valleys, have eroded this "heidezand". The sand of the valleys being formed in the period of the melting away of the first glacier, for the formation of the older "heidezand" only two subsections of the diluvial period rest: 1<sup>st</sup>. the second glacial period and 2<sup>nd</sup>. the period of the melting away of the first glacier."

"The first age is possible for the sand which covers the mentioned vegetable beds. So these vegetable beds must be interglacial. The sand which covers the boulder-clay directly, may also be a deposit of the first glacier."

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Before continuing, I will add some remarks. The old surfaces, observed by Dr. VAN CAPPELLE, prove nothing else but the fact that in the formation of this sand periods of rest have existed, in which organic life could develop on the sand. But this fact does not yet prove that two different geological periods are necessary. Indeed Dr. VAN CAPPELLE himself says that the vegetable beds lie between the sand in the shape of wedge and so are very local. They have not any value for a further determination of the age. I agree perfectly well with Dr. VAN CAPPELLE where he says on page 451:

“this author (Dr. J. MARTIN at Oldenburg) will not believe that the interglacial period has passed without leaving behind traces in our country, though a convincing proof is not to be given, because the ground moraine of the second glacier fails”, and indeed it is not to be thought otherwise that among our so-called postglacial formations, deposits exist which are equivalent to such of the second interglacial period and the third glacial period in Germany, but a decisive proof is not to be given. Old surfaces between the sand have not the least demonstrative power in this matter. To show the point of view of Dr. VAN CAPPELLE in 1899 in regard to the origin of the “heidezand”, I will cite the conclusion at the end of the mentioned communication:

The “heidezand” has been formed in part by the melting waters of the retiring first glacier, in part after the interglacial period by the brooks which were streaming from the gravelhills in the time of the approaching of the second glacier; also the alluvial period has contributed to the increase of the “heidezand” by the washing of the hills.”

Dr. J. LORIE has laid stress upon the fact that the sandy plains which accompany our great rivers and many smaller ones ought to be considered as river-beds of the diluvial times. This sand has been washed away from the banks and removed down the current. Two examples will do.

At the 4<sup>th</sup> Physical and Medical Congress in 1893 (Transactions page 393) Dr. LORIE speaks about “the peat-moors of Brabant-Limburg.” The speaker demonstrates that these moors owe their origin to existing grooves in the surface which had no drainage. Those grooves represent old branches of the Meuse. This whole region ought to be considered as a diluvial delta of the Meuse.

“From the stadium of the “wild waters” when the Meuse was still streaming without a definitive bed, a compound network was born which decreased gradually, until only one current, the present Meuse, remained.”

In the communications on the geology of the Netherlands, collected by the geological committee, number 35, Dr. LORIE shows convincingly that the surface of the "Geldersche Vallei" represents a terrace of a faded branch of the Rhine.

"The peat is followed by a thick layer of sand which has not been washed away from the hills on either side, but has been supplied by a branch of the Rhine which thus built a terrace". (p. 95).

The fact, that the fluvial sand reposes upon the marine fauna of the "Eemstelsel" with temperate character and is still separated from it by peat and clay, proves in my opinion that the terraces have been formed by the rivers in an old-alluvial period with our present climate. I hope to revert soon to this subject.

The third examiner of the Dutch sand districts was Dr. J. L. C. SCHROEDER VAN DER KOLK, and it may be superfluous to draw out his great merits another time, also in regard to this geological problem. To his accurate sand inquiry we owe this division<sup>1)</sup>.

I. Quartz-amfibol-sands:

- a. quantity less than 0,4. Southern Diluvium.
- b. quantity more than 0,4. Northern Diluvium.

II. Quartz-garnet-sands:

- a. small quantity. Increase. Alluvium.
- b. great quantity. Decrease. Alluvium.

He applied his rules to this study of the environs of Deventer with much acuteness.

SCHROEDER VAN DER KOLK could not continue his successful researches because of his busy life in Delft and his feeble health, and his death has put an end to all further expectations.

The difficulties are far from being conquered now. In general the rules of SCHROEDER VAN DER KOLK are quite right. Yet it is not sufficient for the classification of each sand to determine the quantity of heavy minerals. The activity of the forces of nature being too much complicated, the effect cannot appear in a so simple form in all cases. In each case all circumstances must be taken into consideration or we shall often come to an erroneous conclusion. The following example shows this necessity.

The lower parts of the Rhine-diluvium in Limburg are formed by grey sands. In these sands grains of basalt are tolerably numerous. Even when the grains larger than 2 mM. and those smaller than 0,2 mm. are removed, the quantity of heavy minerals is still 0,5 to 0,6, the specific weight of basalt being 2,9 to 3,1. The grains of

<sup>1)</sup> In this form SCHROEDER VAN DER KOLK gave his division at the 6<sup>th</sup> Physical and Medical Congress in 1897 (Transactions page 409).

basalt not being considered as a *mixture* of minerals, it would be concluded that these sands belong to a glacial sheet which had reached our country before the gravel of the Rhine-diluvium had been deposited. Such a contradiction would give rise to many difficulties.

There is still more. In the gravelous diluvium *in situ*, the practical limit of 0,4 % will probably give good results, but in the "zand-diluvium", the materials of which must have been derived from the gravelous diluvium, the quantity of heavy minerals must have been changed, according to the different manners of derivation. Here the greatest prudence is wanted.

When a characteristic can be pointed out which may be considered as the effect of these different manners of derivation, a further step has been made. I believe I have found a specific which may aid in some cases to take a decision, where the rules of SCHROEDER VAN DER KOLK do not help. I add immediately that this specific is not at all universal.

It will be necessary to tell in a very general manner how in my opinion the beginning of the diluvial period found our country and how our gravelous diluvium has been deposited.

As much as we know now, the tertiary base of our country is marine (excepted South-Limburg). In the western part of Zeeuwsch-Vlaanderen the base is formed by the "rupelleem", in the eastern part it is the marine deposit of the Diestien. Along our southern frontiers the marine deposits of the Poederlien, Diestien and Bolderien exist. The sands of the Moséén appertain in my opinion to the old fluvial diluvium. The miocene land- and fresh-water deposits seem to be restricted to South-Limburg. Along our eastern frontiers the base is formed by upper-oligocene sea-sands, to the north these strata are covered by miocene deposits. In Gelderland and Overijssel the same miocene clay forms the surface. In North-Brabant and North-Limburg this miocene is still covered by sands which probably appertain to the pliocene. To the north and west LORÉ has shown a pliocene sea-ground at several places (Grave, Arnhem, Goes, Gorkum, Bergen op Zoom, Utrecht and Amsterdam) which declines to the north-west. So at the beginning of the diluvial period the greater part of our country was covered by the pliocene sea and only in the east and south-east a coast existed.

Now the rivers Rhine and Meuse supplied the enormous quantity of sand and gravel which form everywhere in our country the base (excepted Zeeuwsch-Vlaanderen and South-Limburg). A delta was built which filled up the basin of Holland and the Southern North-sea as far as the chalk rocks of Norfolk and Suffolk.

Then a part of this delta was covered by the northern glacier which deposited its moraines on the surface of the delta. The glacial sheet being retired, a new period begins. The river water remained at the south of the morainal barrier Laren, Rhenen, Nymegen, Cleef, Xanten, and the rivers came from the stadium of the "wild waters" into the stadium of a compound network. The gravelous diluvium has been deposited and we have to examine in what way the surface can have been changed now.

In the sandy areas which are very numerous in our gravelous diluvium, we may expect;

- a. the sand which has been removed by the wind.
- b. the sand washed away from the hills by rain water.
- c. the sand deposited by a river in its bed.

How to distinguish these sands? The sand *a* must be deposited in a depression and does not show a stratification. The composition and the largeness of the grains do not offer a regularity and the surface must be hilly. This origin may be possible for sand districts which are surrounded by gravel-hills.

The sand *c* may be found along the rivers or in a groove which represents a faded river bed. In general the surface declines down the current and the sand is stratified in a horizontal position. The composition and the largeness of the grains give no difference in the direction of the stream, neither in vertical direction.

The sand *b* may be found in depressions as well as in grooves, has also to show a horizontal stratification, but in the composition and the largeness of the grains differences may be expected:

1. in the direction of the groove, when the bordering hills differ in composition, as in the case of the hills of IJolten, Markelo and Lochem.

2. in vertical direction. When grains of sand are washed down the hills by rain water, the grains become smaller, while the inclination decreases gradually. So the grains of the sand *b* has to become smaller in the higher parts of the layer.

The next may show whether this characteristic can practically be used.

In the last year the Dutch Government drilled at three places in the Peel. As appeared the peat reposes on sand and then the gravelous diluvium follows. The question is whether this sand is a sand *b* or a sand *c*. When the lower parts have indeed a greater quantity of large grains than the higher parts, it may be a sand *b*, else we have better consider it as a sand *c*.

The hill-slope from Meyel to Deurne is about 18 K.M. long and has a direction from N. N. W. to S. S. E. At the east of this ridge are situated the three places (at the station of Helenaveen, at the village of Helenaveen and at the north of the village of Helden) which I shall call 1, 2 and 3, from the north to the south.

The position of the sand bed is as follows :

	Meters + A.P.		thickness
	from	to	
at the first place	31 32	24.92	6 40
at the second place	32.01	25.76	6.25
at the third place	30 19	23.54	6.65

I accept four sorts of grains :

Sort A: grains larger than 2 mm.

Sort B: grains smaller than 2 mm. and larger than 1 mm.

Sort C: grains smaller than 1 mm. and larger than  $\frac{1}{2}$  mm.

Sort D: grains smaller than  $\frac{1}{2}$  mm.

The grains were separated by sieving and the quantity was weighed. The results are found in the following tables :

FIRST PLACE.

Depth of the sample in meters + A. P.	Sort	Sort	Sort	Sort
	A.	B.	C.	D.
31.12	0.18	0.30	38.7	60.7
30.42	0.17	0.33	35.5	64.0
29.38	0.43	0.66	41.2	57.7
28.38	0.45	0.75	41.7	57.1
27.62	0.87	0.74	45.9	52.5
26.52	0.93	1.58	47.5	50.0
25.42	2.80	1.88	46.0	49.3

## SECOND PLACE.

Depth of the sample, in meters + A. P.	Sort	Sort	Sort	Sort
	A.	B.	C.	D.
31.36	0.25	0.56	39.2	60.0
29.56	0.58	0.58	37.8	61.0
28.56	0.61	0.92	42.3	56.2
27.56	1.83	2.80	44.3	51.1
26.56	3.50	2.78	44.5	50.2

## THIRD PLACE.

Depth of the sample, in meters + A. P.	Sort	Sort	Sort	Sort
	A.	B.	C.	D.
28.04	0.09	0.52	29.8	69.6
27.04	1.25	2.83	29.5	66.4
25.04	2.79	2.92	34.6	59.6

These lists show that indeed in the higher parts of the sand bed are more small grains and fewer large grains. So the question is decided in favour of the sand *b*.

It occurs to me that we may accept:

1<sup>st</sup>. that the groove originally was the bed of an old branch of the Meuse. However this river did not wash away sand from the banks.

2<sup>nd</sup>. that afterwards the groove has been filled up with sand *b*. As I remarked already, this specific is not at all universal, but can only give an indication in some cases.

Finally a remark. The glacial sheet being retired the glacial period ends for our country. Meanwhile we know that afterwards another approach of the glacier came, which did not reach our country. As Dr. VAN CAPPELLE remarked already, interglacial deposits must exist in our country. We do not know however deposits with an arctic fauna and so the points of comparison fail to divide our postglacial diluvium. Therefore we cannot give a further determination of the age for the deposits between our gravelous diluvium

and the modern formations. In my opinion it is not possible to make a map of our country which is *strictly* geological. But it is just for that reason that a geological survey would have to do good work, by finding means to conquer the difficulties.

For the moment we must be content with a temporary division which I propose as follows:

A. Glacial and fluvial (fluvio-glacial) diluvium. The expression "preglacial" can be applied only to the surface of the delta, where the deposits of the northern glacier repose on it. At the south of the glacial front the surface of the delta may be formed contemporaneously with the glacial diluvium.

B. Postglacial diluvium and old-alluvium.

Only in some cases it will be possible to draw the line.

C. Recent formations.

Within these geological limits only petrographical and genetical distinctions can be made.

Venlo, June 1907.

**Physiology.** — "*On the adsorption of the smell of muscon by surfaces of different material.*" By Prof. H. ZWAARDEMAKER.

(Communicated in the meeting of May 24, 1907).

In 1906 H. WALBAUM discovered the odorous principle of musc in a ketone of constitution  $C_{16}H_{30}O$ , to which the name muscon was given<sup>1)</sup>. Through the kindness of the firm SCHIMMEL & Co. I was enabled to make some olfactological investigations with this preparation, which at my request was mixed with myristic acid for this purpose. With this fatty acid, melting at  $54^{\circ}C.$ , it forms a mixture, containing 0.627% muscon which could easily be cast into an olfactometric cylinder of 8 millimetres lumen. Exposition of 0.15 cm. of such a cylinder to a passing air-current of 100 cubic centimetres per second gives a just recognisable impression of the smell of muscon, a soft perfume, not admitting of further definition and soon growing tiresome. With further dilution this perfume does not change its character. Hence the odorimetric coefficient of the mixture, used by us, was 6,7<sup>2)</sup>.

<sup>1)</sup> H. WALBAUM in SCHIMMEL & Co's Berichte, April 1906, p. 99.

<sup>2)</sup> The odorimetric coefficient of a smelling substance, offered in a certain condition, is defined as the reciprocal value of the length in centimetres of the cylinder, corresponding to the so-called "threshold value" (for olfactometric cylinders of 8 mm.

The olfactometric measurements showed:

1. that the volatilised muscon adheres strongly to the glass walls along which it passes.

2. that rubbing such a glass wall with cotton wool gives rise, instead of an odour of muscon, to a smell, reminding of musc.

This smell of musc was also noticed with glass wool, cotton wool, feathers or paper, placed in the path, but not with asbestos wool and platinum sponge, the time of exposition in all these cases having been about  $\frac{1}{4}$  minute.

This led to a closer investigation, which I undertook the more readily, since an investigation by J. AITKEN in 1905 showed that the odorous principle of musc must be regarded as a gas<sup>1)</sup>. Thus the above-mentioned olfactometric cylinder, containing 0,627 % muscon in myristic acid and having a length of 10 cm. and a diameter of 0.8 cm., was connected by means of a short brass piece with equally long and wide tubes of all sorts of material, in such a way that these tubes could, if required, be kept at a pre-determined temperature by a water-jacket. The thus formed canal passed into an aerodromometer<sup>2)</sup>, i.e. a vertical glass tube in which an aluminium disc is suspended between two spiral springs, the displacement of which indicates the velocity of the air-current by means of an empirical scale. After the aerodromometer finally followed a large tin cone in which an electrically driven fan maintained a suction from the narrow towards the wide end. The connection between the different pieces could be removed and re-established in a moment.

The air, passing through this system, went successively through:

1. the olfactometric cylinder over its full length of 10 cm.
2. the tube of which the adsorption is to be examined.
3. the aerodromometer.

In the experiments here mentioned the velocity of the air-current was perfectly constant; 84 cm.<sup>3</sup> passed per second. Each exposition lasted accurately 5 minutes. Between the experiments the olfactometric

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lumen, i.e. 0.5 cm<sup>2</sup> cross-section). Cf. on this point *Physiol. des Geruchs*, Leipzig 1895, p. 185. The significance of this coefficient, which rises and falls with the smelling power of a substance, is at once seen, when one recognises the close relation between it and the quantity  $b$  in FECHNER's celebrated formula  $\gamma = k \log \frac{\beta}{b}$  (*Psychophysik* II, p. 13). It deserves notice that the odorimetric coefficient of muscon in liquid paraffine is zero.

<sup>1)</sup> J. AITKEN. Evaporation of musk and other odorous substances. *Proc. Roy. Soc.* Vol. 25, p. 894, 1905.

<sup>2)</sup> H. ZWAARDEMAKER. *Arch. f. Anat. u. Physiol. (Physiol. Abth.)*. 1902, p. 417.

cylinder was always kept closed, while controlling experiments with an entirely similar cylinder of pure myristic acid showed that by this alone no lasting adsorption of odour is produced.

Adsorption of odour appeared to be entirely absent with some materials (porous porcelain, carbon, ebonite, steel, iron), with others to exist in a small degree (aluminium, silver, sulphur), with others again to exist in a more or less considerable degree (tin, copper, nickel, glass, lead alloyed with tin, lead). Judging by the impression received immediately after the experiment, the substances may be arranged in the following series of increasing condensation:

Porous porcelain \*, arc lamp carbon, ebonite \*, steel, iron, aluminium\*, silver\*, sulphur\*, tin, copper, nickel, glass, lead alloyed with tin, lead.

The substances marked with an asterisk are not entirely odourless at the temperature of the room.

The first members of this series have no adsorption odour whatever after the muscon-containing air has passed for five minutes, nor do they acquire it by heating. The final members, especially tin, copper, nickel, glass and lead have a distinct adsorption odour which during the first minutes or even hours has an unmistakable muscon character. At last, however, a change takes place, consisting in:

1. an alteration of the quality of the odour, so that finally it resembles musc. This holds for tin, copper, nickel, glass, glazed porcelain, lead alloyed with tin, lead.

2. an increase in the smelling power of the adsorption odour, so that for lead, at any rate, a maximum is obtained after about  $3 \times 24$  hours.

3. a subsequent decrease in the smelling power, so that finally the tubes lose all odour.

Free from any acquired odour the tubes become:

For porous porcelain	in 0 days
„ carbon	„ 0 „
„ steel	„ 0 „
„ iron	„ a few minutes
„ sulphur	„ less than 24 hour
„ aluminium	„ „ „ 24 „
„ glass	„ „ „ 24 „
„ silver	„ „ „ 2 days
„ copper	„ „ „ 4 „
„ tin	„ „ „ 4 „
„ nickel	„ „ „ 4 to 9 days
„ lead alloyed with tin	„ „ „ 6 days
„ lead	„ „ „ 11 to 12 days

Meanwhile these figures have only an approximate value, since the temperature of the room varied considerably during the last spring. In the first place I investigated whether the adsorption of the muscon odour must be explained as an electrical phenomenon. The muscon gas, led over a sensitive electrometer, appeared to impart no charge to it, but it is not impossible that the method was not sensitive enough for this purpose. Therefore in the above described apparatus numbered nickel-plated copper tubes were placed, facing an insulated axially mounted steel rod of 3 millimetres thickness, so that an air condenser was formed with a distance of 2.5 millimetres between the cylindrical charged surfaces. The odd numbers are charged +, the even ones — from the 220 volt continuous current main. Each time, the exposition lasted a minute, the dielectric carrying the muscon passing in the ordinary way at a rate of 84 cm.<sup>3</sup> of air per second. The cylinders appeared to have assumed the odour of muscon with about the same intensity, to acquire later an odour of musc in the same manner and to lose this in about the same time. The comparisons between the tubes were made by three observers, trained in these experiments and independently of each other. <sup>1)</sup>

Next the influence of temperature was investigated, first on the adsorption and next on the change of the smell of muscon into that of musc. For this purpose tubes of an alloy of lead and tin were exposed for ten minutes at 0°, 13° and 100°.

		immediate impression	odourless in
exposition at	0°	strong smell of muscon	5 days
„ „	13°	distinct smell of muscon	2 „
„ „	100°	no smell of muscon	1 day

Then numbered, nickel-plated copper tubes were exposed during two minutes to the ordinary air-current, passing over the muscon-myristic acid. The odd numbers were placed in the ice-box, the even ones were left to themselves at the temperature of the room, each placed in a wide-necked glass stoppered bottle. After 24 hours there appears to be no statistical difference of any importance. All cylinders whether even or odd, appear to have assumed a smell of musc in a distinct though feeble degree. So the temperature coefficient of the surface-action, exerted by nickel on the phenomenon of the transition of muscon into musc, cannot be great.

<sup>1)</sup> One of these observers has an ordinary acuteness of smell for the odour of muscon, but cannot state with certainty the transition of muscon into musc. He also has in other respects strongly deviating peculiarities of his organ of smell which will soon be extensively communicated.

Finally I wish to state that capillary glass tubes of 1 mm.<sup>2</sup> cross-section, after air, carrying muscon, had been passed through them for five minutes, did not show a perceptible change of surface tension with water (the tension being measured by the height of the water column) and that repetition of the other experiments with tubes, heated beforehand and with air that had been dried by means of calcium chloride and cotton wool, gave no deviating results.

At present it is impossible to give a theory of these phenomena. As a preliminary working hypothesis one might suppose the adsorbed muscon to be dissolved in the layer of condensed water vapour and air which covers all objects and it might be further assumed that the change of muscon into musc only then takes place at a perceptible rate when the surface action of the metal, of the glass or of the glazed porcelain produces a particularly great density of the dissolved muscon in immediate contact with the surface in question. This hypothesis is in harmony with equilibrium experiments, made with dried air at 0°, 10°, etc.. These experiments are in progress but not completed yet.

**Physiology.** — *“On the adsorption of the smell of muscon by surfaces of different material”*. By Prof. H. ZWAARDEMAKER.  
Continuation of a former communication.

When air, charged with muscon, is passed through tubes of an alloy of lead and tin, in the manner described in the communication of May 24, the inner surface of these tubes appears to adsorb muscon in quantities, the amount of which may to some extent be estimated from the time, during which the tubes preserve the odour of muscon. This assumption is based on the supposition that the adsorption takes place in one and the same dissolving substance, namely the condensed layer which is said to cover all objects.

The dilution at which the muscon is present in the air in these experiments, can be kept constant when the current velocity is controlled by means of an aerodromometer. Moreover, it may vary between certain limits, since experiments, made to this purpose, showed that it makes no difference in the results whether the muscon, volatilised per second from the smelling source, is contained in 42, 84 or 126 cc. of air. Tubes of lead, alloyed with tin, lose under similar conditions the adsorption odour in the same degree and in the same time, say 5 to 6 days.

Under the just stated conditions the adsorption equilibrium is reached at a temperature of the room of 19° centigrade in about ten minutes, as will appear from the following table:

	after 1 min. exposition	odourless	within 1 day
„ 2 „	„	„	after 1 „
„ 3 „	„	„	„ 2 days.
„ 4 „	„	„	„ 3 „
„ 5 „	„	„	„ 4 „
„ 10 „	„	„	„ 5 „
„ 20 „	„	„	„ 4 „

ADSORPTION ODOUR.

Preceding Exposition	at 0°	at 20°	at 40°	at 60°	at 100°
5 min.	8 days	3 à 5 days	2 days	1½ days	1 day
10 „	10 „	5 „	3 „	2 „	2 days
15 „	a little over 10 days	a little over 5 days	4 „	2 „	2 „

Nickel-plated copper tubes, treated in the same way, show saturation after an exposition of about 5 minutes, it making no difference whether this takes place at 0°, 20° or 40°. Complete loss of adsorption odour was found in these cases after respectively 4, 2 and 2 days.

From these experiments follows that a higher temperature during the exposition causes the state of saturation to be reached only little sooner, but that the degree of adsorption is much smaller at a higher temperature. This proves that with higher temperatures the equilibrium is shifted in the direction of minimum adsorption.

The facts, stated until now, agree very well with the hypothesis of a solution of muscon in the layer of condensed water-vapour, carbonic acid and air which covers all objects. Assuming this, we are led to believe that on nickel-plated copper this layer is thinner than on lead, alloyed with tin, and that consequently in the former case the equilibrium during exposition is reached sooner than in the latter, while temperature has the same influence on them both and in the same degree. The fact that tubes, heated beforehand and treated in dry air, give the same results, is not at variance with this since we may not expect that the condensed layer will by this treatment be completely removed. Also the transition of the smell of muscon into that of musc must take place in this layer, the only curious point being that temperature has so little influence on the rate of

this process of transition which yet must be of a chemical nature:

But a great difficulty to the theory arises from the fact that adsorption of odour on metal surfaces appears to be a general phenomenon. This appears from similar systematic experiments as with musc for two other characteristic smelling substances. I chose ionon, a substance dissolving in water as well as in liquid air and scatol, a substance for which this has not yet been investigated.

Ionon, when diluted 1 to a million in an aqueous solution of 0,5 % antifebrin, and evaporating into a passing air-current which in the well-known manner passes through cylinders of different material, leaves an adsorption which disappears almost immediately with porous porcelain, arc-lamp carbon, glass, silver, sticks to tin for a very short time, to lead, containing tin, scarcely for a day to nickel and copper for about two days, to aluminium for 2<sup>1</sup>/<sub>2</sub> days and to iron and steel for about four days.

Scatol, when dissolved in proportion of 1 to 1000 in liquid paraffin and evaporating into passing air and passing in the well-known manner through cylinders of different material, leaves an adsorption which disappears almost at once with porous porcelain and arc-lamp carbon, in a few hours with glass, sticks to lead, containing tin, to lead, silver and tin for about a day, to copper 3 days, to iron 4 to 5 days, to steel 10 to 13 days, to aluminium over 10 days.

Hence ionon adheres most to the substance which does not take up muscon at all, i. e. to steel; scatol most to aluminium which shows a comparatively very small adsorptive power for muscon (aluminium does not keep muscon for 24 hours).

In order to explain these deviations one is forced either to assume a peculiar modification of the solubility, caused by the dissolution of the specific metallic particles in the condensation layer, or to assume an absorption in the metal itself. To me it would seem that the collected facts do not at present admit of a choice between these two possibilities, although the small influence of the muscon density in the air would point to an adsorption compound with the metal.

**Physics.** — “*Contribution to the theory of binary mixtures.*” V.

By Prof. J. D. VAN DER WAAALS.

Continued. See p. 74.

Up to now we have assumed in the determination of the binodal line that the second component, for which the quantity  $b$  is larger than for the first component, has a lower critical temperature, so that we suppose  $(T_k)_2 < (T_k)_1$ . In the opposite case, so  $(T_k)_2 > (T_k)_1$ , we meet with some new complications, which we shall shortly discuss. So we choose now a region from the general  $p$ -figure, which lies more to the right, and in which the line  $\left(\frac{dp}{dx}\right)_v = 0$  is found. Fig. 14 of These Proceedings April 26, 1907 may be serviceable for this discussion. In this figure the points 1, 2, 3, 4, 5 and 6 are points of the spinodal line. If we had inserted the spinodal line itself in the figure, this curve would have an ordinary shape on the vapour side, remaining all the time at larger volumes than those of the line  $\left(\frac{dp}{dv}\right)_x = 0$ . But on the liquid side the normal course of the spinodal line has been strongly modified by the presence of the line  $\frac{d^2\psi}{dx^2} = 0$ . On the left-hand side it begins in the point  $\frac{dp}{dv} = 0$  of the first component, proceeds then to smaller volumes, till the presence of  $\frac{d^2\psi}{dx^2} = 0$  forces it back to very small volumes, and is the cause that the distance between the spinodal line and the line  $\frac{dp}{dv} = 0$  is abnormally enlarged. In the points where  $\frac{d^2\psi}{dx^2} = 0$  and  $\frac{d^2\psi}{dx dv} = 0$  intersect, the spinodal curve touches the curve  $\frac{d^2\psi}{dx^2} = 0$ . Two plaitpoints occur, viz. the realisable plaitpoint at very small volume, and the hidden plaitpoint in the neighbourhood of the points 2 and 3. This hidden plaitpoint lies in this case on the left-hand side in accordance with the shape of the  $q$ -lines. In fig. 17 this hidden plaitpoint lies on the right-hand side, and the shape of the  $q$ -lines in the region where  $\frac{dp}{dv}$  is positive, is such that there is a  $q$ -line which may be drawn tangent to the spinodal curve, the hidden plaitpoint being the point of contact. In fig. 17 the  $q$ -lines

in this region turn their concave side to the axis of the 1<sup>st</sup> component. In the case to be discussed now they turn their convex side towards the 1<sup>st</sup> component, and hence the hidden plaitpoint must lie on the other side, as a point in which a  $q$ -line touches the spinodal line in the unstable region. The drawn  $q$ -line intersects the spinodal line in 6 points, and the  $p$ -line, thought as function of  $v$ , must have 3 maxima and 3 minima, when this  $q$ -line is followed; a maximum value in the points 1, 3 and 5, a minimum value in the points 2, 4 and 6. In fig. 20 this  $p$ -curve is represented and the different

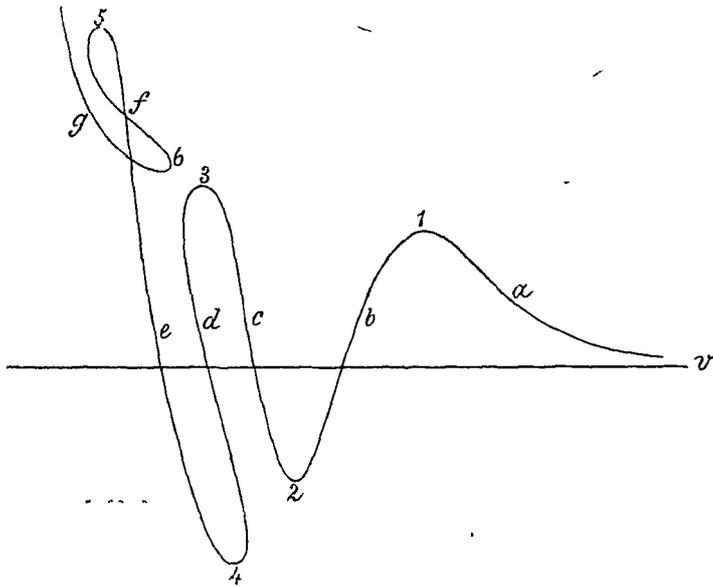


Fig. 20.

branches of this line are indicated by the letters  $a \dots g$ . The branches  $d$  and  $f$  traverse the region where  $\frac{d^2\psi}{dv^2}$  is negative, and accordingly

have two points each, where  $\frac{dp}{dv} = \infty$ . The complication which the  $p$ -line presents in this case compared with the  $p$ -line of fig. 16, consists only in this that the branch  $e$ , which before ran directly to infinity and continually to smaller volumes, has now got a maximum in the point 5, and as soon as the  $q$ -line passes into the region where  $\frac{d^2\psi}{dv^2}$  is negative, runs back to larger volumes. In the point 6 the minimum value has been reached, which however must be larger than the maximum value of the pressure in the point 3. If the

value of  $q$  is lowered, the points 6 and 3 draw nearer to each other, and they coincide for the loop- $q$ -line which passes through the point of intersection of  $\frac{d^2\psi}{dx^2} = 0$  and  $\frac{d^2\psi}{dx dv} = 0$ . Then the branches  $c$  and  $d$  intersect at an acute angle, just as the branches  $f$  and  $g$ . When  $q$  is lowered further, and the  $q$ -line has split up into two separate portions, the  $p$ -line too divides into two separate parts; the branch  $g$  is then the continuation of  $c$ , and the branch  $f$  the continuation of  $d$ . Fig. 21 illustrates the course of  $p$  as function of  $v$

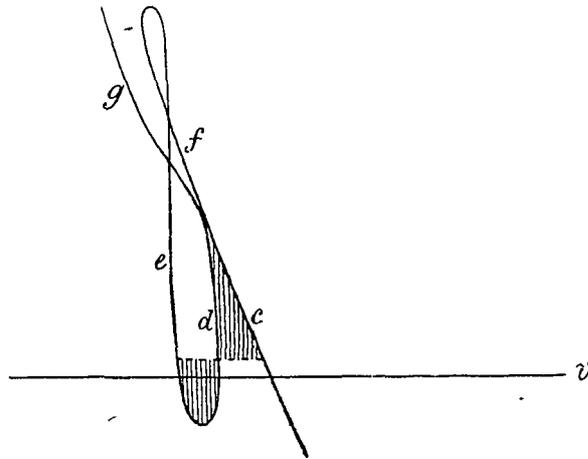


Fig. 21.

for such a  $q$ -line which has divided into two separate portions; then the branches  $c, g$ , which have united to one branch cut the united branch  $d, f$ , and the branch  $e$ .

When applying MAXWELL'S rule for the determination of the binodal line we are confronted with some difficulties, which I will now discuss. Already when the  $p$ -line runs as is represented by the branches  $e, f$  and  $g$  in fig. 20, so when the middle one of the 3 branches cuts one of the outside lines, we must pay proper attention to the sign of the areas when applying the rule for drawing MAXWELL'S line. If the straight line is drawn lower than the point of intersection of  $e$  and  $f$ , the area below this line, which according to the rule must be equal to the area above this line, must of course be all that is contained between the branches  $g$  and  $f$  below this line. But the area above the line, which consists of two parts, viz. the area of the loop, and the part that lies below the double point above the line, must not be considered as the sum of these two parts. On account of the branch  $f$  running back, the latter part must be taken

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negative. This may be considered to be sufficiently self-evident and not to require an elaborate proof. But when the  $q$ -line has divided into two separate parts, and when the  $p$ -line runs as is represented in fig. 21, we meet with another difficulty, which indeed, calls for a somewhat closer discussion. The joined branches  $c$  and  $g$  form a curve which cuts the branches  $d$ ,  $e$  and  $f$ , which have joined to a loop-like curve, in two points, but such a point of intersection must really be considered as two altogether different points. Such a point of intersection represents two perfectly different phases according as it is considered as point of  $c$ ,  $g$  or of  $d$ ,  $e$ ,  $f$ . Hence when drawing the straight line we must bear in mind that the point of intersection of  $c$  and  $d$  and of  $e$  and  $g$  does not represent the same phase, and if the line is drawn as in fig. 21, where the two hatched areas are equal, the points at the extremities of this line are not points of the binodal line. To see how the straight line must be drawn in such cases we revert to the general equation:

$$dM_1\mu_1 = vdp - xdq.$$

Now to get from one point to the point with which it coexists, we can no longer follow one  $q$ -line, but we shall partly have to follow a way which joins the two separate branches of the  $q$ -line, and for this we choose the isobar of the point of intersection that the branches  $c$ ,  $g$  and  $d$ ,  $f$  have in common. We obtain then the equation:

$$(M_1\mu_1)_c - (M_1\mu_1)_e = \int_e^c vdp - \int_e^c xdq,$$

where in  $\int vdp$  the value of  $v$  must be taken which corresponds to the chosen value of  $q$ , and in  $\int xdq$  the value of  $x$  which corresponds to that  $p$ -line that passes through the point of intersection. Let us call the value of the volume of the point of intersection  $v_s$  and the values of  $x$  for the points where the isobar of the point of intersection cuts the two branches of the  $q$ -line,  $x_2$  and  $x_1$ . The above equation assumes then the following form:

$$(M_1\mu_1)_c - (M_1\mu_1)_e = \left[ p(v_c - v_e) - \int_e^c p dv \right] - \left[ q(x_2 - x_1) - \int_1^c q dx \right].$$

Now if  $(M_1\mu_1)_c$  must be  $= (M_1\mu_1)_e$ , then  $p(v_c - v_e) - \int_e^c p dv$  is

not equal to 0, but to  $q(x_2 - x_1) - \int_1^2 q dx$ . For the loop- $q$ -line the length of the isobar along which  $\int x dq$  must be taken, is equal to 0, and  $x_2$  and  $x_1$  coincide. For a  $q$ -line of lower degree  $x_2$  and  $x_1$  differ. In the above equation it is supposed that branch  $e$  is taken as starting point, and that a course is followed necessary to reach branch  $c$ . The point from which we start, lies on the closed circle of the  $q$ -line and in the stable region. We now follow indifferently either the lowest branch of this circle or the highest, but dependent on the pair of coexisting phases that is to be determined. Let us suppose that we follow the lowest course, then we get to branch  $d$ , and meet the point of intersection of the isobar which we must follow to meet the other branch of the  $q$ -line in a point which has equal volume  $v_s$ . As this isobar must pass through the line  $\left(\frac{dp}{dx}\right)_v = 0$ , where maximum volume exists, the equality of the volumes  $v_s$  is possible<sup>1)</sup>, but the values of  $x$  which we have called  $x_2$  and  $x_1$ , are different, viz.  $x_2 < x_1$ . For  $x_1$  the value of  $q$  is the chosen one and for  $x_2$  the value of  $q$  is again the same. Between  $x_1$  and  $x_2$  this value is variable. Now:

$$\left(\frac{dq}{dx}\right)_p = \frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dx dv} \frac{dv}{dx_p}$$

or

$$\left(\frac{dq}{dx}\right)_p = \frac{\frac{d^2\psi}{dx^2} \frac{d^2\psi}{dv^2} - \left(\frac{d^2\psi}{dx dv}\right)^2}{\frac{d^2\psi}{dv^2}}$$

$\frac{d^2\psi}{dv^2}$  (see fig. 14) being positive,  $\left(\frac{dq}{dx}\right)_p$  is positive outside the spinodal line, and negative inside it. Along the  $p$ -line, starting from smaller value of  $x$ , the value of  $q$  is, therefore, increasing, maximum on the spinodal curve, then decreasing, minimum on the spinodal curve, after which it increases continually, as represented in fig. 22.

<sup>1)</sup> The same observation holds for all points which are points of intersection of different branches of the  $p$ -line in figs. 20 and 21. In such a point of intersection  $p$  and  $v$  are equal, and this could only occur when the phases denoted by such a point of intersection lie on either side of the line  $\frac{dp}{dx} = 0$ .

Now :

$$p(v_c - v_e) - \int_e^c p \, dv = - \left\{ q(x_1 - x_2) - \int_2^1 q \, dx \right\}$$

or

$$\int_e^c p \, dv - p(v_c - v_e) = - \left\{ \int_2^1 q \, dx - q(x_1 - x_2) \right\}.$$

For the loop- $q$ -line  $x_1$  and  $x_2$  coincide, and for a  $q$ -line but little lower  $\int_2^1 q \, dx$  is larger than  $q(x_1 - x_2)$ . As  $x_1$  always lies on the left

of the value of  $x$  for which  $q$  has minimum value,  $\int_2^1 q \, dx > q(x_1 - x_2)$

always holds. From this follows that for the lowest pair of coexisting phases of fig. 21 the straight line must be drawn in such a way that the area of the hatched part above this line, to which the area of the hatched part of fig. 22 is added, is equal to the hatched part of fig. 21 which would lie below this line. So the pressure of the lowest pair of coexisting phases for this  $q$ -line is greater than would follow from the application of the rule if the point of intersection of  $c, g$  and  $d, f$  was an identical point, or rather represented one and the same phase. But we shall not pursue this course any further.

Now that we are obliged to include the quantity  $\int x \, dq$  in our considerations, we can find the coexisting phases for the liquid volumes in a simpler way by the aid of this quantity. For such volumes lie on a  $p$ -line which can be followed without interruption when we proceed from one point of the pair of coexisting phases to the second point. And when we proceed along a  $p$ -line  $dM_1 \mu_1 = -x \, dq$ , and so  $(M_1 \mu_1)_2 - (M_1 \mu_1)_1 = -\int_1^2 x \, dq$ . Hence we need only choose two points on the chosen  $p$ -line, satisfying the requirement that  $-\int_1^2 x \, dq = 0$ ,

or

$$q(x_2 - x_1) = \int_1^2 q \, dx.$$

Then we have to carry out the same construction on the  $q$ -line

as was carried out above on the  $p$ -line, and so for the  $p$ -line, for which fig. 22 would represent the course of the  $q$ -line, we have to

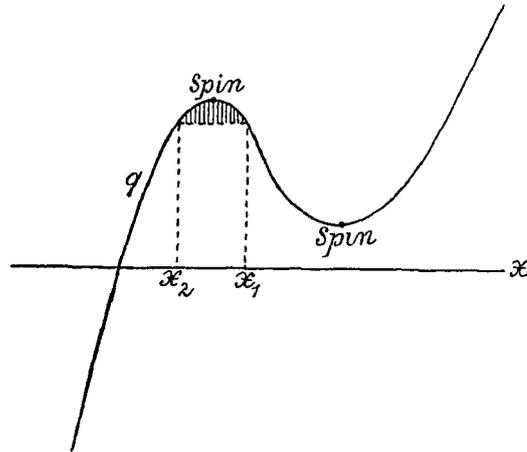


Fig. 22.

draw a straight line in such a way that its height indicates the middle value of the ordinates of the  $q$ -curve. That from the outset we have not followed this course for the determination of the coexisting phases in which the values of  $x_2$  and  $x_1$  for given value of  $p$  are determined, is due to the fact, that this way of determination is again possible without correction term only when the whole  $p$ -line is found between the two coexisting phases without interruption in the  $v, x$ -diagram; and as for the equilibrium between vapour and liquid phases as a rule this condition is not satisfied, and as it is only by way of exception that the  $q$ -line has split up into two branches, the determination of coexistence by the first mentioned method may as a rule be considered as possible. But nevertheless, in some cases the determination by means of the properties of the value of  $q$ , following a  $p$ -line, is to be preferred. If we do so in the case discussed for the determination of the coexistence of a liquid phase with a second liquid phase, we must choose every time other  $p$ -lines, and along each of these  $p$ -lines the course of  $q$  as function of  $x$  is as drawn in fig. 22; and with the simple shape of such a  $q$ -line there is only question of a single straight line along which

$$q_c(x_2 - x_1) = \int_1^2 q dx. \text{ The binodal curve for the coexistence of liquid}$$

with liquid has therefore a simple shape and is restricted to the stable region.

Indeed, this was also to be derived from the  $p$ -figure (fig. 20) where the branches  $f$  and  $g$  must lie higher than the branches  $c$  and  $d$ , and therefore can never combine for the application of the rule for coexistence; but then only for those  $q$ -lines which are of higher degree than the loop- $q$ -line; whereas the rule for finding the conditions for coexistence from the values of  $q$  when a  $p$ -line is followed, holds for all  $p$ -values without exception. Let us consider the case that this part of the plait has got quite detached from the transverse plait as a closed longitudinal plait, and has the two realisable plaitpoints, then a highest and a lowest  $p$ -line may be drawn, along which the maximum and the minimum in the  $q$ -line have coincided, and in the point where they coincide they yield the value of  $x$  for the two plaitpoints.

We had already repeatedly occasion to call attention to the reciprocity between  $\frac{d^2\psi}{dx^2}$  and  $\frac{d^2\psi}{dv^2}$ , and between  $q$  and  $p$  or  $\frac{dq}{dx}$  and  $\frac{dp}{dv}$ . Let us also do so in the case discussed. Here we have intersection in two points of  $\frac{d^2\psi}{dx^2} = 0$  and  $\frac{d^2\psi}{dx dv} = 0$ , and it appeared that then separate portions of  $q$ -lines occur, so that it was not always possible to pass without a leap from one part of a  $q$ -line to another part of such a line. Then it is desirable for the determination of the coexisting phases not to follow such a  $q$ -line, but on the contrary to go along a  $p$ -line and to use the corresponding value of  $q$ . The reciprocal case is found in case of intersection of  $\frac{d^2\psi}{dv^2} = 0$  and  $\frac{d^2\psi}{dx dv} = 0$ , in which case the course of the  $p$ -lines is as is indicated in the middle region of the general  $p$ -figure. Then there are  $p$ -lines, namely those of higher degree than the loop- $p$ -line, which have divided into two separate parts; if we followed a  $p$ -line also then, in order to arrive at the coexisting phases by means of the values of  $q$ , we should be confronted by the same difficulties as we have met now when following the  $q$ -line. If for a  $p$ -line of lower degree than the loop- $p$ -line we draw the value of  $q$ , then such a course for  $q$  follows from

$$\left(\frac{dq}{dx}\right)_p = \frac{\frac{d^2\psi}{dx^2} \frac{d^2\psi}{dv^2} - \left(\frac{d^2\psi}{dx dv}\right)^2}{\frac{d^2\psi}{dv^2}}, \text{ as has been drawn in fig. 23, where}$$

the 1<sup>st</sup>, 3<sup>rd</sup> and 5<sup>th</sup> branches lie in the stable region, and the 2<sup>nd</sup> and 4<sup>th</sup> branches lie in the unstable region, if we take into account that such a  $p$ -line passes 4 times through the spinodal line, in which

points  $\left(\frac{dq}{dx}\right)_p = 0$ , and also 4 times through the line  $\frac{d^2\psi}{dv^2} = 0$ , in which points  $\left(\frac{dq}{dx}\right)_p = \infty$ . Only for the loop- $p$ -line the second minimum

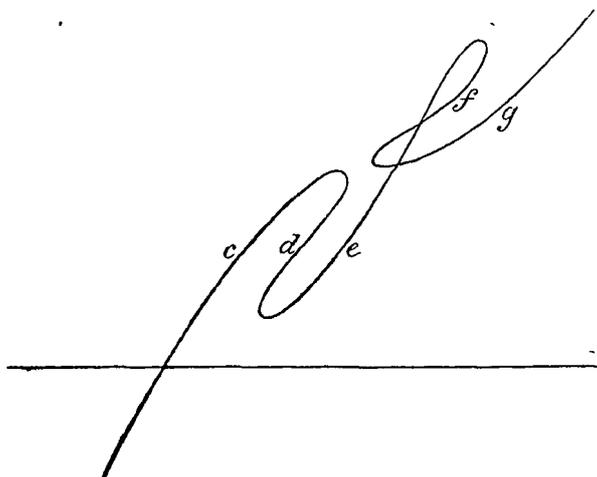


Fig. 23.

coincides with the first maximum, but for lower  $p$ -lines it lies higher, as in the drawing. We have exactly the same shape for  $q$  as function of  $x$ , as in fig. 20 for  $p$  as function of  $v$ . Only one figure must be turned over to cover the other, in accordance with the circumstance that  $q = \frac{d\psi}{dx}$  and  $p = -\frac{d\psi}{dv}$ . The combination  $c, d$  and  $e$  now yields a pair of coexisting phases, and the combination  $e, f$  and  $g$  another pair. No other combinations are possible; and we should be justified in concluding that the binodal line has a simple course and remains limited to the stable region. But this conclusion would be perfectly valid only for all pressures not higher than those of the loop- $p$ -line, though there are also coexisting phases with higher value of  $p$ . In this case it is certainly preferable to follow a  $q$ -line, and to construe  $p$  as function of  $v$ , which we have called preferable already above for other reasons. We know that then a highest pressure exists for the coexisting phases, viz. when  $x_1 = x_2$ ; this is only possible if the chosen  $q$ -line passes through the line  $\frac{dp}{dx} = 0$ , for only then this is the case for values of  $x$  within certain limits. From this circumstance of the reciprocal case we conclude that in the case under consideration, in which  $\frac{d^2\psi}{dx^2} = 0$  is cut by  $\frac{dp}{dx} = 0$ ,

there is a minimum value of  $q$  for the coexisting phases, viz. if  $v_2 = v_1$ . Then the line joining these phases runs parallel to the  $x$ -axis, just as it runs parallel to the  $v$ -axis in the reciprocal case. This too can only occur, if the coexisting phases lie on either side of the line  $\frac{dp}{dx} = 0$ ; for the isobar that passes through the two points of coexistence, can only have two equal values of  $v$  if between them maximum or minimum value for the volume occurs. The equality of  $v_1$  and  $v_2$  for minimum value of  $q$ , to which we have concluded from the principle of reciprocity, follows from the simple equation, which holds for two successive points of a binodal curve, viz.:

$$(v_2 - v_1) dp = (x_2 - x_1) dq.$$

For a pair of coexisting phases  $M_1\mu_1$  is the same, and for a following pair of such phases  $dM_1\mu_1$  is also the same; now the above equation follows from  $dM_1\mu_1 = v_1 dp - x_1 dq = v_2 dp - x_2 dq$ . If  $x_2 - x_1 = 0$  and  $v_2 - v_1$  is different from zero, then  $dp$  must be  $= 0$ ; in the same way  $dq = 0$  involves the equality of  $v_2$  and  $v_1$ , if  $dp$  is not equal to 0. We can also derive from this equation, how the nodal lines lie on either side of the special nodal line for which  $x_2 = x_1$  or  $v_2 = v_1$ , i. e. to which direction they diverge in a fanlike way. Let us first consider the case  $x_2 = x_1$ , so maximum pressure on the vapour-liquid binodal curve. On the left of this nodal line the sign of  $v_2 - v_1$  is positive on the vapour side, and the sign of  $dp$ , if we do not limit ourselves to an infinitely small value of  $dp$ , negative. Then also the sign of  $(x_2 - x_1) dq$  must be negative, and the sign of  $dq$  being negative,  $x_2 - x_1$  must be positive. On the right of this nodal line the sign of  $v_2 - v_1$  and of  $dp$  must be what it was in the preceding case; but  $dq$  now being positive,  $x_2 - x_1$  is negative. So the nodal lines converge towards the vapour side. It would be just the reverse if the pressure was minimum for  $x_2 = x_1$ , for then  $dp$  is positive. Let us now consider the case  $v_2 = v_1$ , so minimum value of  $q$  on the liquid-liquid binodal curve. Let us choose the right side, so where  $x_2 > x_1$ , and let us ascend, so put  $dp$  positive, then  $q$  being minimum,  $dq$  will be positive. The second member is positive, and so we find  $v_2 - v_1$  positive, whereas for negative  $dp$  the value of  $v_2 - v_1$  would be negative. So the nodal lines converge towards the right side, and we may consider the nodal line for which  $v_2 = v_1$ , as axis of such a converging pencil. This shows us at the same time how and where the plaitpoints must lie. As the tangent to the binodal curve in the plaitpoint is to be considered as the limiting direction of the nodal lines, both the  $p$ -line and the

$q$ -line must have such a course in the upper plaitpoint that they descend towards the right, which moreover could be put à priori. For every  $q$ -line when it still lies above the line  $\frac{dp}{dx} = 0$ , and does not pass through  $\frac{d^2\psi}{dx^2} = 0$ , descends when it proceeds towards the right. But in the lower plaitpoint, i. e. in the plaitpoint with the larger volume that lies below the line  $\frac{dp}{dx} = 0$ , the  $q$ -line which touches in that plaitpoint, must descend as it proceeds to smaller value of  $x$ , in accordance with the course of the nodal lines. We should also have found this course of the nodal lines confirmed, if we had paid attention to the course of the  $p$ -lines.

Everything we have discussed in this V<sup>th</sup> communication rests on fig. 14; so we have thought that  $\frac{dp}{dx} = 0$  and  $\frac{d^2\psi}{dx^2} = 0$  intersect. There is, however, also a possibility, and it will even be the rule, that the two curves exist, but do not intersect. Then two cases are to be distinguished, viz. that  $\frac{d^2\psi}{dx^2} = 0$  remains restricted to smaller volumes than those of  $\frac{dp}{dx} = 0$ , or to larger ones<sup>1)</sup>. When tracing the two curves with respect to each other we must take care that the points in which tangents may be drawn to  $\frac{d^2\psi}{dx^2} = 0$  parallel to the  $v$ -axis, lie on the line  $\frac{d^2p}{dx^2} = 0$ , and that also the point in which  $\frac{dp}{dx} = 0$  has minimum volume, lies on this line too. Now the line  $\frac{d^2p}{dx^2} = 0$  has a simple course. The value of  $\frac{dv}{dx}$  for this line is equal to  $\frac{db}{dx} \frac{3}{1 + 2\frac{b}{v}}$ . From this follows that this line  $\frac{d^2p}{dx^2} = 0$  consists of a single branch, which from a point of the 1<sup>st</sup> axis moves regularly to the right to points of continually larger volume. So if the line  $\frac{dp}{dx} = 0$  cuts the line  $\frac{d^2\psi}{dx^2} = 0$ , the two points in which tangents parallel to

<sup>1)</sup> See These Proceedings April 26, 1907, p. 833 seq.

the  $v$ -axis can be drawn to  $\frac{d^2\psi}{dx^2} = 0$ , and the point where  $\frac{dp}{dx} = 0$  has minimum volume must lie in such a way, that the last point lies between the two first mentioned. If the line  $\frac{d^2\psi}{dx^2} = 0$  is restricted to smaller volumes than  $\frac{dp}{dx} = 0$ , then  $\frac{d^2\psi}{dx^2} = 0$  must also lie at smaller  $x$  than the point where  $\frac{dp}{dx} = 0$  has the smallest volume and the

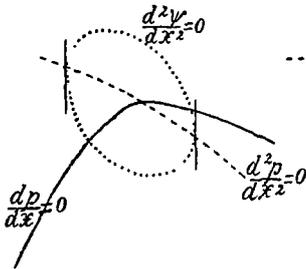


Fig. 24a

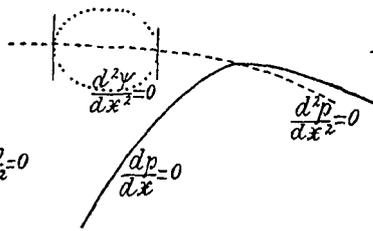


Fig. 24b

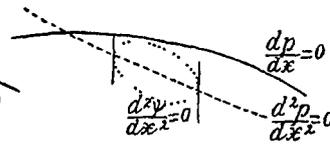


Fig. 24c

reverse; this has been represented in fig. 24a, fig. 24b and fig. 24c, but has not always been kept in view in preceding schematical figures, which were plotted for the representation of other particularities.

After these remarks we may examine more in details what happens when  $\left(\frac{dp}{dx}\right) = 0$  and  $\frac{d^2\psi}{dx^2} = 0$  intersect, and the temperature is raised. With rise of  $T$   $\frac{d^2\psi}{dx^2} = 0$  contracts to the point in which this curve must disappear. Also the curve  $\frac{dp}{dx} = 0$  contracts. If the point in which  $\frac{d^2\psi}{dx^2} = 0$  must disappear, lies at smaller volume than  $\frac{dp}{dx} = 0$ , then with contraction of  $\frac{d^2\psi}{dx^2} = 0$  the right-hand point where the latter curve is directed //  $v$ -axis, will have to pass through the minimum volume of  $\frac{dp}{dx} = 0$ . Even then there is still intersection, but with further contraction the two curves will touch, and get detached. Above the temperature at which they touch, the complicated course of the  $q$ -lines has disappeared in so far that no  $q$ -lines occur any more which have split up into two separate branches; then we get a group of  $q$ -lines as drawn in

fig. 3, These Proc. March 30, 1907 with a maximum and a minimum volume, but moreover when they afterwards cut  $\frac{dp}{dx} = 0$ , with a maximum value of  $x$ . But when the point in which  $\frac{d^2\psi}{dx^2} = 0$  must disappear lies at larger volume than  $\frac{dp}{dx} = 0$ , then with rise of  $T$  the left-hand point where  $\frac{d^2\psi}{dx^2} = 0$  is directed parallel to the  $v$ -axis, must pass through the point where  $\frac{dp}{dx} = 0$  has minimum volume. Then intersection still takes place, but with further rise of  $T$  the curves touch and get detached — and then the  $q$ -lines run as has been drawn in fig. 5. So contact between  $\frac{d^2\psi}{dx^2} = 0$  and  $\frac{d^2\psi}{dx dv} = 0$  may take place in two ways and we may already conclude to this from the condition for contact. From the equality of  $\frac{dv}{dx}$  for the two curves follows namely:

$$-\frac{d^3\psi}{dx^3} \frac{d^2p}{dx dv} = \left(\frac{d^2p}{dx^2}\right)^2.$$

The value of  $\frac{d^2p}{dx dv}$  being negative for the points of  $\frac{dp}{dx} = 0$ ,  $\frac{d^3\psi}{dx^3}$  must be positive in the point of contact. That is to say, that for the curve  $\frac{d^2\psi}{dx^2} = 0$  the point of contact must lie to the right of the line which joins the minimum and the maximum volume. Only with the two kinds of contact which we have described, this condition can be fulfilled. If the first described contact takes place, the minimum volume of  $\frac{dp}{dx} = 0$  must lie to the right of the point of contact. In the second case of contact this point must lie on the left, or even be entirely wanting in the figure, in which case  $\frac{dv}{dx}$  is positive in all points of the line  $\frac{dp}{dx} = 0$ .

From all this follows that if the spinodal curve entirely envelops the curve  $\frac{d^2\psi}{dx^2} = 0$  in a closed line, and the latter remains entirely restricted to smaller volume than the volumes of  $\frac{dp}{dx} = 0$ , there are

indeed still two realisable plaitpoints on this spinodal line, but that the course of the nodal lines in all this longitudinal plait is as was the case in the upper half of the above discussed longitudinal plait — so that in both plaitpoints the tangent  $p$ -line and the tangent  $q$ -line descend to the right. All over this-longitudinal plait  $v_2 > v_1$ , if  $v_2$  represents the right-hand point of coexistence. But if  $\frac{d^2\psi}{dx^2} = 0$  remains restricted to volumes larger than those of  $\frac{dp}{dx} = 0$ , the course of the nodal lines is such that  $v_2 < v_1$ , and the plaitpoint has such a situation that  $\frac{dv}{dx_p}$  and  $\frac{dv}{dx_q}$  is negative for the  $p$ -line and the  $q$ -line which pass through the plaitpoint. I speak of the plaitpoint, because I think I can demonstrate that then there cannot be question of two realisable plaitpoints, nor of a detached closed longitudinal plait. For when a spinodal line splits up, not only  $\frac{dv}{dx_p} = \frac{dv}{dx_q}$  in this splitting point, but also  $\frac{d^2v}{dx_p^2} = \frac{d^2v}{dx_q^2} = 0$ . Properly speaking I have already discussed this point (These Proc. April 26, 1907 p. 848), but on account of the great importance of the question further elucidation is perhaps not uncalled for. The following remarks may serve for this purpose.

Let us in the first place consider a mixture represented by a region of the general  $p$ -figure lying on the right side, and so much to the right that the point where  $\frac{dp}{dx} = 0$  has minimum volume, no longer occurs, or lies at very small value of  $x$ . Then the point where  $\frac{d^2\psi}{dx^2} = 0$  disappears at  $T = T_g$ , because it must lie on the line  $\frac{d^2p}{dx^2} = 0$ , lies at smaller volume than those of the line  $\frac{d\tilde{p}}{dx} = 0$ ; and if this curve is still found at temperatures below  $T_g$ , the points in which this curve intersects the line  $\frac{dp}{dv} = 0$ , lie in the region where  $\frac{dp}{dx}$  is negative. If we now suppose that the temperature rises, and the spinodal line might split up, this splitting point must lie between the larger volumes of  $\frac{d^2\psi}{dx^2} = 0$  and the volumes of  $\frac{dp}{dv} = 0$ , so also in the region in which  $\frac{dp}{dx}$  is negative. Now the question is if in this

region a point of inflection of the  $p$ -lines and of the  $q$ -lines can lie. It appears from what has been observed about the loci of these points of inflection (These Proc. March 30, 1907 p. 736) that this is possible for the  $q$ -lines. But from what has been observed on the course of the locus of the points of inflection of the  $p$ -lines (These Proc. Febr. 23, 1907 p. 628) appears that in the stable part of that region no point of inflection can occur for these lines.

Let us now take the other case, viz. that the point with minimum volume of  $\frac{dp}{dx} = 0$  exists, and is not found at very small value of  $x$ . If the spinodal line has split up into two parts, then there is a part which we might consider as belonging to  $\frac{dp}{dx} = 0$ , and another part that surrounds  $\frac{d^2\psi}{dx^2} = 0$ . Now the splitting point lies again in the region where  $\frac{dp}{dx}$  is negative, but in a part of that region where as well points of inflection of the  $p$ -lines as of the  $q$ -lines may occur, at least if  $\frac{dp}{dx} = 0$  still intersects the curve  $\frac{d^2\psi}{dx^2} = 0$ . Two branches on which  $\frac{d^2v}{dx^2_q} = 0$ , start from the point in which  $\frac{dp}{dx} = 0$  cuts the curve  $\frac{d^2\psi}{dx^2} = 0$ . One of these branches passes through the region where  $\frac{d^2\psi}{dx^2}$  is negative, and leaves this region only at the point where  $\frac{d^2\psi}{dx^2} = 0$  has the maximum volume. The second branch runs right of the loop- $q$ -line to larger volumes. But there is also a locus on which  $\frac{d^2v}{dx^2_p} = 0$ , which runs right of  $\frac{dp}{dx} = 0$ , and passes through the two following points. 1<sup>st</sup> the point where  $\frac{dp}{dx} = 0$  has minimum volume, and 2<sup>nd</sup> the point where  $\frac{dp}{dx} = 0$  cuts the line  $\frac{dp}{dv} = 0$ . If the spinodal line splits up, this will have to take place in the point of intersection of the line on which  $\frac{d^2v}{dx^2_p} = 0$  with the second mentioned branch on which  $\frac{d^2v}{dx^2_q} = 0$ . If this case of splitting occurs,

the detached closed longitudinal plait is cut by the line  $\frac{dp}{dx} = 0$ , and has the above discussed plaitpoints.

But though on the supposition of this way of splitting up we do not meet with a definite contradiction, yet there is one circumstance which makes me doubt whether it will occur frequently or universally. If we draw the point of intersection of the mentioned loci on which  $\frac{d^2v}{dx^2p} = 0$  and  $\frac{d^2v}{dx^2q} = 0$ , we find a point which lies on the left side of  $\frac{d^2\psi}{dx^2} = 0$ , whereas after the detaching we should sooner expect the place of the plaitpoint with the largest volume, according to the course of the nodal lines, on the right side of  $\frac{d^2\psi}{dx^2} = 0$ . Indeed, another way of detaching is possible. The splitting may take place in a point on the left of  $\frac{dp}{dx} = 0$ . Then  $\frac{d^2\psi}{dx^2} = 0$ , which curve must disappear in a point of  $\frac{d^2p}{dx^2} = 0$ , must already have contracted so far that it lies entirely in the region where  $\frac{dp}{dx}$  is positive. As we observed before, there runs a branch on which  $\frac{d^2v}{dx^2p} = 0$  also there and for the loop-line on which  $\frac{d^2v}{dx^2} = 0$  (These Proc. March 30 1907 p. 736) there must be a closed figure, which has got detached from the branch right of  $\frac{dp}{dx} = 0$ , because the double point, the point in which  $\frac{dp}{dx} = 0$  and  $\frac{d^2\psi}{dx^2} = 0$ , no longer exists. Then we have again a detached closed longitudinal plait, but one which is not intersected by  $\frac{dp}{dx} = 0$ , and which has two plaitpoints in which the  $p$ - and  $q$ -lines which touch have  $\frac{dv}{dx_p} = \frac{dv}{dx_q} =$  positive, in accordance with the course of the nodal lines. In fig. 25 the circumstances after the splitting have been represented for this case. First of all the lines  $\frac{dp}{dx} = 0$  and  $\frac{dv}{dx} = 0$  occur in the figure; further  $\frac{d^2p}{dx^2} = 0$ , which passes through the point where  $\frac{dp}{dx} = 0$  has minimum volume.

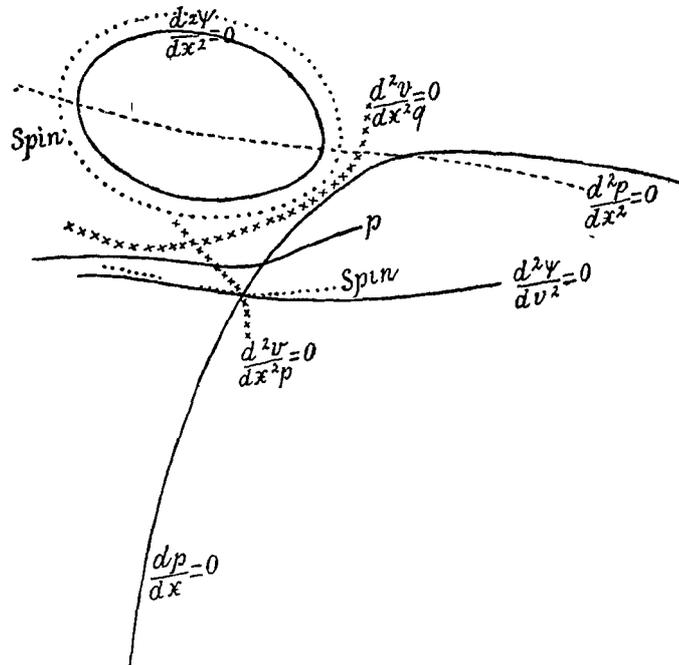


Fig. 25.

On the left of  $\frac{dp}{dx} = 0$  and at smaller volumes also  $\frac{d^2\psi}{dx^2} = 0$  has been drawn. Where this curve passes through  $\frac{d^2p}{dx^2} = 0$  it has tangents //  $v$ -axis. The spinodal line has split up and the two parts have been drawn far apart for the sake of lucidity. One part surrounds  $\frac{d^2\psi}{dx^2} = 0$ , and the other part touches  $\frac{dp}{dv} = 0$  in the point in which this curve is intersected by  $\frac{dp}{dx} = 0$ . Further a  $p$ -line has been drawn with two points of inflection. The right-hand point of inflection is of no importance for our case. And finally the detached branch of the locus of the points of inflection of the  $q$ -lines has been drawn. Now too the point in which  $\frac{d^2v}{dx^2 p} = 0$  and  $\frac{d^2v}{dx^2 q} = 0$  intersect, is to be expected on the left side of the spinodal curve, which has got detached. But for this case  $v_2 > v_1$  for all nodal lines of the longitudinal plait, and the second plaitpoint is really to be expected on the left. I suspect these two ways of detaching to be connected with the two series of values of  $x_g$ , for which  $\frac{d^2\psi}{dx^2} = 0$  disappears in the

region where  $\frac{dp}{dx}$  is positive (These Proc., April 26, 1907, p. 833) — either for a very great difference in the size of the molecules of the components, or for a small difference. In the latter case the highest and the lowest points of  $\frac{d^2\psi}{dx^2} = 0$  are to be found at almost the same value of  $x$ . But this is one of the many particularities which is to be left to a later investigation.

Particularly the last described way of splitting up of the spinodal curve takes place far to the left of the point where  $\frac{dp}{dx} = 0$  has minimum volume, and so at a value of  $x_1$  not very different from that for which  $x_2 = x_1$  on the vapour binodal curve, and maximum pressure exists; and so this leads to the opinion that this detaching of a longitudinal plait is to be found for mixtures with minimum pressure and very different size of the molecules; but also this supposition must be further defined by a fuller investigation.

The following remarks may serve for a full characterization of the course of the spinodal line before and after the splitting. Before the splitting the curves  $\frac{d^2\psi}{dx^2} = 0$  and  $\frac{d^2\psi}{dv^2} = 0$  must be thought as intersecting, as in fig. 8 (These Proc. March 30, 1907), but the line  $\frac{d^2\psi}{dx^2} = 0$  as having moved to smaller volumes. This figure holds indeed for a left-hand region of the  $p$ -figure, but this figure would change little in its essential features if we also insert the line  $\frac{dp}{dx} = 0$  in it, but place it on the right so that  $\frac{d^2\psi}{dx^2} = 0$  is no longer intersected by it. For a region of the left-hand side extended towards the right is the same as a region of the right-hand side extended towards the left. If  $\frac{d^2\psi}{dx^2} = 0$  and  $\frac{d^2\psi}{dv^2} = 0$  intersect there is a complicated plait, with the hidden plaitpoint on the right side. If now with rise of temperature the two curves get further apart, because they both contract, splitting up of the spinodal curve does not always immediately follow. For this to be brought about the curves must be pretty far apart, and intersection of  $\frac{d^2v}{dx^2_p} = 0$  and  $\frac{d^2v}{dx^2_q} = 0$  must take place between the two curves, and the temperature must be reached at which this point of inter-

section lies on the spinodal line. Then a point of the left-hand side of the spinodal line coincides with a point of the right-hand side of this line, but not in the hidden plaitpoint. Consult also fig. 17 (These Proc. May 24, 1907 p. 68). Then there are 4 plaitpoints, viz.  $P_1, P_2$  and the double plaitpoint in the splitting point of the spinodal line. The course of the binodal curve on the liquid side has been represented in fig. 26. On the liquid side the binodal curve of

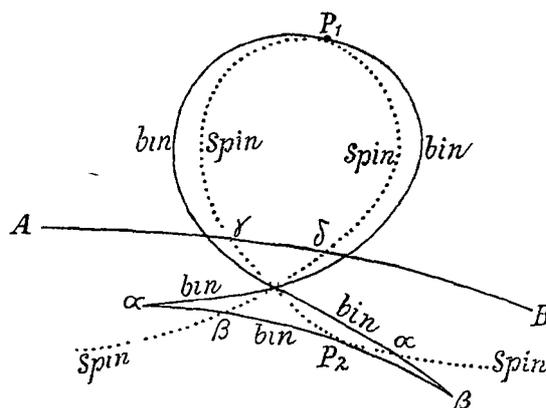


Fig. 26.

the vapour-liquid equilibria passes in two more points,  $\gamma$  and  $\delta$ , through the spinodal curve. And so nothing appears yet of the detaching of the longitudinal plait for the experiment. Only at higher temperature the detached binodal curve, and then with its newly obtained plaitpoint, will pass through the binodal curve  $AB$ , and with still higher value of  $T$  the binodal line has split up into two quite separate branches.

(To be continued).

(September 3, 1907).



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

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PROCEEDINGS OF THE MEETING

of Saturday September 28, 1907.

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(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 28 September 1907, Dl. XVI).

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**Physiology.** — “*Quantitative researches on phagocytosis. A contribution to the biology of phagocytes.*” By Prof. H. J. HAMBURGER and Dr. E. HEKMA.

(Communicated in the meeting of June 29, 1907.)

I. *Introduction and method of investigation.*

The investigations of which an abridged account is given in this paper <sup>1)</sup> are a continuation of those begun several years ago by one of us <sup>2)</sup>, with the object of ascertaining the influence exercised by solutions of various concentration on the red corpuscles and other cells. These researches had been for the greatest part confined to the study of chemical and volumetrical alterations experienced by the cells through the modification of their media and of their significance with regard to the functions of the body. But until now, *the influence of these agents on the life of the cell itself*, had not been the object of a systematic investigation, although the plan had existed for some time and the expediency of the method had been proved <sup>3)</sup>. The importance of such an investigation will be readily admitted. In the first place, because it enhances the value of the chemical and volumetrical researches mentioned above, and secondly, because the phenomena produced by the agency of solutions undangerous to life, are in fact nothing else but the effects of reaction, which finally will help us to penetrate farther into the chemical structure of the living cell. The red corpuscles, which were mostly used for the chemical and volumetrical researches, however, are no suitable objects for the study of the influence of reagents upon life, for they do not afford sure tests of vitality, nor is it possible to measure the value of their life functions.

We therefore looked elsewhere for our material and our choice fell on the phagocytes, for the twofold reason that they are simple, isolated cells in which it is possible to follow the effect of the chemical exchange with their natural medium, and to rate their very life by quantity; besides the phagocytosis is an essential factor in the functions of life. In support of this latter contention, we refer to the important place assigned by METCHNIKOFF to these cells in the struggle of the body against disease; a theory which he has

<sup>1)</sup> For detailed account, see “*Biochemische Zeitschrift*”.

<sup>2)</sup> HAMBURGER, Zittingsverslag der Koninkl. Akad. v. Wetensch. 29 December 1883.

<sup>3)</sup> HAMBURGER, Het gedrag van witte bloedlichaampjes tegenover cyaankalium, Bijdrage tot de kennis der celpermeabiliteit. Feestbundel voor Rosenstein, 1902.

defended with such admirable acumen and unflagging energy. According to the same investigator, the part they play in the healthy body is no less important. The only thing therefore which remains to be done with regard to these cells, is to get a nearer insight into their conditions of life; as yet scarcely anything is known on this subject, a fact mentioned with regret by METCHNIKOFF, in the paper he read last year before the students of the University of Amsterdam, on: "Réactions phagocytaires" <sup>1)</sup>.

The method of investigation employed by us was the following: White corpuscles from the blood of a horse, after having been transported into various media, were brought into contact with carbon and afterwards it was ascertained what percentage of the leucocytes had taken up particles of carbon. *This percentage was the measure for the degree of phagocytosis and gave the value of the influence of various agents on that function of life.*

These calculations were based on the principle that the phagacytorian power of the phagocytes present in a suspension is of unequal extent; i. e. the more detrimental the action of the agent is, the smaller must be the number of phagocytes able to take up carbon.

Our selecting a neutral indifferent substance of bacteria, had its ground in the fear that otherwise our work would have become too complicated. We here refer to the recently established fact that most kinds of bacteria, before they can be taken up by the phagocytes, must undergo a certain amount of preparation <sup>2)</sup>. Hence it follows that not only will the intensity of phagocytosis be influenced by the agent as such, but also by the degree of preparation it has undergone. Another fact which had to be borne in mind, is that the bacteria sometimes secrete poisons which have an injurious effect on the phagocytosis.

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1) "Nous ne sommes qu'an début. Lorsqu'on connaîtra mieux *la physiologie des phagocytes* (the italics are ours) on cherchera des méthodes pour augmenter l'activité de ces éléments dans la lutte contre les microbes et on cherchera d'autres pour préserver contre l'attaque des phagocytes les cellules nobles de notre corps. En poursuivant ce but, il faudra tenir compte de ce que les phagocytes sont non seulement les destructeurs des microbes, mais qu'ils sont capables aussi de s'incorporer des poisons solubles et de les rendre inoffensifs. Leur rôle n'en devient que plus important."

2) WRIGHT and DOUGLAS, Proceed. of the Royal Society 72, 1903, p. 357 and later studies prepared under WRIGHT. Further HEKTOEN and RÜDIGER, Journ. of Infect. diseases 2, 1905, p. 128 and other studies prepared under HEKTOEN.

The selection of the indifferent substance carbon, instead of the usual grains of carmine was based on the greater facility and more accurate certainty with which the taking up of carbon can be ascertained. It was also for this reason that carbon had been the substance selected in former investigations on the action of carbonic acid<sup>1)</sup> and the action of cyanate of potassium<sup>2)</sup> on phagocytosis.

On the present, as well as on the former occasion, the leucocytes used in our investigations, were taken from the blood of a horse<sup>3)</sup>. They were obtained by shaking blood with pieces of glass in a closed bottle and straining the defibrinated blood through a piece of muslin. The red corpuscles sink to the bottom, and the serum which covers them holds all the leucocytes. When this turbid fluid has been poured off we have a suspension of leucocytes in serum; this suspension can be made richer in leucocytes, by centrifugalizing it, removing part of the clear serum and mixing the leucocytes which have fallen to the bottom, with the remaining serum. A detailed description of this method, the process of preparing the carbon, the mode of bringing it into contact with the leucocytes, and the method of determining the percentage of the cells which have taken up carbon, will be found in our article in the *Biochemische Zeitschrift*<sup>4)</sup>.

## II. *The effects produced on phagocytosis by the addition of water.*

Our first experiments were directed to the solution of the question in how far phagocytosis is affected by the addition of water.

With this object in view, equal quantities of the suspension of leucocytes were mixed with serum, previously diluted with known quantities of water. The following table shows the results of one of the series of experiments. It will need no further explanation.

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<sup>1)</sup> HAMBURGER. VIRCHOW'S Archiv, 156, 1899. S. 329. Osmot. Druck u. Ionenlehre. 1. S. 416.

<sup>2)</sup> HAMBURGER. Het gedrag van witte bloedlichaampjes tegenover Cyaankalium in ROSENSTEIN'S Feestbundel. 1902.

<sup>3)</sup> At Groningen we experienced great difficulty in obtaining a regular supply of horses' blood. Mr. K. HOEFNAGEL, the Director of the abattoir at Utrecht, had the great kindness fully to meet our wants, for which we here beg to tender him our best thanks.

<sup>4)</sup> Compare also HAMBURGER, Osmot. Druck u. Ionenlehre, Bd. 1. S. 401.

TABLE I.

Effect of lessening the concentration of the serum.

Serum diluted with	Number of examined white corpuscles	Number of white corpuscles which have taken up coal	Percentage of number of white corpuscles containing coal	Decrease of the phagocytarian power
0% water	886	331	37	
20 "	754	246	32	13.5%
50 "	732	154	21	43.2 "
100 "	636	81	12½	66.2 "
140 "	530	0	0	
200 "	546	0	0	

From this table it appears that in serum, to which no water has been added, of the 886 examined leucocytes, 331 had taken up carbon, i.e. 37 %.

We must here point out that in the circulating, and also in the coagulated blood, the percentage of phagocytes is actually much smaller.

By a certain proceeding, however, we contrived that in our experiments, the leucocytes used for examination should contain a great number of phagocytes. This process is based on the fact that among the leucocytes, the phagocytes are the cells which soonest sink to the bottom. After this explanation, it will cause no surprise to find that, in normal serum, the percentage of the phagocytes which have taken up carbon, continually varies in different series of our experiments.

An addition of 20 % water, already lessens the phagocytarian power with 13½ %. In calculating this loss on an addition of 5 % water, supposing the diminution to be proportionate, the decrease of the phagocytarian capacity would have amounted to:  $\frac{5}{20} \times 13.5\% = 3.4\%$ . In other words, *when the osmotic concentration of the blood plasma is lessened by 5%, a loss which in a healthy individual may be of daily occurrence*<sup>1)</sup>, *the phagocytarian power falls about 3.4 %.*

By the side of this great sensitiveness of the phagocytes to the increase of their percentage of water, stands the fact, as shown from

<sup>1)</sup> Compare a o. KOEPPE, PFLÜGER'S Archiv. 62, 1896. S. 567. In his experiments, KOEPPE noticed a decline below the mean osmotic pressure of over 10 %.

the table, that on the other hand, there are a great number of phagocytes which can stand a dilution of their serum with 100% of water. Former experiments have proved that this dilution causes an increase in the bulk of the cells, of considerably over 30%.<sup>1)</sup>

We will now pass on to the following question: *Is this decrease in the phagocytosis of a permanent nature?*

In order to find an answer, we brought the white corpuscles which had been submitted to the action of diluted serum back into the normal, undiluted serum, and then tested again their power of taking up coal.

T A B L E II.

After exposure to the action of diluted serum, the phagocytes are brought back into normal serum.

Serum diluted with	Number of white corpuscles examined	Number of white corpuscles which have taking up carbon	Percentage of white corpuscles containing carbon, in normal serum
0% water	500	105	21
20 "	500	99	19.8
50 "	500	107	21.4
70 "	500	96	19.2
100 "	500	78	15.6
200 "	500	61	12.2

This table shows that phagocytes, which had some time remained in serum, diluted with 20% or 50% water, dilutions which as the former series of experiments indicates, caused a reduction of the phagocytarian capacity of 13.5% and 43.2% respectively, after having been brought back into normal serum, *entirely recovered their original phagocytarian power.*

The addition to the serum of 100% water, has on part of the phagocytes a lasting deleterious effect; the addition of 200% water is even more detrimental. Still, it is interesting to observe that, although in serum which had been diluted with 200% water, all the phagocytes

<sup>1)</sup> HAMBURGER. Archiv. f. (Anat. u.) Physiol. 1898. S. 317.

had lost the power to take up carbon, after being replaced in the normal serum, over 50% of the phagocytes recovered their original capacity.

*So, the greater part of the phagocytes can support a considerable volume of water without permanent loss of their phagocytarian capacity.*

Here may be asked: On what does it depend, whether a phagocyte will regain its phagocytarian power? It is not impossible, nay, it is even probable, that here as well as in the case of the red corpuscles some lose their contents in serum diluted with 70% of water<sup>1)</sup>. If the quantity of water added be raised to 100%, the number of destroyed erythrocytes will be found considerably larger. When the red corpuscles, which *have not lost their haemoglobin*, are removed from the serum diluted with 100% of water into undiluted serum, they entirely recover; they change from small globules into biconcave discs, which even arrange themselves like piles of coins.

However, this only applies to the cells which have not lost their colouring matter. These which have actually lost haemoglobin cannot recover. Now our microscopical investigations have revealed the fact, that in serum + 70% water, some of phagocytes lose a part of their contents: in that case we see a granular substance lying by their sides. In serum to which 100% water has been added, the effect is more apparent still. Then the number of leucocytes which have expelled granular matter is still larger. It is easy to understand that these cells, when again placed in normal serum, have lost the power of taking up carbon. The difficulty of ascertaining this with certainty however, is very great; in the transmission there is every chance of disturbing the granular substance by the side of the cells, and it is impossible to know whether one deals with a phagocyte which has lost part of its contents or not. Anyhow, taking into consideration the striking analogy existing between white and red corpuscles, both with regard to their permeability and to the osmotic pressure of their interior substance, and even to the percentage of the volume of their watery contents<sup>2)</sup>, we seem justified in our conjecture that the same fluid, which causes a loss of colouring matter in the least resisting of red corpuscles, also brings about the irremediate destruction of the phagocytarian power of the least resisting phagocytes.

It is a fact worthy of notice that the resisting power of the phagocytes reaches a higher maximum than that of the erythrocytes. In serum diluted with 200% water, all the erythrocytes of the horse are destroyed, and not quite half of the phagocytes.

### III. *Effect on phagocytosis by the reduction of water.*

A similar method as had been used for studying the effect on phagocytosis by dilution of the serum, was now applied to ascertain the

<sup>1)</sup> HAMBURGER. Transactions of the Royal Academy of Sciences, 26th March 1885.

<sup>2)</sup> Osmot. Druck u. Jonenlehre I, S. 401—435.

influence of concentration. With this object in view, common salt was dissolved in the serum in quantities of 0.1, 0.2, 0.3, 0.4 % and more. The results of these experiments are shown in the following table:

T A B L E III.

Effects on phagocytosis by increased concentration of the serum.

Serum in which is dissolved	The liquids in the preceding column are corresponding to:	Percentage of leucocytes which have taken up carbon	Decrease of the phagocytarian power
0 % Sod. Chl.	Sod. Chl. 0 90%	$\frac{208}{832} \times 100 = 26\%$	
0.1 "	" 1	$\frac{184}{874} \times 100 = 21.5$	17.30%
0.2 "	" 1.1	$\frac{184}{1005} \times 100 = 18.3$	29.6
0.3 "	" 1.2	$\frac{76}{941} \times 100 = 8$	69.2
0.4 "	" 1.3	$\frac{43}{793} \times 100 = 5.4$	79.2

Here we see that the injurious effect is very great, much greater than is the case when the osmotic concentration has been diminished. Then we observed that by diluting the serum with 20 % water, phagocytarian capacity fell 13.5 %; here we find that by raising the osmotic concentration by 10 %, the phagocytarian power is lowered by 17.3 %. This effect must already be perceptible within the physiological boundaries in which the osmotic pressure of the blood plasma usually varies in the normal body. For it may happen every day that in a normal individual the osmotic pressure of the liquor sanguinis, a few hours after dinner, is still raised by that of 0.1 % common salt <sup>1)</sup>).

Here again, as we did before when studying the decrease of osmotic pressure, we ask whether the loss of phagocytarian power

<sup>1)</sup> KOPPE, l. c.

D. SCHOUTE. Het fysisch-chemisch onderzoek van menselijk bloed in de kliniek. Diss. Groningen 1903.

See also Osmot. Druck u. Ionenlehre B. I S. 540 ff.; B. II S. 279 and 310 ff.

can be restored, by replacing the white corpuscles in the normal serum. The answer will be found in the following table.

T A B L E IV.

After being exposed to the action of increased concentration,  
the leucocytes were replaced into normal serum.

Serum in which is dissolved	After replacement into normal serum, the phagocytarian power stands at
0% Sod. Chl.	$\frac{273}{700} \times 100 = 39\%$
0.2 "	$\frac{246}{646} \times 100 = 38.4$
0.7 "	$\frac{226}{685} \times 100 = 33$
1.2 "	$\frac{170}{567} \times 100 = 30$
1.5 "	$\frac{149}{713} \times 100 = 21$
2 "	$\frac{87}{625} \times 100 = 14$
3 "	$\frac{57}{590} \times 100 = 9$

From this table it may be seen that after exposure to the action of serum in which 0.2 % common salt had been dissolved, a solution which had lowered the phagocytarian capacity by 29.6 % (see table III), replacement in normal serum brings it back to its original value. The action of serum in which 0.7 % of salt had been dissolved, however, causes a permanent loss of phagocytosis. Still, this loss is not so great considering that, in the serum with 0.7 %, not a single cell has taken up carbon, — in other terms, the phagocytosis has been entirely paralysed.

Now the phagocytes had only been exposed for half an hour to the action of the concentrated media. This certainly may be considered long enough for the small cells to readjust themselves to their new medium. Still, it may be asked whether *after a more prolonged exposure the normal value of the phagocytarian power would be restored too*. This question is of great importance for the functions of normal life, in

which the increase of osmotic concentration often lasts longer than half an hour. For this reason, the experiments in which the leucocytes were exposed to an action of much longer duration, were made with serum containing only 0.1 and 0.2% NaCl; higher osmotic concentration does not occur in the body. The leucocytes were placed in the serum of increased osmotic concentration for 2, 24 and 48 hours, and then transferred into normal serum.

The experiment showed that after an exposure of 24 and 48 hours, the phagocytarian power had been diminished; but an *equal* decrease of vitality was also observed in phagocytes which had remained for 24 and 48 hours respectively in *normal* serum. This proved that the prolonged action of serum of increased osmotic concentration had had no *permanent* injurious effect on the phagocytarian capacity.

*Thus we may conclude that, in the living body an increase in the osmotic concentration of the blood plasma, as well as a decrease of the same, has a deleterious effect on the phagocytarian power, but that the loss may be recovered; for as soon as the osmotic pressure has been restored to the normal, the phagocytes also entirely regain their inherent power.*

If from these experiments we may conjecture, that what we have observed in the phagocytes, will also be applicable to other cells with semipermeable walls, it is reasonable to conclude from the results shown in tables II and III, *that the vital functions of the cell are in a large measure influenced by slight oscillations in the osmotic concentration of the environment and consequently of the cells themselves.*

#### IV. *Effect of simple solutions of Salt.*

##### 1. Solutions of Sodium Chloride.

Now the question arises whether the loss of vitality described above, must be attributed to the variations of the quantity of water as such, or to the modification in the concentration of one or more of the substances.

In order to examine this question systematically, we might have alternately reduced the several elements in the diluted serum to their original concentration and then studied the extent of the improvement. But as in the mean time it had been clearly demonstrated to us that in a pure solution of Sodium Chloride of 0.9%, the phagocytes take up carbon in equal or almost equal quantities as in normal serum, we decided to abandon this mode of investigation.

Here we must incidentally remark that, after all that has been said by

LOEB<sup>1)</sup> and others, of the injurious action of a pure solution of a simple salt on the life of young moving larvae and the vital processes of higher animals, such as the beating of the heart and the movements of the intestines, we were at first rather astonished at the almost perfect innocuousness of similar solutions in regard to the phagocytes. However, we can easily find an explanation for this seeming inconsistency. Whenever a cell is surrounded by a simple isotonic solution of salt, two things are likely to happen: an exchange of ions may take place, thus causing a modification in the chemical structure of the cell, which interferes with certain of its vital functions. This is the case with the larvae of fundulus with the muscle of the heart and that of the intestines. A supply of specified ions is then required to restore the chemical structure of the cell to its normal state. But — and this is the second possibility — if the permeability of the cell to ions is highly limited, a pure isotonic solution of salt will not cause any, or only a very slight alteration in the chemical structure of the cell. This is the case with the white corpuscles, the slight permeability of which to ions of salts has already been demonstrated in the most convincing manner.<sup>2)</sup>

Bearing this fact in mind, it can cause no surprise that, contrary to the results of the observations on eggs and muscles, a pure solution of Sodium Chloride leaves the phagocytarian power entirely or almost entirely intact.

Under these circumstances, for determining the influence of the water as such, it was indicated to take solutions of Sodium Chloride of various strength.

Table V shows the action of diluted solutions of Sodium Chloride on phagocytosis.

TABLE V.

Effect of hyper-isotonic solutions of Sodium Chloride on phagocytosis.

Solutions of Salt.	Percentage of leucocytes which have taken up carbon.
NaCl-sol. 0.9%	$\frac{235}{756} \times 100 = 31 \%$
NaCl 0.75% = NaCl 0.9% + 20% water	$\frac{208}{741} \times 100 = 28$
„ 0.6 = „ 0.9 + 50 „	$\frac{221}{1012} \times 100 = 21.8$
„ 0.45 = „ 0.9 + 100 „	$\frac{83}{745} \times 100 = 11.1$

<sup>1)</sup> J. LOEB, American Journal of Physiol. 3 1900 p. 327 and 383; 5 1901 p. 362 Pflüger's Archiv 80 1900 S. 229.

LINGLE, Americ. of Journal of Physiol. 4 1900 p. 265.

MISS MOORE, Ibid. 1900 p. 386 etc.

<sup>2)</sup> HAMBURGER. Zeitschr. f. Biol. 35. 1897 S. 252 and S. 280; Proceed. of the Royal Academy of Sciences 11 April 1897.

Archiv f. (Anat. u.) Physiol. 1898 S. 31 and S. 317.

VIRCHOW'S Archiv 156 1899 S. 329

HAMBURGER and VAN DER SCHROEFF, Archiv f. (Anat. u.) Physiol. 1902. S. 251.

Here we see the marked effect of a diminution in the concentration of the salt solution.

TABLE VI.

Effect of hyper-isotonic solutions of salt.

Solutions.	Percentage of leucocytes containing carbon.	Decrease of the phagocytarian power.
NaCl 0.9%	$\frac{250}{722} \times 100 = 34.6\%$	
" 0.95	$\frac{293}{875} \times 100 = 33.5$	30%
" 1	$\frac{95}{802} \times 100 = 11.84$	60.6
" 1.1	$\frac{105}{981} \times 100 = 10.8$	69
" 1.2	$\frac{7}{990} \times 100 = 0.7$	98
" 1.3	$\frac{0}{200} \times 100 = 0$	
" 1.4	$\frac{0}{150} \times 100 = 0$	
" 1.5	$\frac{0}{150} \times 100 = 0$	

*The surprisingly rapid decline of phagocytosis observed in serum of increased concentration (table III) is again clearly demonstrated in this instance.*

Even the slight increase of 0.9 to 1% lowers the phagocytarian power already 60.6%. Another illustration of this rapid decline is afforded by the observation that in the 1% concentration of Sodium Chloride, the amount of carbon present in the coal containing phagocytes is far less than in those that have stayed in the solution of 0.9%.

Now, by comparing tables VI and III, we see at a glance that, when the experiments were made with a solution of Sodium Chloride of 0.9%, to which afterwards salt had been added, *the decline in the phagocytarian power is more marked than when they are*

made in serum supplemented with an equal quantity of salt. This proves that besides the osmotic pressure, which must principally be made accountable for the decline, there is still another factor at work, and this factor can be no other than the modification — however slight — produced by a pure solution of  $\text{NaCl}$  in the chemical structure of the phagocytes. Some time ago, one of us, in conjunction with Dr. VAN DER SCHROEFF<sup>1)</sup>, already demonstrated that the leucocytes the same as the red corpuscles are in any case permeable to anions. It is therefore evident that, owing to their chemical structure being interfered with, the cells most lose some of their vitality (phagocytarian power) under the action of pure salt solutions, — or rather, that they should lose more than in an isosmotic serum.

We have submitted this hypothesis to further experiments, starting from the following reasoning: If it is a fact that in a hyper-isotonic solution of salt, the phagocytes undergo a chemical variation through exchange of ions, it must be possible to restore this loss of phagocytarian capacity resulting from their modification in their structure, by replacing them in normal serum, and that this recovery will not be complete by immersion in a 0.9% solution of salt. The following table proves that we were correct in our surmise.

TABLE VII.

Effect of solutions of salt on the chemical structure  
of the phagocytes.

White corpuscles immersed for 2½ hours in the following solutions.	Phagocytarian power after being transferred into.	
	Normal Serum	Salt solutions of 0.90%
NaCl 0.90%	$\frac{319}{942} \times 100 = 33.9\%$	$\frac{284}{811} \times 100 = 35\%$
" 1	$\frac{258}{775} \times 100 = 33.3$	$\frac{251}{760} \times 100 = 33$
" 1.1	$\frac{233}{790} \times 100 = 29.5$	$\frac{209}{735} \times 100 = 28.6$
" 1.2	$\frac{202}{722} \times 100 = 28$	$\frac{175}{677} \times 100 = 26$

<sup>1)</sup> HAMBURGER and VAN DER SCHROEFF. l. c.

*It is clearly demonstrated that the phagocytes, which have been exposed for two hours to the action of solutions of Sodium Chloride, exhibit a greater phagocytarian power when they are transferred into serum, than when they are placed into salt solution of 0.9 %.*

No doubt the observation will strike the attentive reader as contradictory, that this is only the case with the phagocytes which had been exposed to the action of sodium chloride of 1 %, 1.1 % and 1.2 %, but not with those which for the same space of time had been immersed in a similar solution of 0.9 %; then the effect of this salt-solution and the serum is quite the reverse. This, however, is not actually the case; for in serum the phagocytes are likely to stick together and on this account do not offer as large a surface to the carbon as in the salt-solutions in which they remain more isolated. If then, as must be the case in an *isotonic* solution, the injurious effects of the Cl-ions of the pure salt solution are comparatively small, they may easily be exceeded by the unfavourable position of the cells caused by the serum.

When, however, by the use of *hyper-isotonic* solution of sodium chloride, the injurious action of the Cl-ions be increased, it may exceed the detractory influence of the agglomeration of the cells, and produce the results shown in the table.

With regard to these statements it may here be asked why, in *isotonic* solutions of sodium chloride, the injurious effect on the phagocytes cannot be determined, but is easily demonstrated when *hyper-isotonic* solutions are used, and the more readily in proportion as the concentration of the salt solutions are increased in strength. This question is very natural, because it concerns such a small increase in the considerable amount of ions of Cl or of Na already present. Here we are involuntarily reminded of the fact stated by HEDIN<sup>1)</sup> with regard to the red blood-corpuses. The minute investigations of this scientist have brought to light the fact, that in isosmotic *isotonic* solutions of salt, the corpuscles possess an equal volume, but that in isosmotic *anisotonic* solutions their relative volume is no longer equal. HEDIN has not given an explanation of this important fact; but anyhow, it proves that simple solutions of salt, when *anisotonic*, exercise still another kind of action beyond that of their osmotic pressure. We propose to investigate this matter somewhat further: it is very probable that by a modification in the dissociation of the contents of the cell, an altered condition for the exchange of ions is produced.

<sup>1)</sup> HEDIN. Skandinavisches Archiv f. Physiol, 1895 S. 377.

## 2. Solutions of Chloric Potash.

In our description of the influence of sodium chloride, we attributed it to the ions of chlorine. This was based on the results of investigations in which we compared the action of sodium chloride and of potassium chloride, of which a few items here follow.

These investigations proved that isosmotic solutions of sodium chloride and potassium chloride have almost the same effects on phagocytosis.

T A B L E VIII.

Comparison of isosmotic quantities of sodium chloride and potassium chloride.

	Percentage of leucocytes containing carbon.
Serum	$\frac{253}{722} \times 100 = 35\%$
NaCl-sol. 0.9%	$\frac{300}{836} \times 100 = 36$
KCl-sol. 1.15% (isot. m. NaCl-sol. 0.9%)	$\frac{258}{277} \times 100 = 34$
Serum + 0.1 % NaCl	$\frac{183}{672} \times 100 = 27$
„ + 0.127 „ KCl	$\frac{181}{715} \times 100 = 25$
„ + 0.3 „ NaCl	$\frac{45}{630} \times 100 = 7$
„ + 0.38 „ KCl	$\frac{54}{683} \times 100 = 8$
„ + 0.3 „ NaCl	$\frac{184}{600} \times 100 = 30$
„ + 0.38 „ KCl	$\frac{185}{621} \times 100 = 30$

Two other parallel-experiments in solutions of 0.9% of sodium chloride produced the following results:

$$\frac{198}{863} \times 100 = 23\% \text{ of leucocytes containing carbon}$$

$$\text{and } \frac{146}{677} \times 100 = 21.5\% \text{ „ „ „ „}$$

in the isosmotic solution of KCl 1.15 %:

$$\frac{128}{615} \times 100 = 21 \% \text{ leucocytes containing carbon}$$

$$\text{and } \frac{165}{732} \times 100 = 22.5 \% \quad \text{,,} \quad \text{,,} \quad \text{,,}$$

*Hence we may conclude, that there is no difference between the action of chloride of potassium and chloride of sodium.*

### 3. Effect of chloride of calcium.

The great importance which, according to the most recent investigations must be ascribed to the ions of calcium,<sup>1)</sup> in the constitution of the fluid-matter of the tissues, induced us to test also the effect of this medium on phagocytes.

With this object in view, we dissolved various quantities of chloride of calcium in the serum of the blood of a horse and mixed the suspension of leucocytes thus obtained with carbon.

T A B L E IX.

Effect of calcium chloride.

Serum +	Percentage of leucocytes containing carbon	Increase of the phagocytarian power
0% CaCl <sub>2</sub> 6 aq.	$\frac{132}{612} \times 100 = 21.2\%$	
0.01%	$\frac{225}{861} \times 100 = 26$	22.6%
0.1	$\frac{180}{652} \times 100 = 27.6$	30.2
0.5	$\frac{162}{598} \times 100 = 27$	27.3
1	$\frac{0}{724} \times 100 = 0$	

*An addition of 0.01 % of Ca Cl<sub>2</sub> 6 aq. to the serum already produces an increase of the phagocytarian capacity of 22.6 %; by the addition of 0.1 % Ca Cl<sub>2</sub> 6 aq., the effect is somewhat*

<sup>1)</sup> See especially the investigations of LOEB. Publications of the University of California and of LANGENDORFF and HUECK. Pflüger's Archiv 96 1903 S. 473; for the complete bibliography on the subject until 1904, see Osmotischer Druck und Ionenlehre B. III, S. 107 etc. Comp. also A. NETTER, Importance biologique du Calcium. Paris. Masson et Cie. 1907.

greater, and by the addition of 0.5 % Ca Cl<sub>2</sub> 6 aq., it again decreases.

The result registered in the first instance, which is produced by the addition of 0.01 % Ca Cl<sub>2</sub>, must be considered the most valuable, for it denotes the nearest unalloyed effect of the calcium chloride. In the experiments where quantities of 0.1%, 0.5% and 1% of Ca Cl<sub>2</sub> were added, the increase of phagocytosis is counteracted by the unfavourable influence of the raising of osmotic pressure.

This experience is in strict accordance with the observations made by LANGENDORFF, who found that the injection of very small quantities of calcium, causes the heart to beat with greater force. We ascribe this manifestation to the action of the ion of calcium on the contractile substance, and we may conclude that the muscular fibre and the phagocytes also, are permeable to this cation.

#### 4. Effect of citras naticus.

The frequent use which, in consequence of the experiments of WRIGHT and DOUGLAS,<sup>1)</sup> is made of this medium at the present day by the bacteriologists, in order to prevent the coagulation of the blood, actuated us also to experiment with this substance for the sake of determining its action on the phagocytosis. The following table gives a survey of the results.

The customary solutions of 1 % and 2 % of citras naticus in 0.9 % solution of sod. chl. were used in these experiments.

T A B L E X.  
Effect of citras naticus.

	Percentage of leucocytes containing carbon
(a) 1 cc. suspension of leucocytes + 2 cc. solution of 1% citras natr. in 0.9% Sod.Chl.	0
(b) 1 cc. suspension of leucocytes + 2 cc. solution of 2% citras natr. in 0.9% Sod.Chl.	0
(c) leucocytes from (a) transferred in Sod.Chl. 0.9 %	$\frac{260}{686} \times 100 = 38\%$
(d) leucocytes from (b) transferred in Sod.Chl. 0.9 %	$\frac{255}{731} \times 100 = 35\%$
(e) 1 cc. suspension of leucocytes + 2 cc. solution of 0.9 % Sod.Chl. (Control test)	$\frac{369}{725} \times 100 = 50\%$

<sup>1)</sup> WRIGHT and DOUGLAS, Proceed. of the Roy. Soc. 72, 1903, p. 357; 73, 1904, p. 128.

From the above table it is shown: 1. That in 1—2 % solutions of citras naticus in 0.9 % of Sod. Chl. the phagocytarian power is nil.;

2. that the phagocytarian capacity again *partially reappears*, when the cells are transferred into 0.9 % solutions of Sod. Chl. *The permanent decline of the phagocytarian power still amounts to 28 %.*

#### 5. Effect of Fluornatrium.

Fluornatrium being also much used for preventing the coagulation of the blood, it seemed important to us also to study the effect of this medium on the phagocytosis.

T A B L E XI.  
Effect of Fluornatrium.

	Percentage of leucocytes containing carbon	
	Before being transferred into 0.9% Sod. Chl.	After being transferred into 0.9% Sod. Chl.
2cc suspension of leucocytes + 2cc NaFl 0.65% (isot. with NaCl 0.9%)	0%	$\frac{91}{677} \times 100 = 14\%$
"                    + 2cc NaFl 1%	0	$\frac{90}{511} \times 100 = 6$
"                    + 2cc NaFl 2%	0	0
"                    + 2cc NaCl 0.9%		$\frac{369}{725} \times 100 = 50$

Here we see that when the leucocytes have been exposed to a solution of Fluornatrium of 2 %, 1 % or 0.65 % (isot. with 0.9 % NaCl) the phagocytarian power is entirely paralysed, yea, that even after transferring of the phagocytes in a solution of 0.9 % Sod. Chl. it shows to have been entirely destroyed for ever. *Hence we may conclude that NaFl is a powerful poison for the protoplasm of the phagocytes.*

#### V. Effect of acid and alkali.

##### 1. Effect of acid.

The important part which the alkaline reaction of the blood-plasma seems to play, not only in connexion with the degree of

oxydation taking place in the body, but also in infectious diseases, induced us to study its effects on the increase or decrease of the phagocytarian power.

The results of one of the experiment are shown in the following table.

T A B L E XII.  
Diminution of the alkaline reaction of the serum.

l cc $\frac{1}{2}$ n. $H_2SO_4$ +	Amount of acid added	Percentage of white blood corpuscles containing carbon
9 cc serum	$\frac{1}{20}$ norm.	0
14 cc "	$\frac{1}{30}$ "	$\frac{13}{308} \times 100 = 4.3\%$
19 cc "	$\frac{1}{40}$ "	$\frac{35}{398} \times 100 = 9$
49 cc "	$\frac{1}{100}$ "	$\frac{165}{724} \times 100 = 21.4$
299 cc "	$\frac{1}{1000}$ "	$\frac{255}{612} \times 100 = 41.7$
499 cc "	$\frac{1}{1000}$ "	$\frac{256}{530} \times 100 = 48.5$
normal serum		$\frac{227}{530} \times 100 = 43$

We observe that even the small addition of  $\frac{1}{1000}$  n-acid is injurious to the phagocytosis.

Now, we know that according to titration with laemoide, 100 c.c. horse serum in the mean is equivalent to 75.5 cc.  $\frac{1}{25}$  n-acid<sup>1)</sup>; consequently it is calculated that serum represents an alkaline fluid of  $\frac{1}{30}$  normal.

The addition of  $\frac{1}{1000}$  n-acid, therefore lowers its alkaline reaction by 5 %.

*Consequently, a diminution of the alkaline reaction of the serum by 5 % is already injurious to the phagocytes.*

This result is in strict accordance with the injurious effect experienced

<sup>1)</sup> HAMBURGER, Verhandl. d. Koninkl. Akad. v. Wetensch. Second section, Vol. VI, N<sup>o</sup>. 1, 1897.

by administering acid per os, and we are fully justified in ascribing the poisonous effects of the acid, to a diminution in the process of oxydation.

The results agree also with the observations recently published by J. LOEB, on the influence of the traces of NaOH (OH-ions) on the artificial fructification of the eggs of sea-urchins. The author has clearly demonstrated that the primary cause of this effect might be found in the acceleration of chemical reactions. <sup>1)</sup>

T A B L E XIII.

Increase of the alkaline reaction of the serum.

1cc $\frac{1}{2}$ n. NaOH +	Amount of alkali added	Percentage of white corpuscles containing carbon.
29cc Serum	$\frac{1}{100}$	$\frac{25}{622} \times 100 = 4$
37cc "	$\frac{1}{76}$	$\frac{57}{840} \times 100 = 6.8$
49cc "	$\frac{1}{100}$	$\frac{114}{707} \times 100 = 16$
99cc "	$\frac{1}{200}$	$\frac{179}{716} \times 100 = 25$
199cc "	$\frac{1}{400}$	$\frac{143}{531} \times 100 = 27$
399cc "	$\frac{1}{800}$	$\frac{149}{580} \times 100 = 25.7$
normal serum		$\frac{177}{664} \times 100 = 26.5$

It is seen from this table that, within a large margin, the addition of OH-ions to the serum does not exercise a perceptible influence on the phagocytarian power, it remains unaltered until the value is increased by  $\frac{1}{200}$  normal: i.e., with 15 % of the original alkaline reaction. An additional supply of alkali causes a lessening of the phagocytarian power.

*More pronounced still is the effect of acid and alkali on the phagocytes, when these substances, instead of being added to serum, are*

<sup>1)</sup> J. LOEB, PFLUGER'S Archiv 118, 1907, H. 3/4, S. 181.

introduced in solutions of 0.9 % sod. chl. A more detailed account of the results of these investigations will follow later.

We also made a number of experiments to test the influence of other media on the phagocytarian power, e.g. with *ureum*, *chinine*, *argentum colloidalale*, *heterogenous serum*, etc., the results of which will appear in a subsequent paper.

*Summary.*

The following are the principal conclusions derived from the above described experiments.

1. The action exercised by various media on the phagocytarian power of white corpuscles, can be accurately determined by counting the percentage of cells which have taken up particles of carbon.

2. *The addition of water to the inherent medium of the phagocytes i.e. to their own serum, acts injuriously on the phagocytarian power. Even a decrease in the osmotic concentration as may daily occur in a normal individual, causes a perceptible decline in the phagocytarian power.*

So, it was shown in one of the experiments that, whilst in normal undiluted serum 37 % of the leucocytes had taken up carbon, in serum which had been diluted with 20 % of water the amount of cells containing carbon was only 32 %: this corresponds to a decline in the phagocytosis of  $\frac{37-32}{37} \times 100 = 13.5$  %.

By the addition of 50 % water, the percentage of phagocytes containing carbon fell to 21 %, thus in this case a decrease of phagocytosis of  $\frac{37-25}{37} \times 100 = 43$  %.

By addition of 140 and of 200 % water, the percentage of the carbon-containing leucocytes was lowered to nil, — in other words the phagocytarian power had been suspended, but only *temporarily*, for

3. *by replacing the cells damaged by the addition of water, into their own serum, the phagocytarian power is entirely or partially restored.*

So the recovery was complete, when the serum had been diluted with 20 % or 50 % of water, and only partial when 70 tot 100 % water had been added. Even when it had been diluted with 200 %,

a figure at which, it is shown under 2, the phagocytosis had been entirely suspended, — a recovery took place in the phagocytarian power to half of its original amount.

4. *The observations, here made with the phagocytes, correspond with those previously observed in the red corpuscles.*

1. The phagocytes, the same as the red corpuscles, can support a considerable quantity of water ( $\pm 60\%$ ) without a single cell being destroyed;

2. The modifications produced in the phagocytes by the addition of water, unless they have led to their entire destruction, may, judging from the phagocytarian capacity, be entirely obviated by replacing them in normal serum.

5. *A heightening of the osmotic concentration of the serum, as well as a lowering of the same, (comp. sub 2) has a very injurious effect on the phagocytosis. It was obvious that an increase of the osmotic concentration had even a more pronounced deleterious action than the decrease at the same ratio.* Already an addition of  $0.1\%$  NaCl to the serum caused the phagocytarian power to decline  $17.3\%$ .

By the addition of  $0.4\%$  NaCl this decrease amounted to  $79.2\%$ , and by the addition of  $0.5\%$  Sod. Chl., the phagocytarian power was reduced to nil; but this considerable loss was but temporary, for

6. *when the cells which had been damaged by an addition of sodium chloride to the serum, were replaced in their original blood-serum, their phagocytarian capacity was again entirely or partially restored; entirely when only from  $0.1\%$ — $0.2\%$  of the substance had been added; partially when a greater amount had been used.*

7. If thus, as shown under 2 and 5, the phagocytarian power is specially impaired by modification of the normal osmotic concentration of the blood-serum, this capacity will be entirely restored as soon as the blood-plasma, principally owing to the activity of the kidneys, has recovered its normal osmotic concentration. The experiments have demonstrated that this recovery is still possible after the agency of the anisotonic serum for 24 hours and more.

8. *In solutions of  $0.9\%$  NaCl the phagocytarian power is almost equal to that of serum.* It considerably decreases under the action of weaker and stronger solutions of this salt, even more so than in serum which has been made isosmotic with these salt-solutions.

9. *This result leads to the conclusion that the decline of the phagocytarian capacity produced by anisotonic serum, has its cause principally in the alteration of the amount of water in the cells.*

10. *Besides the modification of the amount of water in the cells, another factor comes into play, namely the chemical change, which takes place consequently on the exchange of the contents of the cells with those of their environment and which, as a matter of course, is greater when the cell is surrounded by a simple solution of NaCl than when placed in an isosmotic serum. This accounts for the fact, that phagocytes which have been submitted to the action of hyperisotonic solutions of NaCl, when replaced into serum, exhibit a somewhat greater phagocytarian power, than when they are transferred to a 0.9 ‰ solution of NaCl. In the latter case they have not the opportunity, given them in the former, of regaining the ions which they have lost in the anisotonic solutions of salt.*

11. *It is very probable that the ions of Ca and of OH belong to this category.*

With regard to calcium, it has been proved that by the addition to the serum of the minute quantity of 0.01 ‰  $\text{CaCl}_2$  6 aq, i.e. about 0.005 ‰  $\text{CaCl}_2$ , the phagocytarian power was raised by about 22.6 ‰. The inference is that ions of calcium must have penetrated into the phagocytes.

On the other hand it may be surmised that the phagocytes will lose ions of calcium when the amount of calcium in the medium is lower than that to which the phagocytes are accustomed. This loss of ions of calcium must cause a diminution of the phagocytarian power.

We observe a similar result in the case of the OH-ions; for our experiments have demonstrated that decrease of these ions causes a lowering of the phagocytarian power. A 5 ‰ diminution of the alkaline reaction of the serum, which necessarily must lower the amount of alkali in the phagocytes, produces a noticeable decline in the phagocytarian capacity.

12. LÖBB and after him other investigators have pointed out, that a pure solution of NaCl must be considered injurious to the larvae of lower sea animals, the muscles of the heart, and those of the intestines. *This opinion does not hold for the phagocytes.* The proof of this assertion is found in the fact that in a solution of NaCl isotonic with serum, the phagocytosis is almost as powerful as in the serum itself.

This seeming contradiction may be met by the explanation that the exchange of substance between the leucocytes and the solution of NaCl, especially when the latter is isotonic with the serum, is very small; whilst in the case of other cells (ciliated cells, muscular fibre cells) the conditions of the exchange of ions are not so restricted, and consequently the chemical structure of these cells is more easily modified. And it is obvious that a modification of their chemical structure causes a disturbance in their inherent functions.

13. From the facts here recorded, it is evident that in studying the action of the phagocytes on bacteria *in vitro*, the degree of osmotic concentration and of the alkaline reaction of the medium, must be taken into account. This condition has been lost sight of in several of the experiments. They ought therefore to be repeated.

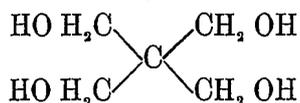
Groningen, June 1907.

**Chemistry.** — “*The decomposition of penta-erythritol tetraformate on heating.*” By Prof. P. VAN ROMBURGH.

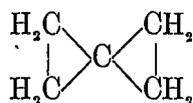
(Communicated in the meeting of June 29, 1907).

As the heating of the diformate of *s.* divinylglycol had led in such a simple manner to hexatriene 1.3.5, investigations have been set on foot in my laboratory for studying the decomposition of formic esters of polyhydric alcohols, the results of which will be gradually communicated.

If for penta-erythritol we accept the formula:

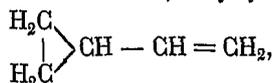


and if the reaction took place in a similar manner as with *s.* divinylglycol diformate, we might expect on heating the tetraformate<sup>1)</sup> the formation of a hydrocarbon of the formula:



in which occurs twice a 3-ring.<sup>1)</sup>

<sup>1)</sup> GUSTAVSON C. R. 123 (1896) 242 obtained from the tetrabromide of penta-erythritol, by the action of zinc and alcohol, vinylcyclopropan:



instead of the above cited hydrocarbon.

The reaction, however, proceeds in quite a different sense, for instead of the hydrocarbon we only obtain carbon monoxide, while penta-erythritol is regenerated.

In order to prepare the tetraformate of penta-erythritol, this substance is heated with an excess (8 mols.) of concentrated formic acid in a flask connected with a condenser, in such a manner that the excess of acid distils over slowly with the water formed in the reaction. When the thermometer placed in the liquid shows  $120^{\circ}$ , the heating is stopped, and the distillation is repeated with a fresh quantity of formic acid. After this the heating is repeated twice with 100% acid. There then remains in the flask an oily liquid, which, when placed in a dish over sulphuric acid, abundantly deposits crystals after some time. These are collected at the pump, and then thoroughly pressed between filterpaper.

The solid substance thus obtained, after having been recrystallised from dry benzene, melts at  $55^{\circ}$ . After repeated recrystallisation from that solvent, the melting point rose to  $57^{\circ}$  and then remained constant.

This formate is sparingly soluble in ether; from a solution in benzene it is precipitated by ether. It has a slightly bitter taste.

On boiling with a titrated solution of potassium hydroxide the formic acid formed may be readily estimated.

Found 74.21 and 74.16% formic acid

Calculated = 74.18%.

The ultimate analysis gave the values expected for penta-erythritol tetraformate :

	Found	Calculated for $C_9H_{12}O_8$
C	43.6 43.75	43.57%
H	5.26 5.16	4.88%

On heating this formate, a plainly visible evolution of gas commences at  $220^{\circ}$ , which is fairly strong at  $230^{\circ}$ . The gas evolved consists of pure carbon monoxide and when the evolution of gas has ceased, there remains in the flask pure penta-erythritol, which may be readily identified as such by its properties. The amount of gas evolved is that required by theory.

I wish to express my thanks to Mr. VAN ENDT, who has assisted me in these experiments with care and zeal.

Mr. RENIER, who is engaged in the study of the formates of glycols found that from 2.5 dimethyl-hexandiol 2.5, the well known tetramethyldihydrofuran, is formed by simply heating with formic acid.

On the other hand the formic ester of pentandiol 2.4 is very stable towards heat.

At about 400°, however, the ester is decomposed and a liquid is formed boiling at 42° which is most probably 1.2 dimethylcyclopropane.

Mr. VAN MAANEN, is engaged in the study of the decomposition of the formic esters of mannitol.

Utrecht. Org. Chem. Lab. University.

**Botany.** — “*On the influence of wound stimuli on the formation of adventitious buds in the leaves of Gnetum Gnemon L.*” By Mr. J. VAN BEUSEKOM. Communicated by Prof. F. A. F. C. WENT.

(Communicated in the meeting of June 29, 1907).

It had been observed for a long time already that adventitious sprouts were formed on the leaves of a specimen of *Gnetum Gnemon L.*, cultivated in the Botanic Garden at Utrecht.

In January 1906 my attention was drawn to this circumstance by Prof. WENT, who advised me to study the development of these adventitious sprouts, and to try to discover the origin of their formation.

The results of this investigation will be concisely communicated here.

The adventitious buds appear on the tips of the leaves, while these are still attached to the plant.

As far as I have been able to find out, the formation of these adventitious buds has never before been observed with *Gnetum Gnemon*, neither in its natural sites, nor in botanic gardens<sup>1)</sup> except at Utrecht. The Utrecht Garden possesses three specimens of *Gnetum Gnemon*. One of these has been continually cultivated in a hothouse where in winter the temperature is kept at about 25° C., and the air is very damp. The other two were, when I began my investigation, in an other hothouse where the temperature is lower (in winter on an average 15° C.), and the humidity less. Whereas of the former I have always obtained leaves in different stages of bud-formation, the other two showed the phenomenon only after they had been conveyed to the warmer and damper hothouse.

Although all three plants, apart from the formation of adventitious buds, are evidently healthy and do not make a morbid impression

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1) On this point I gained information from the other botanic gardens in our country, from that at Munich and also from that at Buitenzorg.

at all, they flower very rarely. Personally I only observed it with one of the plants from the cooler hothouse. This latter plant produced one single ♂ inflorescence, which enabled me to check the accuracy of the determination.

The first external change, noticed with a leave which will form adventitious buds, is that on the tip extremely small yellow dots appear, which are seen best when light is falling through the leaf. They remind us in this respect of the oil dots in the leaves of the *Rutaceae* or *Hypericum*, but as a rule they are bigger and less densely spread than these.

With the bigger ones a hand-magnifier will show that where the dots are, the epiderm of the upper or lower side or of both together is slightly bulged, so that we have to do with small vesicles.

It will be shown presently that these vesicles are caused by the sting of a scale-insect *Aspidiotus* spec., and as such are not restricted at all to the tip of the leaf. Normally, however, it is only the tip which can form adventitious buds. The remaining part of the leafblade can only form adventitious buds when the organic relation with the tip has been disturbed in some way or other. But even then they arise apically in this part. Hence only the vesicles which have originated on the apical part of a leaf, form the introduction to the process of bud-formation.

For the sake of simplicity we shall in what follows, only mention the tip of the leaf, since the statements referring to the tip also apply to the other cases.

After some time also the region, surrounding the vesicles, becomes discoloured; as a rule the tip of the affected leaf soon becomes distinctly yellow, although in some cases it long keeps a more or less greenish tint.

At the same time with this discoloration the tip of the leaf becomes thicker. This thickening is at first not easy to observe macroscopically; gradually, however, it becomes stronger and at last generally advances so far that the tip becomes stiff and difficult to bend.

Of the yellow vesicles nothing can then be seen any longer.

The extent of this region of discoloration and thickening varies much in a basal direction; along the edge it generally extends farther basipetally than in the middle; always, however, the phenomenon is restricted to the apical part of the leaf. A new stage sets in, when the surface of the thickened leaf-tip which until now had remained smooth, on account of the swelling being even, becomes uneven: as well on the lower as on the upper surface this may as a rule be observed; on the upper surface it is generally more pronounced.

During the first weeks generally no striking changes are observed until after about a month a varying number of local elevations, yellow like the leaf-tip that produces them, becomes prominent and reveals the differentiation of special proliferating centres.

As a rule we see these grow to real knobs, especially in the direction perpendicular to the surface of the leaf.

While the knobs are still relatively small, brownish grey streaks begin to appear on their tops, which gradually extend, so that finally the whole knobbed surface becomes brown.

For some time such a knob shows nothing particular, except that it becomes larger and thicker. Next on a certain day a small opening is formed in its top, through which a small green point projects, which will grow out into a leafed sprout.

As well on the lower as on the upper surface of the leaf-tip knobs may form. Mostly they form on the upper surface, though. With some leaves I have observed knobs on both sides at the same time.

The observations on the time, needed by a leaf in order to form "ripe" knobs, after the yellow vesicles have appeared, have led to somewhat diverging results. The shortest period was observed with leaves on the upper branches or in the periphery of the crown, which consequently occupied the most favourable position with regard to light. On these good-sized, brown knobs had generally formed half a year after the appearance of the yellow vesicles.

Also for the question, how old and how large a knob must be in order to open and give the adventitious bud an opportunity for sprouting, no rule can be fixed. I saw one sprout five weeks after the knob had first been observed as a special elevation, while others were still closed after five to seven months.

About the size of the knobs we may state that some knobs, scarcely rising more than a millimetre above the surface of the leaf-tip, opened, while others of double and even treble the height remained obstinately closed. Yet these latter contain as well an adventitious bud and not seldom even more than one.

The microscopical investigation was for the greater part carried out on microtome preparations. For fixing the material I used the mixture: zincchloride-glacial acetic acid-alcohol, (2 grams of zincchloride and 2 ccm. of glacial acetic acid to 100 ccm. of alcohol of 45—50 pCt), recommended by JUEL<sup>1)</sup>. The particular hardness of

<sup>1)</sup> H. O. JUEL, Ueber den Pollenschlauch von Cupressus. (Flora. Bd. 93. 1904. pag. 56—62).

the leaf tissue made it necessary to treat the material, before being embedded in paraffin, during 3 to 4 × 24 hours with a 40 pCt. aqueous solution of hydrofluoric acid. After this treatment it was then washed for 8 to 10 hours in streaming water, dehydrated by the usual method and after treatment with chloroform embedded in paraffin (melting point 62° C.).

For staining the sections I used at first Haematoxylin-Delafield and saffranin, according to the prescriptions given in CHAMBERLAIN'S "Methods in Plant Histology" <sup>1)</sup>; but this method proved unsatisfactory for differentiating the very thin-walled meristem cells. Therefore I afterwards always stained with methyl green and acid fuchsin <sup>2)</sup>, by which very good results were obtained.

A consequence of the treatment with hydrofluoric acid was that the microtome preparations were not suitable for all observations. In these cases I used hand-cut preparations, if necessary stained with Haematoxylin-Delafield.

The anatomy of the normal leaf, on which something may be found in literature with BERTRAND <sup>3)</sup>, DE BARY <sup>4)</sup>, SCHEIT <sup>5)</sup> and HABERLANDT <sup>6)</sup>, is as follows.

The epiderm of the lower and upper surface consists of relatively small, cubical cells, the outer wall of which is strongly thickened and provided with a strong cuticle and from which capriciously shaped and canaliculate outgrowths project into the lumen of the cell. (cf. BERTRAND, l. c. Pl. II fig. 6, 7, 8.). In the epiderm of the lower side numerous, irregularly placed stomata are found.

Under the upper epiderm lies the palissade parenchyma, formed by one continuous row of cells, slightly elongated in the direction perpendicular to the leaf surface. (dimensions 13—21  $\mu$  by 21—30  $\mu$ ). Between the palissade cells and the lower epiderm lies the spongy parenchyma, consisting of tubular cells, the diameter of which is on the average 18  $\mu$ , as a rule is not more than 9  $\mu$  at a partition wall between two tubes and does not reach more than 28  $\mu$ . Between the cells of the spongy parenchyma remains a system of large inter-

<sup>1)</sup> C. J. CHAMBERLAIN, Methods in Plant Histology 2nd ed Chicago. 1905. pag. 30, 38 and 54.

<sup>2)</sup> CHAMBERLAIN. l. c. p. 40, 44 and 68.

<sup>3)</sup> C. E. BERTRAND, Anatomie comparée des tiges et des feuilles chez les Gnétacées et les Conifères. (Annales d. Sc. nat. Botanique 5<sup>ème</sup> série Tome XX. 1874).

<sup>4)</sup> A DE BARY. Vergl. Anatomie der Vegetationsorgane der Phanerogamen und Farne. (Handb. der Physiol. Botanik von W. HOFMEISTER. Leipzig. 1877.)

<sup>5)</sup> M. SCHEIT, Die Tracheiden-Säume der Blattbündel der Coniferen etc. (Jenaische Zeitschr. f. Naturw. Bd. XVI. Neue Folge Bd. IX. 1883.)

<sup>6)</sup> G. HABERLANDT, Physiologische Pflanzenanatomie 2te Aufl. Leipzig. 1886

cellular spaces. In the spongy parenchyma numerous thick-walled sclerenchyma fibres are found, which are generally ramified and often have an enormous length.

A section through a leaf-tip on which yellow vesicles are found, shows that these vesicles are caused by hypertrophy of cells of the spongy parenchyma which have there entirely lost their tubular shape and among which specimens are found, measuring 91 by 109  $\mu$ , 100 by 73  $\mu$ , 100 by 113  $\mu$  etc. Among the cells, constituting the vesicle, some are always found which in unstained preparations are conspicuous by their wall being more or less swollen and brown. In preparations, treated with acid fuchsin and methyl green, the wall of these cells is blue, those of the other cells red. Applying the usual reactions we find that these walls have become suberized. Also of the palissade parenchyma some cells may have become larger, but always in a small degree.

While in the vesicles themselves the process goes a little further still on account of partition walls forming in some of the enlarged cells, whose walls have not become suberized, also the region, surrounding the vesicles, evidently answering to a stimulus, proceeding from them, begins to undergo similar changes. Macroscopically we detect this by the more or less yellow tint, assumed by the vicinity of the vesicles. A microscopical examination of the section shows that now also outside the vesicles the cells of the spongy parenchyma are hypertrophical. As with the formation of the vesicles the chlorophyll is disorganised in the hypertrophical cells.

At this stage no function of importance may be ascribed yet to the cells belonging to the palissade parenchyma.

In most preparations now already the peculiar behaviour is noticed of those spongy parenchyma cells which border immediately on the palissade parenchyma. While the other cells of the spongy parenchyma swell as evenly as possible in all directions, those which lie immediately below the palissade parenchyma become enlarged especially in a radial direction, thus making the impression of a second layer of palissade cells. Since also in later stages they will repeatedly draw our attention, I shall in what follows call these cells subpalissade cells, instead of using the cumbersome longer definition.

This extension, especially in a radial direction, of the subpalissade cells, is illustrated by the following two tables.

A Subpaliss. cells of a normal leaf-tip	Height $\mu$ : 16	16	14.5	18	14.5	16	14	14.5	14.5	22
	Breadth $\mu$ : 31	18	16	25.5	27	27	18	25.5	31	31
B Subpaliss. cells of a yellow leaf-tip	Height $\mu$ : 33	26	38	44	47	42				
	Breadth $\mu$ : 31	29	18	31	33	33				

In a leaf-tip which macroscopically is distinguished, besides by the yellow colour, by a distinct thickening, the intercellular cavities of the spongy parenchyma are found to have entirely disappeared, excepting a small corner here and there. The mutual pressure which the cells consequently begin to exert on each other, causes them to assume a more polygonal shape. The cells, bordering on the subpalissade cells and often also the rows, turned towards the lower epiderm, show a tendency to stretch themselves in a direction perpendicular to the surface of the leaf. In many spongy parenchyma cells partition walls have formed.

The part, played by the subpalissade cells in the process of thickening, is generally a very important one. So I found in a leaf-tip in a place, where it was 332  $\mu$  thick (the section of a normal tip is on the average 170  $\mu$ ), cell rows, formed of subpalissade cells, partitioned by two or three walls and measuring 90, 110, 115 and 127  $\mu$  in height. — The palissade rows were in these places not sensibly enlarged.

That the different tissues also in the same leaf-tip do not everywhere play the same part in the process of thickening, appears from the following figures, from measurements in two different places of the same leaf-tip;

Height of the palissade cells.	36 to 45 $\mu$ } most cells with 2 or 3 partitions	27 $\mu$ non-partitioned.
Height of the subpaliss. cells.		
Height of the spongy parench.	273 $\mu$ .	273 $\mu$ .

The special thickened outgrowths, mentioned on page 3, are caused by the same processes of proliferation which cause the thickening of the whole leaf-tip, and which in some places go on with particular activity, while the surrounding region seems to come to rest.

On the upper surface they are formed by locally strong proliferation of the subpalissade cells. Sometimes also the underlying cells, originating from the spongy parenchyma contribute to them and then it cannot be ascertained as a rule what part is derived from the subpalissade cells and what from the original spongy parenchyma. In most cases the contribution of the palissade parenchyma to the formation of the special elevations is rather unimportant.

The special thickenings on the lower surface of the leaf are entirely formed by cells which genetically belong to the spongy parenchyma but for the rest in exactly the same way as those on the upper surface. Since the cells from which they are built up, divide parallelly to the surface of the leaf and the so-formed division-

cells stretch themselves again, these special thickenings, which at first appear as small unevennesses, grow out into the knobs, already mentioned on p. 3.

How has the epiderm been able to follow the increase of surface, accompanying these thickening processes?

In a normal leaf-tip we find for the dimensions of the epiderm cells 9 to 18  $\mu$  height and 9 to 29  $\mu$  breadth, while in the epiderm, covering a special thickening, amidst cells of normal dimensions others are found which measured :

Height $\mu$ :	9	11	13	13	13	9	11	11	9	9
Breadth $\mu$ :	31	36	45.5	36	49	45.5	45.5	42	54.6	45.5

Hence some epiderm cells seem really to broaden; whether this is only an extension or active growth, I dare not decide.

Besides, the epiderm soon gives way and is rent. Like the part of the epiderm which gives way to the pressure, some cells of the tissue underneath die off, the cell-walls turning brown. In this way arise the brown streaks on the surface of the knobs which finally by extension in tangential direction of this suberizing process becomes entirely brown. A special suberizing meristem, a phellogen, is not formed.

The regular structure of these cell-hills is lost as soon as the differentiation of a meristem commences. Some cells, assembled in a small group, then enter a new stage of strong growth, which makes them conspicuous in the preparations by a more rounded form amidst the adjoining cubical cells. A number of the surrounding cells are compressed by the pressure which these primordial cells cause by their growth, and die.

Soon the primordial cells divide into a number of small filial cells with extremely thin walls and dense contents, after which the primordium has become meristem.

For answering the question in what place in a knob the meristem is formed and what is the descent of the initial cells, we have the following data. An otherwise 415 to 450  $\mu$  thick leaf-tip had by local swelling to about 840  $\mu$ , formed a knob, which by a small depression in the middle was, so to speak, divided into two halves, each of which contained a primordium of a meristem. The surface of the knob was entirely suberized to a fairly considerable depth. In one half the primordium lay 220  $\mu$  below the top of the knob and its cells in all probability descended from the subpalissade cells, in the other half the primordium lay 180  $\mu$  below the surface and was of the same origin as in the former case.

While in another case a primordium was noticed which genetically belonged to the original spongy parenchyma I found in a small knob which was still covered by an intact epiderm, and did not rise more than 85  $\mu$  above its surroundings, and in this case had been formed by special proliferation of the palissade parenchym, a distinct young meristem immediately below the epiderm. *The epiderm cells themselves however, did not take part in the formation of the meristem.*

In a word, meristem formation may take place as well by cells, descending from the spongy parenchyma and the subpalissade cells, as from such as have been formed by hyperplasia of the palissade parenchyma, the epiderm, however, plays no part. In other words: *the adventitious buds on the leaves of Gnetum Gnemon are endogenic formations.*

In the beginning the young meristem increases in size by its own active growth as well as by new cells from the immediate vicinity becoming meristematic.

When the meristem has reached certain dimensions, it partly becomes loose from the surrounding tissue. This is brought about by some of the cells, forming the transition between the meristem and the surrounding tissue, being dissolved and resorbed.

This dissolution process proceeds along the whole upper side of the meristem, so that the growing point of the adventive bud comes to be placed in a slit-shaped space.

The greater the depth at which the meristem was originally formed inside the knob, the thicker is the layer of tissue which ultimately separates the bud from the outer world and the further the development within the enclosure proceeds. This explains how it is possible that knobs, no larger than 1 millimetre, open, while much larger ones remain persistently closed.

The appearance of two meristems within the same knob is a very common occurrence; once I found as many as four meristems in one knob.

The buds assume a green colour while they are still entirely enclosed within the knob and hence must have the power, like the germinating plants of Ephedra and the Coniferae, to form chlorophyl independent of light.

The sprouts growing out of the adventitious buds always remain short and tender. The biggest I observed reached a height of about 3,5 centimetres and consisted of a stem with 5 internodes (including the basal part) of which the upper one reached the greatest length (almost 2 centimetres), while the leaflets on the last node became

largest (about 3 cms. long). The position of the leaves is alternating, the innervation of the leaf the typical one for *Gnetum Gnemon*<sup>1)</sup>. The leaflets on the first node as a rule remain scale-shaped; in some cases, however, they develop to leaflets, differentiated into stalk and blade.

Although in the axils of the leaflets axillary buds are certainly formed, I never saw the adventitious sprouts ramify themselves, except in a single case, when, as I surmise, of the basal piece of an adventitious sprout the terminal bud did not develop for some reason or other, and instead the buds in the axils of the scale-leaves sprouted.

On a differentiation of histogens at the vegetative cone I have not been able to form a definite opinion from my preparations of adventitious sprouts.

The numerous attempts which I made, in order to induce the adventitious sprouts to produce roots, have all failed. This agrees with the circumstance that in my preparations I have never been able to discover anything that resembled root-formation. The sprout-carrying leaves which had been planted in wet sand did not form roots either. As far as I know formation of adventitious roots does not occur at all with *Gnetum Gnemon*.

A connection between the vascular system of an adventitious sprout and the nerve system of the mother leaf is established by procambial bundles, formed by cells of the tissue, situated between the meristem and a leaf bundle.

As a rule we find as the first indication of this vascular bundle connection in the immediate vicinity of very young meristems even, some tracheids and cells, changing into them. The degree of development, reached at a certain moment by this vascular bundle connection, is not directly dependent on the degree of development of the adventitious bud in question, but seems to me to stand in close relation to the distance between meristem and leaf bundle and to the diameter of this latter. When a complete connection has been established we see the vascular bundles of the adventitious sprout within the knob in which the bud has formed, bend towards each other and unite with a more or less cylindrical group of locally formed vessels and tracheids, the ramifications of which are connected with the vascular bundles of the mother leaf.

When describing the changes, macroscopically observed with a

<sup>1)</sup> Viz. Nr. 3 of the leaf nervations, distinguished by KARSTEN for the species of *Gnetum* [G. KARSTEN, Untersuchungen über die Gattung *Gnetum*. I. (Ann. du Jardin Bot. de Buitenzorg Volume XI. 1893. p. 195—218)].

leaf in which adventitious buds are forming, it has already been briefly stated that the yellow vesicles, initiating the process of bud-formation, are caused by a scale-insect, *Aspidiotus* spec.

That suspicion fell on this *Aspidiotus* had a very simple reason.

Although not nearly all the leaves, showing yellow vesicles, carried scale-insects, yet the reverse was generally true and it soon became apparent that the leaves, carrying scale-insects generally also had some yellow vesicles.

But unexpected difficulties were experienced when it was attempted by means of microtome preparations to obtain certainty and a clearer insight in what had been rendered probable by macroscopical observation. A great difficulty was that the majority of the insects refused to stick to the bits of leaf from which the microtome preparations were going to be made. While a great part already loosed their hold during the treatment preceding the embedding itself, their example was followed by most others when they were put into the melted paraffin. It was supposed that perhaps the reason of this was that the scale-insects, when coming into the fixing solution, withdrew their suction organ from the tissue of the leaf, possibly on account of a pre-mortal reactional movement. After this unfavourable result the leaves carrying the insects were always treated before fixation with an anaesthetic, namely aether. This precaution, however, did not materially improve the results.

Among the microtome preparations which I obtained in spite of these difficulties, there is not a single one in which a scale-insect may be seen in a sucking position. But always in the places where an insect was on the leaf, in the tissue the changes were found which we described as characteristic for the yellow vesicles.

Here also hypertrophy, accompanied by disorganisation of the chlo-rophyll, of cells, belonging to the mesophyl; some of these cells have brown walls. Also in the epiderm on which the scale-insect is found, some cells are found, the walls of which are suberized and which besides are sometimes slightly swollen.

I was more fortunate with hand-made preparations, some of which show the suction apparatus of the scale-insect inside the leaf tissue. From these we see that in the yellow vesicles those cells, the wall of which has become suberized, have been in direct contact with the suction apparatus of the scale-insect and that the other cells, which become hypertrophical, only react to a stimulus, exercised by the wounded cells. On the character of this stimulant action we shall speak presently.

That here the enlargement of the cell should take place at the

expense of its own contents, as is stated for many similar hypertrophical processes, is not the impression I received. Although in many of the very strongly hypertrophical cells a large central vacuole may be observed, yet I saw nowhere reduction of the protoplasm to a very thin wall-lining. The nucleus does not show any deviation and the cell-wall does not become perceptibly thinner.

That the sting of the scale-insect not only causes the formation of the yellow vesicles but through them also all further changes, including the formation of the adventitious buds, has become clear to me by :

1. the microscopical examination of a very large number of preparations, relating to these stages;

2. the continued observation of a number of leaves on the tree, showing that those leaves on which scale-insects or the yellow vesicles caused by them, were seen, underwent the above described changes, while the control leaves remained free from them. On Sept. 13, 1906, the top of that plant which forms adventitious buds most strongly and one of its branches were each surrounded by a muslin balloon, after they had first been carefully inspected and cleaned. These balloons were supported by skeletons of galvanised iron wire and closed below by pulling them on to a pad of cotton wool, placed round the sprout. At the top of the plant were then only young leaves, on the branch full-grown ones, all of them free from scale-insects and vesicles. The balloon, surrounding the top of the plant had repeatedly to be replaced by a bigger one as the top grew.

On January 22, 1907, the balloon was removed from the branch and the leaves were examined. Of two of these leaves the extreme part of the top had turned yellow. A microscopical examination of these leaf-tips showed, however, that here was no initial stage of bud-formation. Hypertrophical cells, such as we ought to have found in this case in the mesophyl, were not present. The yellow colour was caused by the dying of the tissue, the cell-contents then discolouring.

On May 10 the top of the plant was liberated. A number of full-grown leaves which at the beginning of the experiment were still young and young leaves at lateral sprouts which during the isolation had been formed by sprouting of the axillary buds, were now seen. All these leaves were perfectly normal, healthy and strong with a normal green colour; on none of them anything could be detected of yellow vesicles or spots, of none the top showed any discoloration or thickening. The isolation by means of the muslin balloon

had not hindered these leaves at all in their normal development. Only scale-insects and other animals had been prevented from settling on the leaves with the formerly described result.

Similar tumours as the yellow, thickened leaf-tips of *Gnetum Gnemon* really are, have also been repeatedly observed with other plants and described under the name of "yellow specks" (Gelbfleckigkeit), oedemata or intumescences. The word "Intumescencia" was introduced into phytopathological nomenclature by SORAUER with the definition <sup>1)</sup>: "Intumescencia" sind "diejenigen Erscheinungen, die das gemeinsame Merkmal haben, als kleine knotchenförmige oder drüsige Auftreibungen der Blätter aufzutreten, die meist an diesen Stellen gelb verfarbt erscheinen und eine aussergewöhnliche Zellstreckung ohne wesentliche Zellvermehrung zeigen". That the thickened leaf-tips of *Gnetum Gnemon* are not indeed "kleine Auftreibungen" and do present "wesentliche Zellvermehrung" need not necessarily prevent us from counting them among the intumescences, since as well very large <sup>2)</sup> or mutually coalescent <sup>3)</sup> as typically hyperplastic <sup>4)</sup> intumescences have been described for other plants.

We cannot now deal with the very divergent views of different investigators about the cause of the formation of intumescences; we will only mention that in most cases it has been stated that a high temperature and great humidity of the air are essential factors.

Experiments enabled me to form an idea about the character of the stimulus exerted by the scale-insects on the tissue of the leaf of *Gnetum Gnemon*, on which the formation of the intumescences is the reaction. After I had tried artificially to produce intumescences in leaves by mechanically wounding them in all sorts of ways and treating them with poisons, without obtaining the desired result, I arrived at the conclusion that either my method of wounding, compared with that of the scale-insects, was too coarse or that the insect injected some stimulating substance into the leaf. In order to settle these points the following experiments were carried out: 1). In

<sup>1)</sup> P. SORAUER, Die symptomatische Bedeutung der Intumescenzen (Bot. Zeitg. 48 Jahrg. 1890. p. 241).

<sup>2)</sup> H. v. SCHRENK, Intumescences formed as a result of chemical stimulation. (Missouri botan. garden. 16<sup>th</sup> ann. report. 1905. p. 125).

<sup>3)</sup> Miss G. E. DOUGLAS. The formation of intumescences in potato plants. (Bot. Gazette Vol XLIII. 1907. p. 233.)

<sup>4)</sup> E. KUSTER, Über experimentell erzeugte Intumescenzen. (Ber. deutsch. bot. Ges. Bd. XXI. 1903. pag. 452). P. SORAUER, Ueber Gelbfleckigkeit. (Forsch. a. d. Geb. d. Agrik. Phys. h. v. Dr. E. WOLLNY. Bd. IX. 1886. pag. 387). and Intumescenz bei *Solanum floribundum*. (Zeitschr. f. Pflanzenkrankh. Bd. VII. 1897. p. 122).

the leaf-tips extremely small wounds were made by means of the sterilised, very fine point of an injection syringe. 2). The same was done after the point had first been stuck into yellow vesicles, caused by the scale-insects. 3). A number of yellow and thickened leaf-tips were ground in a mortar and a very small portion of the so obtained pulp, mixed with some diluted glycerin, injected in several places in leaf-tips. 4). The same operation as in 3 was applied after the pulp had first been heated to 100° C.

The result was exactly the same in *all* cases.

After some ten days small, brown specks were visible in the wounded places, which afterwards could still increase somewhat in size. A month after the wounding the brown specks had become surrounded by a very thin, more or less transparent, yellow margin. The brown specks were formed by the cells which had died in consequence of the wounding, and the walls of which had turned brown. In the yellow margin a complex was found of relatively small cells, leaving no intercellular cavities. These cells had thick walls and their protoplast still contained remnants of the chlorophyl grains. The complex was formed by hyperplasia of the whole mesophyl. On the border between this complex and the normal tissue some cells of the spongy parenchyma had become greatly enlarged, their chloroplasts having become disorganised. After another month it was noticed that the leaf-tips in the neighbourhood of the wounded spots assumed a somewhat yellow colour, which gradually became more and more distinct. Microscopically it could be stated that where externally this yellow discoloration was visible, the tissue round the wounded spots had undergone precisely the same changes as take place round the yellow vesicles, caused by the scale-insects, namely a general hypertrophy of the cells of the spongy parenchyma, while here and there even a partition wall had already been formed in the enlarged cells.

As was stated above, this result was obtained in all cases, also in those in which small wounds had been made without anything else. From which we may conclude that the leaf of *Gnetum Gnemon* may be stimulated to the formation of intumescences and hence of adventitious buds by wounding, provided this is very light and that consequently the process must be regarded as a reaction on a *wound stimulus*.

In a disease of carnations which also consists in the formation of a sort of intumescences<sup>1)</sup> and for which it has been shown by

<sup>1)</sup> H. v. SCHRENK 1, c. p. 39.

WOODS<sup>1)</sup> that it is caused by the sting of aphides, among others, WOODS thinks the growth of the yellow, thickened spots must be ascribed to the diffusion of an irritant, injected by the insect<sup>2)</sup>.

That a similar hypothesis is superfluous for the "stigmonose" of *Gnetum Gnemon*, appears clearly enough from our experiments. The specific point about the wound, made by the suction organ of the scale-insect is only that it is so trifling. Only a few cells, namely those which are distinguished in the yellow vesicles by brown walls, have undergone the direct consequences of it, while the whole subsequent formation of the intumescences takes place as a reaction on the stimulating action, proceeding from these few wounded cells.

KÜSTER<sup>3)</sup> calls all cataplasms after vulneration, as far as they have a parenchymatical character, callus. According to this terminology also the tissue of which the thickened leaf-tips of *Gnetum Gnemon* consist, is a "callus" and the buds, formed in them, are callus-buds<sup>4)</sup>.

Why the two plants from the cooler hothouse did not form callus or buds on their leaves, is now also clear. The *Aspidiotus*, playing such an important part in this formation of callus, is also found in the cooler hothouse; but for callus-formation the chief condition is humidity. This condition was only to some extent fulfilled by the cooler, but completely by the hotter house, while also the higher temperature in this latter could not but favour the formation of callus with these tropical plants.

Why only the apical part of a leaf is capable of forming callus and buds, may be explained in the following manner. The small wound causes an afflux of nutrient matter in an apical direction. If now an accumulation of this matter, which is necessary for the hyperplastic formation of callus, shall be possible, the afflux must not be able to pass by, i.e. it must be stopped apically of the wound. And this condition is normally only fulfilled in the tip of the leaf, in another part of the blade only when the organic relation with the tip has been disturbed.

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<sup>1)</sup> A. F. WOODS, Stigmonose: a disease of carnations and other pinks. (Bull. no. 19. U. S. Dept. Agr. Div. Veg. Phys. and Path. 1900).

<sup>2)</sup> l. c. p. 24.

<sup>3)</sup> E. KÜSTER, Pathologische Pflanzenanatomie. Jena. 1903. p. 154.

<sup>4)</sup> See also: E. KÜSTER, Histologische und experimentelle Untersuchungen über Intumescenzen. (Flora oder allgem. bot. Zeitg. 96 Bd. 1906, p. 527—537).

**Crystallography.** — “*The system of crystallization of the diamond*”

by Mr. A. L. W. E. VAN DER VEEN, candidate mining engineer.

(Comm. by Mr. MOLENGRAAFF).

(Communicated in the meeting of June 29, 1907).

There still exists some doubt about the system of crystallization of the diamond. Although the tetrahedral hemihedrism of the diamond is pretty generally accepted, still the opinion that it belongs to the regular system, also finds support.

The existing uncertainty is caused by the lack of physical research with regard to this question. Such a research into the existence or non-existence of polarity of the trigonal axes has now been made. With that object in view the trigonal axes of the diamond were tested for pyro-electricity according to P. P. KOCH's method<sup>1</sup>). Tourmaline, boracite and quartz, which evinced strongly pronounced pyro-electrical characteristics, were used as testminerals. The result arrived at is absolutely negative. The diamond is not pyro-electric, and the trigonal axes do not possess polarity.

Besides, researches were made into the crystalline form of the diamond out of a collection of 367 uncut diamonds collected by Mr. MOLENGRAAFF. Practically all types of crystallization were represented here, to explain which tetrahedral hemihedrism for the diamond had been accepted in numerous writings of GROTH, SADEBECK, MARTIN and others. The result of this investigation, which is not yet at an end, is that a rational explanation of all irregular and apparently tetrahedral-hemihedral crystalline forms of the diamond can be found in the peculiar octahedral lamellar structure of the diamond.

On this ground it may be accepted that the diamond crystallizes in the holohedral division of the regular system.

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<sup>1</sup>) P. P. KOCH, Ueber eine neue Methode zur Untersuchung auf Pyroelektricität. Inaug. Dissert. München, Mainz 1902.

**Physics.** — “*Contribution to the theory of binary mixtures. VI. The plaitpoint line.*” By Prof. J. D. VAN DER WAALS.

Continued. See p. 123.

By the plaitpoint line we understand the continuous series of points, in which the mixture is in the plaitpoint state. If we think the points of the surface of saturation determined by the coordinates  $T$ ,  $p$  and  $x$ , then the plaitpoint line is a curve lying on this surface, and its projections on the planes of coordinates are expressed by:  $p = f_1(T)$ ,  $p = f_2(x)$  and  $x = f_3(T)$ . If the surface of saturation is given by the coordinates  $T$ ,  $v$  and  $x$ , its projections have the form:  $v = f_4(T)$ ,  $v = f_5(x)$  and  $x = f_3(T)$ . The two surfaces of saturation mentioned may be derived from each other by the aid of the relation  $p = \varphi(x, v, T)$ . If we have the first mentioned surface, the substitution of  $p$  leads to the second. However, we might also have eliminated  $T$ , and obtained a surface of saturation of the form  $F(p, v, x) = 0$ , also one of the form  $F_1(p, v, T) = 0$ . A point of saturation being determined and known in all respects if the 4 quantities  $T$ ,  $x$ ,  $v$ , and  $p$  are known and the equation of state giving a relation between these 4 quantities, we may imagine as many surfaces of saturation as the number of combinations of 4 quantities three and three. The number of projections of the plaitpoint line is then the number of combinations two and two. For the direction of the projections  $\frac{dT}{dx}$ ,  $\frac{dp}{dx}$ ,  $\frac{dv}{dx}$ ,  $\frac{dp}{dT}$ ,  $\frac{dp}{dv}$ , and  $\frac{dv}{dT}$  present themselves for consideration, which of course, are not independent of each other.

The best known shape of the plaitpoint line is that for which the initial point lies in the critical point of the first component, and the final point in the critical point of the second component.

In this case there is a point in which the plaitpoint line begins, and another in which it terminates; but such initial and final points lie necessarily in such places as are to be considered as natural boundary points. Thus initial and final points might also occur for boundary volumes ( $v = b$ ) — but a plaitpoint line can never have an initial or final point for arbitrarily chosen value of  $v$  and  $x$ . Thus in the case that there is minimum or maximum  $T_k$  the mentioned well-known shape of the plaitpoint line will, it is true, make its appearance only in a certain point with gradual increase or decrease of the temperature for certain definite value of  $T$  — but such a point is then necessarily a double plaitpoint, and the plaitpoint line itself retains its character of continuous series of points; the double

plaitpoint mentioned is then an homogeneous double plaitpoint. If then in the  $v, x$ -projection the plaitpoint line is drawn, it proceeds again continuously from the left to the right side -- and this continues to be the case also when the plaitpoint line mentioned has more intricate properties, e. g. when there are two heterogeneous double plaitpoints, as discussed in "Contribution etc." and also treated in These Proc. March 25, 1905, p. 621 and These Proc. June 24, 1905, p. 184. However, besides this plaitpoint line, another is possible. The latter does not cross from the left side to the opposite side. So only the possibility is left either that it is a closed curve in the  $v, x$ -projection, or that it begins and terminates on the borders  $v = b$ .

We shall proceed to discuss some properties of the special points of this line, particularly of the double points of this line. KORTEWEG has demonstrated that these double points are of two kinds. Either it is a double point in which two homogeneous plaitpoints originate or coincide -- or it is a double point in which this is the case for two heterogeneous plaitpoints. Though physically such plaitpoints bear such different characters -- mathematically they satisfy the same criteria, and on the plaitpoint line such an heterogeneous double point is the transition point for a series of plaitpoints which might be realized, and for a series of unrealisable plaitpoints.

*Minimum or maximum temperature for the plaitpoint line.*

If we suppose a double plaitpoint to originate or to disappear on the  $\psi$ -surface at a certain value of  $T$ , two plaitpoints are found at somewhat higher or lower value of  $T$ . This holds both for the case that the double point is an homogeneous and an heterogeneous double point, as we shall briefly call them. For the plaitpoint line  $\frac{dT}{dx}$  and  $\frac{dT}{dv} = 0$  in this case. But for an homogenous double point  $\frac{dT}{dp}$  is also  $= 0$ . This property follows from the shape of  $\frac{dp}{dT}$ , which has been derived in Verslag Kon. Ak. v. Wet. Deel IV p. 20 and p. 82 because  $\frac{d^2v}{dx^2_p} = 0$  in an homogeneous double point (Contribution etc. These Proc. March 30, 1907, p. 745). For an heterogeneous double point  $\frac{dT}{dp}$  is not equal to 0, as also appears from the value given for  $\frac{dp}{dT}$ , as for such a double point  $\frac{d^2v}{dx^2_p} = 0$ , but  $\frac{d^2v}{dx^2_p} = \frac{d^2v}{dx^2_q}$ . That in an heterogeneous

double point  $\frac{dT}{dp}$  is not equal to 0, is also immediately seen when we consider that for such a point also  $dp = 0$ , and  $\frac{dT}{dp}$  appears therefore in an indefinite form, the value of which we shall presently determine. Hence  $\frac{dv}{dx} = \left(\frac{dv}{dx}\right)_p$  for such a double point, which is not the case for an homogeneous double point.

Of the 6 differential quotients which come in for discussion, three are equal to 0 for an homogeneous double point, and three are left the value of which is still to be determined, viz.  $\frac{dv}{dx}$ ,  $\frac{dv}{dp}$  and  $\frac{dp}{dx}$ .

If we write:

$$\frac{dv}{dx} = \frac{\frac{dT}{dx}}{\frac{dT}{dv}}$$

$$\frac{dv}{dp} = \frac{\frac{dT}{dp}}{\frac{dT}{dv}}$$

and

$$\frac{dp}{dx} = \frac{\frac{dT}{dx}}{\frac{dT}{dp}},$$

in all these three expressions both numerator and denominator is equal to 0. If in the first we differentiate numerator and denominator with respect to  $x$ , in the second with respect to  $v$ , and in the third with respect to  $p$ , we find:

$$\frac{dv}{dx} = \frac{\frac{d^2T}{dx^2}}{\frac{d^2T}{dv^2} \frac{dv}{dx}}$$

$$\frac{dv}{dp} = \frac{\frac{d^2T}{dp^2} \frac{dp}{dv}}{\frac{d^2T}{dv^2}}$$

and

$$\frac{dp}{dx} = \frac{\frac{d^2 T}{dx^2} \frac{dx}{dp}}{\frac{d^2 T}{dp^2}}$$

or

$$\left(\frac{dv}{dx}\right)^2 = \frac{\frac{d^2 T}{dx^2}}{\frac{d^2 T}{dv^2}}, \quad \left(\frac{dv}{dp}\right)^2 = \frac{\frac{d^2 T}{dp^2}}{\frac{d^2 T}{dv^2}} \quad \text{and} \quad \left(\frac{dp}{dx}\right)^2 = \frac{\frac{d^2 T}{dx^2}}{\frac{d^2 T}{dp^2}}$$

We may verify these properties by writing for the immediate neighbourhood of the minimum or maximum plaitpoint temperature

$$T = T_1 \pm \alpha (x - x_1)^2 = T_1 \pm \beta (v - v_1)^2 = T_1 \pm \gamma (p - p_1)^2,$$

in which the sign + holds for minimum value of  $T$ , and reversely the sign - for maximum value.

From this follows:

$$\alpha (x - x_1)^2 = \beta (v - v_1)^2 = \gamma (p - p_1)^2,$$

or

$$\pm (x - x_1) \sqrt{\alpha} = \pm (v - v_1) \sqrt{\beta} = \pm (p - p_1) \sqrt{\gamma},$$

and

$$\frac{dv}{dx} = \pm \sqrt{\frac{\alpha}{\beta}}, \quad \frac{dp}{dv} = \pm \sqrt{\frac{\beta}{\gamma}} \quad \text{and} \quad \frac{dx}{dp} = \pm \sqrt{\frac{\gamma}{\alpha}}.$$

As  $\frac{dv}{dx} \times \frac{dp}{dv} \times \frac{dx}{dp} = +1$ , we have to take all the signs positive, or one positive and two negative. Thus in the case that there is minimum or maximum plaitpoint temperature, and we choose the direction of  $x$  such that  $\frac{dx}{dp}$  is positive,  $\frac{dv}{dx} > 0$  and  $\frac{dp}{dv} < 0$ , and so also  $\frac{dp}{dx}$  negative. It is, however, not always the case that  $\frac{dp}{dv}$  is negative.

Thus for a plaitpoint line with maximum value of  $p$ ,  $\left(\frac{dp}{dT} = 0\right)$  also  $\frac{dp}{dx} = 0$  and  $\frac{dp}{dv} = 0$ . So in such a case reversal of the sign of  $\frac{dp}{dv}$  must take place.

If we examine the criteria for an heterogeneous double point, we have in the first place  $\frac{dT}{dx} = 0$  and  $\frac{dT}{dv} = 0$ . Then  $\frac{dT}{dp}$  is not equal to 0. But in its stead there are two other differential quotients which

are equal to 0. From  $\frac{dp}{dT} = \frac{dp}{dx} \frac{dx}{dT}$  follows, if we take into consideration that  $\frac{dp}{dT}$  has a finite value, and  $\frac{dx}{dT} = \infty$ , that  $\frac{dp}{dx}$  must be  $= 0$ , and also  $\frac{dp}{dv} = 0$ . That  $p$  has maximum or minimum value in the case of an heterogeneous double point has already been represented by us in a drawing. (These Proc. March 25, 1905, p. 621, and June 24, 1905, p. 184). So of the 6 differential quotients for the projections of the plaitpointline 4 are zero. Two are left whose value is to be determined, viz.  $\frac{dp}{dT}$  and  $\frac{dv}{dx}$ .

If we write:  $\frac{dp}{dT} = \frac{\frac{dp}{dx}}{\frac{dT}{dx}}$ , we find by differentiation of numerator and denominator.

$$\frac{dp}{dT} = \frac{\frac{d^2p}{dx^2}}{\frac{d^2T}{dx^2}}$$

If we write:  $\frac{dv}{dx} = \frac{\frac{dT}{dx}}{\frac{dT}{dv}}$ , we find.

$$\left(\frac{dv}{dx}\right)^2 = \frac{\frac{d^2T}{dx^2}}{\frac{d^2T}{dv^2}}$$

What follows may serve as a verification. Let us again write as holding in the immediate neighbourhood of the double point:

$$T = T_0 \pm \alpha (x-x_0)^2 = T_0 \pm \beta (v-v_0)^2$$

and

$$p = p_0 \pm \gamma (x-x_0)^2 = p_0 \pm \delta (v-v_0)^2.$$

For minimum value of  $T$  and  $p$  the positive sign must be chosen, and reversely. So we have the following relations:

$$\alpha (x-x_0)^2 = \beta (v-v_0)^2,$$

and

$$\gamma (x-x_0)^2 = \delta (v-v_0)^2$$

from which

$$\frac{\alpha}{\gamma} = \frac{\beta}{\delta}.$$

Further

$$\frac{T-T_0}{\alpha} = \pm \frac{p-p_0}{\gamma}.$$

In this last equation the sign  $+$  must be chosen, if, as is the case,  $T$  and  $p$  have at the same time either maximum or minimum value. We find then:

$$\frac{dp}{dT} = \frac{\gamma}{\alpha}$$

and

$$\frac{dv}{dx} = \pm \sqrt{\frac{\alpha}{\beta}} = \pm \sqrt{\frac{\gamma}{\delta}}.$$

That this value of  $\frac{dv}{dx} = \left(\frac{dv}{dx}\right)_{p,T}$  follows from the derivation.

So we find a definite value for  $\frac{dp}{dT}$ , and as no lower value of  $T$  exists for minimum value of  $T$ , and no higher value for maximum value, the  $p, T$ -projection of the plaitpoint curve must possess "cusps". That this value of  $\frac{dp}{dT}$  is positive, and so  $p$  and  $T$  are at the same time maximum or minimum, follows inter alia from the equation:

$$dp = \left(\frac{dp}{dv}\right)_{xT} dv + \left(\frac{dp}{dx}\right)_{vT} dx + \left(\frac{dp}{dT}\right)_{vx} dT.$$

For, as  $\frac{dv}{dx} = \frac{dv}{dx_{pT}} = -\frac{\left(\frac{dp}{dx}\right)_{vT}}{\left(\frac{dp}{dv}\right)_{xT}}$ , this equation reduces to:

$$\frac{dp}{dT} = \left(\frac{dp}{dT}\right)_{vx}.$$

*Other special points of the plaitpoint curve.*

It appears from the form for  $\frac{dp}{dT}$  (Versl. Kon. Ak. Deel IV p. 20) that also the case that  $\frac{dp}{dT} = 0$  is possible, and for some mixtures a maximum value of  $p$  in the  $p, T$ -projection has been experimentally

shown. As  $\frac{dp}{dT} = \frac{dp}{dx} \frac{dx}{dT} = \frac{dp}{dv} \frac{dv}{dT}$ , we derive that in this case also  $\frac{dp}{dx} = 0$  and  $\frac{dp}{dv} = 0$ , save in exceptional cases. Then  $p$  is the highest, or the lowest pressure that can occur on the plaitpoint curve. Of the 6 differential quotients 3 are again equal to zero, and 3 others are again to be determined, viz:  $\frac{dx}{dT}$ ,  $\frac{dv}{dT}$  and  $\frac{dv}{dx}$ . We find then from:

$$\frac{dx}{dT} = \frac{\frac{dp}{dT}}{\frac{dp}{dx}}$$

$$\left(\frac{dx}{dT}\right)^2 = \frac{\frac{d^2p}{dT^2}}{\frac{d^2p}{dx^2}}$$

From

$$\frac{dv}{dT} = \frac{\frac{dp}{dT}}{\frac{dp}{dv}}$$

we find:

$$\left(\frac{dv}{dT}\right)^2 = \frac{\frac{d^2p}{dT^2}}{\frac{d^2p}{dv^2}}$$

And from:

$$\frac{dv}{dx} = \frac{\frac{dp}{dx}}{\frac{dp}{dv}}$$

we find:

$$\left(\frac{dv}{dx}\right)^2 = \frac{\frac{d^2p}{dx^2}}{\frac{d^2p}{dv^2}}$$

which may be again verified from the equations:

$$p = p_1 \pm \alpha(T - T_1)^2 = p_1 \pm \beta(v - v_1)^2 = p_1 \pm \gamma(v - v_1)^2$$

For plaitpoint lines which do not run from  $x = 0$  to  $x = 1$ , and which therefore either form a closed figure, or run from a point of

the line  $v = b$  to another point of this line, the value of  $x$  may be maximum or minimum. Then  $\frac{dx}{dT}$ ,  $\frac{dx}{dv}$  and  $\frac{dx}{dp} = 0$ , and the three remaining differential quotients must be determined — and lastly also  $v$  might be maximum or minimum; then  $\frac{dv}{dT}$ ,  $\frac{dv}{dp}$  and  $\frac{dv}{dx}$  would be equal to zero, and  $\frac{dT}{dx}$ ,  $\frac{dp}{dx}$  and  $\frac{dp}{dT}$  would have to be determined.

*Three phase pressure and final point of the three phase pressure on the plaitpoint line.*

If at a certain temperature three phase pressure exists, there must be a hidden plaitpoint on the  $\psi$ -surface, as appears from the foregoing remarks. If the spinodal curve is closed on the side of the small volumes there is moreover a realisable plaitpoint, and there can even be another realisable plaitpoint if the temperature is above the  $T_k$  of one of the components. Let us call  $x_1$  and  $v_1$ ,  $x_2$  and  $v_2$ ,  $x_3$  and  $v_3$  the compositions and volumes of the three phases, assuming the first two to be liquid phases and the third to be a gas-phase, and let us put  $x_2 > x_1$ . Now three cases may occur, viz.:  $x_3 > x_2 > x_1$ ;  $x_3 > x_1 > x_2$  and  $x_2 > x_3 > x_1$ . The first case occurs when the gas phase contains more of the second component than each of the liquid phases, and so when  $\left(\frac{dp}{dx}\right)_{vT}$  is always positive; the second case when the gas phase contains less of the second component, and so when  $\left(\frac{dp}{dx}\right)_{vT}$  is negative, and the third case requires that the line  $\left(\frac{dp}{dx}\right)_{vT} = 0$  runs between the two liquid phases. Of the first case an example may be found in the mixture water in  $\text{SO}_2$ , mixtures of ethane and some alcohols (above methylalcohol) constitute an example of the second case, and of the third case the mixture water and phenol is an example.

As we have an equilibrium which is independent of the size of the volume, when for a mixture of 2 substances there exists equilibrium of 3 phases, the formula of CLAPEYRON may serve for the computation of the value of  $\frac{dp}{dT}$ , and we may put:

$$T \frac{dp}{dT} = \frac{W}{u}$$

if  $W$  represents the heat which is released with decrease of volume when part of the middle phase is converted into the state of the

two other phases, and  $u$  the degree of this decrease of volume. We arrive at the same result if we follow the course (Verslag Kon. Akad. v. Wetensch. Deel V, p. 482) indicated there, viz.:

$$\frac{dp}{dT} = \frac{\begin{vmatrix} 1 & x_1 & \eta_1 \\ 1 & x_2 & \eta_2 \\ 1 & x_3 & \eta_3 \end{vmatrix}}{\begin{vmatrix} 1 & x_1 & v_1 \\ 1 & x_2 & v_2 \\ 1 & x_3 & v_3 \end{vmatrix}} = \frac{(x_1 - x_3)(\eta_2 - \eta_3) - (x_2 - x_3)(\eta_1 - \eta_3)}{(x_1 - x_3)(v_2 - v_3) - (x_2 - x_3)(v_1 - v_3)}$$

We find the same equation when we have three phase equilibrium for a binary system of solid, liquid, and gaseous. And the course of the line  $p = f(T)$  is then known. It is a line, consisting of two branches lying above each other, which smoothly pass into each other at a certain maximum temperature, and the upper branch of which possesses maximum pressure. In this case, however, the course is simpler. For the equilibrium of solid, liquid, and gaseous two branches occur; on one branch the liquid is richer in one of the components than the solid body, and on the other branch the reverse. Where these branches meet, the value of  $x$  has the same amount for the solid body and for the liquid, and in that point the line  $p = f(T)$  has an element in common with the melting-point line. This is seen from the value of  $\frac{dp}{dT}$ , if e. g.  $x_2 = x_3$  is put in it, in

which case  $\frac{dp}{dT} = \frac{\eta_2 - \eta_3}{v_2 - v_3}$ . And it has, therefore, often been stated

as a fixed rule, that when two phases have the same concentration, the variation of equilibrium with the temperature depends only on these two phases, and is independent of the third. Also for equilibrium of 2 liquid phases and one gas phase, however, equality of concentration may occur between two phases. Thus one of the liquid phases may get the same concentration as the gas phase, or the two liquid phases may get the same value of  $x$ . Then the above mentioned rule does not hold. When a solid body has the same concentration as a liquid, and e. g.  $x_2 = x_3$ , then  $\eta_2$  is not equal to  $\eta_3$ , and  $v_2$  not equal to  $v_3$ . Then there are, indeed, two phases of the same concentration, but not two *identical* phases. But when a liquid phase has the same concentration as a gas phase this expression means that in the three phase triangle one of the sides has been reduced to zero, and these two phases have become identical. Then we find

after division of numerator and denominator by  $x_1 - x_3$ :

$$\frac{dp}{dT} = \frac{\eta_1 - \eta_3 - (x_1 - x_3) \left( \frac{d\eta_3}{dx_3} \right)_{pT}}{v_1 - v_3 - (x_1 - x_3) \left( \frac{dv_3}{dx_3} \right)_{pT}}$$

or

$$T \frac{dp}{dT} = \frac{W_{13}}{v_{13}}$$

It appears from the form for  $\frac{dp}{dT}$ , that this value is equal to  $\left( \frac{dp}{dT} \right)_{x_3}$ , if a section is made through the surface of saturation for  $x = x_3$ .

In other words: The three phase triangle in its extreme position touches the section mentioned — and to this we might also at once have concluded. It will also be immediately seen, that the coinciding of the points  $x_2$  and  $x_3$  of the three phase triangle takes place in a plaitpoint, and that therefore the final point of the line  $p = f(T)$  lies on the plaitpoint line. Then we have a plaitpoint in the point where  $x_2$  and  $x_3$  coincide, and the  $p, T$ -projection of the plaitpoint line being the envelope of the  $p, T$ -projection of the sections of the surface of saturation for constant values of  $x$ , the plaitpoint line and the  $p, T$ -projection of the sections touch, and so also the final point of the  $p, T$ -projection of the three phase pressure, as in that final point the last element of this pressure coincides with the section mentioned. This contact has not yet been taken into consideration in former diagrams. If there are two final points of the three phase pressure, then there are two separate portions of the realisable portion of the plaitpoint line, which are joined by the three phase pressure, the meeting-points being again *cusps*, just as is the case with the hidden portion of the plaitpoint line. Now, however, rises the following question. We know from the shape of the section of the surface of saturation at given value of  $x$ , that in the simplest case it consists of two branches, and that on the upper branch the value of  $\frac{dp}{dT}$  may also be negative. Can now also  $\frac{dp}{dT}$  be negative for the three phase pressure? As far as I know this has never been observed; but the observations on the rise of the three phase pressure with the temperature, and the other circumstances, viz. the values of  $x$  and  $v$ , have been only little examined

as yet. If it should be possible that  $\frac{dp}{dT}$  becomes negative, and for the present I do not see any reason to consider this impossible, this can only take place in the case of a plaitpoint line descending with the temperature. Accordingly the final point of the three phase pressure, so the plaitpoint, lies on that part of the section of the surface of saturation which lies between minimum pressure and critical point of contact, and it is known, that then also the plaitpoint line must descend in its  $p, T$ -projection, because it is the envelope of the sections of the surface of saturation. If  $\frac{dp}{dT}$  is negative at the final point, this value must have passed through 0; this will then require that no heat is released with conversion of the middle phase into the two others, and so that if heat is released with conversion into one of the two extreme phases, the conversion into the other extreme phase is attended by heat-absorption<sup>1)</sup>. And without further investigation this cannot be pronounced as impossible.

Finally we point out that  $\frac{dp}{dT}$  cannot become infinite. For this it would be required that the denominator is equal to zero without this being the case with the numerator. Then the area of the three phase triangle must be equal to zero or the 3 points must lie on a straight line. This is the case when two points coincide, but then the numerator is also equal to zero. Now a  $p$ -line — for the three points always lie on the same isobar — can indeed be intersected by a straight line in 3 points, but in this case this would have to occur in the same three points with a  $q$ -line; this observation will most likely suffice to put down this case as one that does not occur. So we have in the  $p, T$ -projection of the threephase pressure a curve which, at least as a rule, ascends with the temperature; under every point of this line is a point of the plaitpoint line (hidden point) and above every point is a second point of this line (realisable point). This second point is wanting if the plait should not be closed at the bounding volume.

*Shapes of plaitpoint lines ( $p, T$ -projection).*

According to the above considerations I shall describe a possible shape of plaitpoint line for the case of two components, for which

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<sup>1)</sup> The diagrams p. 126 Cont. II, in which the value of  $v_{21}$  and  $w_{21}$  for coexisting phases has been represented, must be supplemented, when also incomplete miscibility is assumed.

the ratio  $\frac{T_{k_2}}{T_{k_1}}$  is a high value, and for which the temperature, at which  $\frac{d^3\psi}{dx^3} = 0$  has contracted to a point, is much higher than  $T_{k_1}$ .

As an example take the mixture helium and hydrogen investigated by KAMERLINGH ONNES and KEESOM partly experimentally and further theoretically, or the mixture helium and water. As, however, there are two shapes possible, I shall describe them both, not stating as yet, which of these shapes is the correct one in these cases.

As  $b$  for hydrogen will be higher than  $b$  for helium, helium is the first component. In the first place we observe that there must be a complex plait for  $T < T_{k_1}$ , which extends over the whole width.  $\frac{d^2\psi}{dv^2} = 0$  has closed on the helium side for  $T > T_{k_1}$ ; but  $\frac{d^2\psi}{dx^2} = 0$  is a closed curve, which extends outside  $\frac{d^2\psi}{dv^2} = 0$  on the helium side, and so there is intersection of  $\frac{d^2\psi}{dv^2} = 0$  and  $\frac{d^2\psi}{dx^2} = 0$ . The spinodal curve, which remains near  $\frac{d^2\psi}{dv^2} = 0$  on the side of  $H_2$ , moves further away from this line as we approach the helium side, and remains also outside  $\frac{d^2\psi}{dx^2} = 0$ . I shall continue to assume that the spinodal line remains closed on the side of the small volumes. The changes which must be made if this should not be the case, will be easily applied in the result at which we arrive. Then there are three plaitpoints for this  $T > T_{k_1}$ . With very small difference of  $T$  and  $T_{k_1}$  there is first the ordinary plaitpoint on the helium side; and further there are two heterogeneous plaitpoints, viz. a realisable one at the very small volumes, and a hidden one (see inter alia figs. 12 and 13 of the preceding communications).

If now the first mentioned plaitpoint should coincide with the hidden one, as is assumed in the discussion of these figures, only one single plaitpoint would remain; but another, more intricate case is possible. If  $\frac{d^2\psi}{dv^2} = 0$  and  $\frac{d^2\psi}{dx^2} = 0$  are quite detached, as will happen with increasing temperature, the spinodal line may viz. either continue to run round the two curves, as I have repeatedly drawn, or it may split up between the two curves. For splitting it will be required that they are so far apart that a point is found between them, in

which not only  $\frac{d^2\psi}{dx^2}$  and  $\frac{d^2\psi}{dv^2}$  are positive, but the product is equal to  $\left(\frac{d^2\psi}{dx dv}\right)^2$  — which may the sooner take place when the line  $\left(\frac{dp}{dx}\right)_{vT} = 0$  is in the neighbourhood. In this case there originate two new realisable plaitpoints. Then there are 5 plaitpoints at somewhat higher temperature, because 2 new ones have been added to the three above mentioned ones. And now, as I demonstrated when I discussed such a splitting up, at somewhat higher temperature the hidden plaitpoint will coincide with one of the newly formed realisable ones, and vanish as a couple of heterogeneous plaitpoints. So there are 3 realisable plaitpoints left viz one that is the plaitpoint of the half of the plait (transverse plait) on the hydrogen side. And the two others, which are the upper and lower plaitpoint of the half of the plait which has got detached (longitudinal plait). In other words: one half is a plait that surrounds the curve  $\frac{d^2\psi}{dv^2} = 0$ , and the other half runs round  $\frac{d^2\psi}{dx^2} = 0$ . In this half  $\frac{d^2\psi}{dx^2} = 0$  performs in many respects the function which  $\frac{d^2\psi}{dv^2} = 0$  performs as a rule. The splitting up of the spinodal line, so that a closed longitudinal plait detached itself, can, therefore, take place in such a way that this longitudinal plait is found at temperatures at which  $\frac{d^2\psi}{dv^2} = 0$  still exists for the same value of  $x$ , but is then restricted to very small volumes (mixtures of water and phenol); or it may take place in such a way that  $\frac{d^2\psi}{dv^2} = 0$  no longer exists for the same value of  $x$ , but then the volumes need not be so very small. We might say: the detaching might take place in such a way that the two parts of the plait exist above or by the side of each other.

Moreover the case may occur that  $\frac{d^2\psi}{dv^2}$  has quite disappeared, and  $\frac{d^2\psi}{dx^2}$  alone exists. Then only a longitudinal plait is found. This can only take place for temperatures above  $T_{k_1}$  and  $T_{k_2}$ , and if what I have called  $T_g$ , is larger than  $T_{k_1}$  and  $T_{k_2}$ .

In fig. 27 I have drawn the  $p, T$ -projection of the plaitpoint line, which in the  $v, x$ -plane is again a line which proceeds continuously from the left to the right side. At  $T_k$  for  $H_1$  there are three points

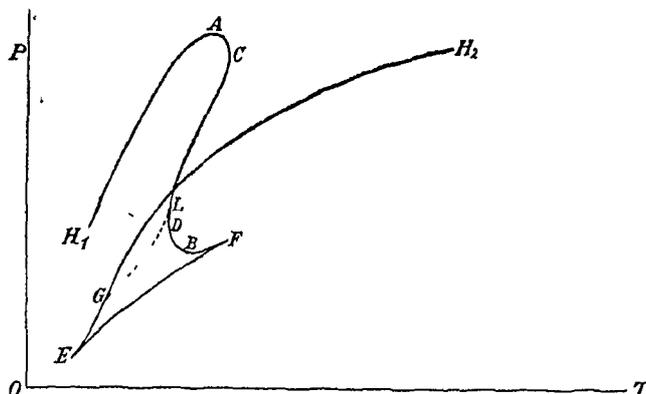


Fig. 27.

of this line; the downmost is the hidden plaitpoint lying between  $E$  and  $F$ . The place of the points  $E$  and  $F$  has been arbitrarily chosen, so that it may also be possible that  $E$  must lie more to the right than  $T_{k_1}$ . At the value of  $T_D$ , the splitting temperature, 2 new points appear. At  $T_F$  a couple of heterogeneous plaitpoints unite. At  $T_C$  the detached longitudinal plait would disappear. Between  $T_C$  and  $T_D$  there are two plaitpoints for the detached plait. The three phase pressure runs between  $G$  and  $L$ , the extremity  $L$  having been chosen such that the point  $D$  (splitting point) lies below the three phase triangle, and can, therefore, not be observed. Hence only the following 3 parts can be realized by means of the experiment: 1.  $H_2G$ , 2.  $H_1. ACL$ , 3.  $GL$ . And now, if the hypothesis that the plait is closed on the side of the limiting volumes, should be incorrect, we have only to open the upper part at  $A$  and  $C$ , and to make the open branches run asymptotically towards infinitely high. So this plaitpoint line is essentially the same as that with the double point which I have drawn. Only one of the branches, i.e. the left branch, has in addition got a maximum and a minimum pressure, and a maximum and a minimum temperature. If we drew the  $T,x$ -projection, there would be 2 maxima and two minima — also in the  $p,x$ -projection. But the  $v,x$ -projection remains simple. If the plait is closed at the limiting volumes, there is a minimum volume, in

<sup>1)</sup> In this figure the shape of the plaitpoint line has been drawn when really the spinodal line could run between  $\frac{d^2\psi}{dv^2} = 0$  and  $\frac{d^2\psi}{dx^2} = 0$ . Further investigation will have to decide whether or no this complication can occur. If it occurs, the righthand side of the plait (transverse plait) will be much narrower, then when this complication is not met with. In the latter case the righthand part of the plait is a complex plait.

the opposite case two points for which  $v = b$ , come in its stead. For neither with an homogeneous double point, nor for an heterogeneous double point,  $\left(\frac{dv}{dx}\right)_{pl} = 0$ . And in the point in which  $\left(\frac{dv}{dx}\right)_{pl} = 0$  or  $\left(\frac{dx}{dv}\right) = 0$ , (see p. 185)  $\frac{dp}{dT}$  has not a value which presents any particularity.

The second form will differ from the one described here in so far that the temperature at which the detaching of the longitudinal plait takes place, is assumed to be equal to  $T_{k_2}$  (critical temperature of the second component).

This may take place if the temperature at which  $\frac{d^2\psi}{dx^2} = 0$  disappears, is not only higher than  $T_{k_1}$ , but also higher than  $T_{k_2}$  (a case to which I alluded already before in these Contributions).

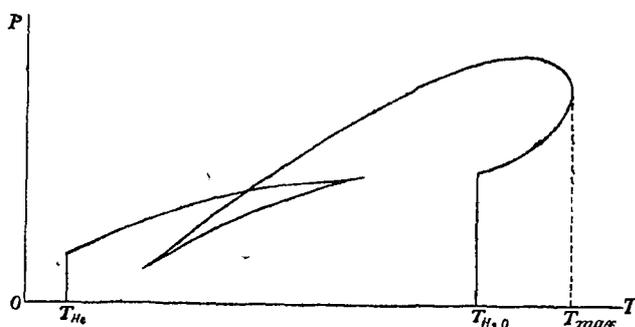


Fig. 28.

Then the  $p, T$ -projection is given by fig. 28. The highest temperature which then occurs, is that at which  $\frac{d^2\psi}{dx^2} = 0$  disappears.

That for the mixture helium and hydrogen the second shape of the plaitpoint line can occur, and that therefore  $T_g$  can be  $> T_{k_2}$ , follows immediately from the formula for the value of  $T_g$  (These Proc. May 24, 1907) viz.:

$$MRT_g = 2 \frac{a_1 + a_2 - 2a_{12}}{b} x(1-x) \frac{1-y}{(1+y)^2}$$

For the case, namely, that  $a_1$  and  $a_{12}$  may be neglected, and  $b_1 < b_2$  and  $x > \frac{1}{3}$ , we find really  $T_g > T_{k_2}$ . Thus we find for  $x = 0,4$ , which belongs to  $\frac{b_1}{b_2 - b_1} = 0,3704$ ,  $MRT_g > \frac{8}{27} \frac{a_2}{b_2}$ . For still higher value of  $x$ , this value of  $T_g$  would be found still higher, but

if  $a_1 + a_2 - 2a_{12}$  becomes appreciably smaller than  $a_2$ , this may, of course, be different. In this case the plait remains a complex plait as far as  $T = T_{k_2}$ . At this value of  $T$  has  $\frac{d^2\psi}{dv^2} = 0$  disappeared, and  $\frac{d^2\psi}{dx^2} = 0$  still exists. So above  $T_{k_2}$ , the complex plait is to be considered as a longitudinal plait.

If in the case described above we have a plaitpoint line that proceeds continuously in the  $v, x$ -plane, starting on the left hand side in the critical point of the first component, and terminating in the critical point of the second component, though a maximum value of  $x$ , and then also a minimum value may be possible, still another case is possible, and most likely this case is met with in the mixture water and phenol. Of course the first mentioned line, which starts and terminates in the critical point of the components, must continue to exist, if we continue to assume that the plait remains closed on the side of the limiting volumes. Else it splits up into 2 parts, which I, however, consider as two parts of one and the same branch of the plaitpoint curve. If another branch is possible, it must be a separate closed curve — which, however, if the plait is supposed open on the side of the limiting volumes, may be considered as starting in a point of the line  $v = b$ , and terminating in another point of this line. We meet with this case when the longitudinal plait detaches itself at a temperature which is lower than  $T_{k_1}$  and  $T_{k_2}$ . As has been described above, the longitudinal plait will have quite retreated to volumes smaller than those of the liquid branch of the binodal line of the transverse plait at a certain value of  $T$  higher than the temperature of detaching. Then the three phase pressure no longer exists, and the first mentioned branch of the plaitpoint line, which joins the critical points of the components, has its simplest shape. In fig. 29

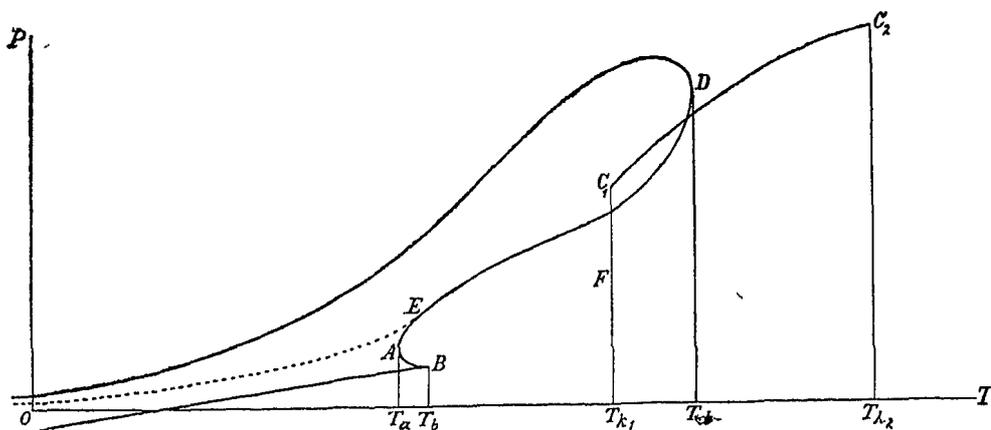


Fig. 29.

the  $p, T$ -projection has been drawn. At  $T = T_d$ , which is lower than  $T_{k_1}$  and  $T_{k_2}$ , the detaching takes place, and there is an homogeneous double point. At  $T = T_b$  there is an heterogeneous double point, and at  $T_d$  again an homogeneous double point. If we suppose the longitudinal plait to be open towards  $v = b$ ,  $p_D$  must be thought infinitely large, and the upper part of this second branch disappears. Without doubt the three phase pressure line, which terminates in  $E$ , will have its other extremity, i. e. its initial point, at  $T = 0$ .

We should have a very simple and remarkable case of a closed curve for the second branch of the plaitpoint line if the lowest temperature at which an heterogeneous double point is formed, lies little below the temperature at which this double point vanished again — and this temperature lies below  $T_{k_1}$  and  $T_{k_2}$ . Then also the temperature at which again an heterogeneous double point exists,

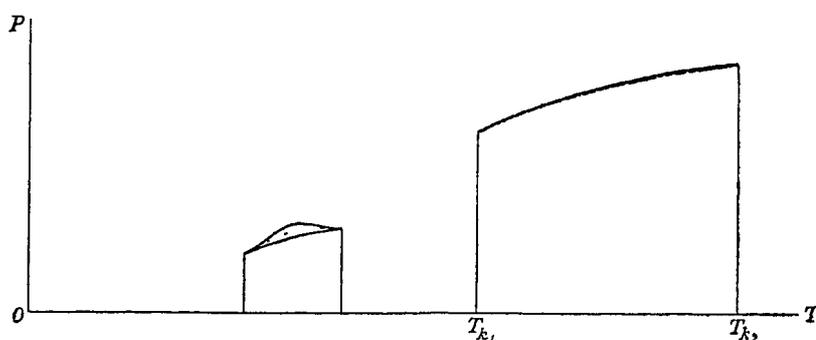


Fig. 30.

will lie only little higher than the first. Fig. 30 gives then again the  $p, T$ -projection for such a case. There can then be a three phase pressure indicated by a dotted line. Then the liquid begins to split up into two phases at a temperature lying much below  $T_{x_1}$  and  $T_{x_2}$ , becoming homogeneous again at somewhat higher temperature — at least if the value of  $x$  has been chosen between that belonging to the extremities of the three phase pressure. In the  $v, x$ -projection we have then a small closed figure with maximum and minimum volume.

So many different shapes of plaitpoint lines, however, may be deemed possible, that they would require a special study. If they are found by the experiment, I expect that the rules given in these contributions, will prove sufficient to render them intelligible.

However, I intend shortly to indicate the circumstances in which the forms discussed are met with, more fully by means of some mathematical developments.

**Physics.** — “*On the measurement of very low temperatures. XV. Calibration of some platinum-resistance thermometers.*” By Prof. H. KAMERLINGH ONNES and J. CLAY. Communication N<sup>o</sup>. 99<sup>b</sup> from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 29, 1907).

§ 1. *Introduction.* The investigation on the variation of the resistance of metals (pure ones and those with known admixtures) set on foot many years ago (see Comm. N<sup>o</sup>. 77 § 1 These Proc. Febr. 1902) at Leiden, comprises besides the determination of the galvanic resistance of conductors made of the different metals, also the determination of the expansion for each of these metals. We have only little advanced as yet with the latter part of this investigation, the expansion has only been investigated for platinum, which was chosen as standard metal, and then only down to  $-182^{\circ}$ .<sup>1)</sup> We hope shortly to publish a Communication on the expansion down to  $-252^{\circ}$  C. For the present, however, the knowledge of this expansion is not yet of much importance for the investigation of the variation of the specific resistance with the temperature. When in this investigation we descend to very low temperatures, the correction for the expansion becomes so small compared with the disturbance in consequence of other influences which are still further to be investigated, that we may disregard it for the moment.<sup>2)</sup>

The investigation consists then in the calibration of different resistance thermometers. The wires treated in this Communication being chiefly of importance to us as resistance thermometers, we have inserted their calibration in this series.

<sup>1)</sup> In Comm. N<sup>o</sup>. 85 (These Proc. April 1905) it was observed for the first time that in order to represent the expansion of glass from  $-180^{\circ}$  to  $0^{\circ}$  a formula of the second degree with other constants was required than for the range from  $0^{\circ}$  to  $+100^{\circ}$ . We found this confirmed in Comm. N<sup>o</sup>. 95<sup>b</sup> (These Proc. Sept. '06), and also applicable to platinum, for which a formula of the third degree, as we gave one for glass, proved necessary between  $-180^{\circ}$  and  $+100^{\circ}$ . Afterwards (Dec. '07) SCHEEL, who was at first (Zeitschr. f. Instr.k. April '06) of opinion that a formula of the second degree could be found for platinum between  $-190^{\circ}$  and  $+100^{\circ}$ , come to the same opinion as we, and gave the three constants for platinum. Our formula of the second degree for platinum between  $0^{\circ}$  and  $-180^{\circ}$  quoted by SCHEEL was used by us to prove, that for platinum between  $-180^{\circ}$  and  $+100^{\circ}$  a formula of the second degree is *not sufficient*, but that a formula of the third degree is required. In order to show this with given values at  $+100^{\circ}$ ,  $0^{\circ}$  and  $-190^{\circ}$  observations at a temperature about halfway between  $0^{\circ}$  and  $-190^{\circ}$ , as our  $-87^{\circ}$ , are more suitable than observations at a temperature between  $0^{\circ}$  and  $+100^{\circ}$ , as those by SCHEEL at  $+56^{\circ}$ .

<sup>2)</sup> Here it is left entirely undecided whether the variation of the resistance with the temperature is not in close connection with the expansion.

§ 2. *Particulars on the comparison and on the investigated wires.* In these calibrations we have taken the platinum wire which was compared with the hydrogen thermometer in Comm. N° 95<sup>c</sup> (These Proc. Sept. '06) and which we shall call  $Pt_I$ , as standard. We determined the variation of the resistance of the other wires by bringing them together with  $Pt_I$  at the desired temperature, and by then comparing their resistance with that of  $Pt_I$ . The two platinum wires  $Pt_{III}$  and  $Pt_V$  were brought in the same cryostat (see § 4 Comm. 95<sup>c</sup>) together with  $Pt_I$ , and whereas the temperature was kept constant with one resistance according to the indication of the WHEATSTONE-bridge, the ratio of the resistance of the other to  $Pt_I$  was determined by means of the differential galvanometer.  $Pt_V$  was also measured separately with the WHEATSTONE-bridge. The difference of the results by the two methods amounted only to 0,02 % at the lowest temperatures.

Just as  $Pt_I$ ,  $Pt_{III}$  and  $Pt_V$  were supplied by HERÆUS; they were delivered at the same time, but later than  $Pt_I$ . The diameter of all three was 0.1 m.m. After having been treated and wound round the glass (see Comm. N°. 95<sup>c</sup> § 3) in the same way, they were heated for a long time in an annealing furnace for glass.  $Pt_{III}$  and  $Pt_V$  differed only in this respect that after being heated  $Pt_V$  was partly unwound, and then wound again, and was not heated in the annealing furnace again.

To obtain also a resistance thermometer of very small dimensions a platinum wire of 0,05 m.m. diameter was wound round a tube of 1 c.m. diameter and about 8 c.m. long. The thin platinum wire was welded to thick platinum wires which were fused in the glass. Consequently the thermometer could be cleaned by means of acids if necessary. The thin wire  $Pt_{II}$  used for this thermometer, was also furnished by HERÆUS.

A fourth wire was investigated to get an idea of the

§ 3. *Invariability of the resistance thermometers for low temperatures with the time*, viz. the resistance thermometer with which the observations were made by MEILINK in 1902, and which we shall call  $Pt_M$ . The zero point appeared to have remained unchanged to one 300000<sup>th</sup>). This was also the case with  $Pt_I$ , after measurements had been made at very low temperatures with the resistance thermometer for two years.

Repetition of the calibration at low temperatures of 1902 did not give an equally good harmony. We found:

<sup>1)</sup> The thermometer had got defect in consequence of the bursting of the glass cylinders. However carefully it was repaired, yet this gave rise to a diminution of length of the wire of 3 mm. or 0,039 %, for which a correction was applied.

Hydrogen th.	1902	1907	Deviation in $\Omega$	Deviation in $^{\circ}$ C.
$0^{\circ}$	110.045	110.048	- 0.003	
-182.63	28.692	28.605	+ 0.087	+ $0.25^{\circ}$
-197.08	21.877	21.999	- 0.022	- 0.05
-209.93	16.025	15.934	+ 0.089	+ 0.25

We think that we cannot draw another conclusion from it than that the reliability of the measurements with the hydrogen thermometer in 1902 was not yet so great as it has become now as appears from Comm. N<sup>o</sup>. 95<sup>d</sup>.

§ 4. *Results.* The measurements have yielded for the resistance of each of the wires expressed in that at  $0^{\circ}$  as unity:

Temperature	$Pt_I$	$Pt_{III}$	$Pt_V$	$Pt_M$	$Pt_d$
$0^{\circ}$	1.	1.	1.	1.	1.
- 30.53	0.87892	0.87846	0.87799		
- 58.58	0.76685	0.76632	0.76643		
- 87.55	0.64991	0.64918	0.65039		
-103.83	0.58345			0.58720	
-109.09	0.56204	0.56025	0.56126		
-140.19	0.43311	0.43195	0.43182		
-159.11	0.35368	0.35240	0.35214	0.35979	
-182.75	0.25283	0.25141	0.25069	0.26022	0.27374
-195.10	0.20045	0.19894	0.19858	0.20812	0.22298
-204.68	0.15974	0.15816	0.15880		0.18355
-212.20	0.12816	0.12653	0.12625	0.13622	0.15285
-216.63	0.11024	0.10853	0.10824		
-252.82	0.01421				0.040637
-255.18	0.01244				0.03766
-259.10	0.01053				0.03645

It appears that wires delivered at the same time show the same course with only small deviations. A considerable difference in deformation of the wire has had only a slight influence for  $Pt_V$ . The great difference with wires delivered at different times points to the fact that the originally used material and the treatment in drawing the wires out decide on the change of the resistance. How great the influence of the treatment in drawing is appears from the comparison of  $Pt_{III}$  and  $Pt_d$ . They were supplied by HERAEUS about the same time and are therefore probably made of platinum of the same degree of purity. Yet the thinner wire  $Pt_d$  decreases much less in resistance than the thicker one. At the temperature of liquid hydrogen the differences become very large. In view of the results obtained for gold, which have been inserted in the following Communication (N<sup>o</sup>. 99<sup>c</sup>), the most plausible explanation is this that the admixtures in the platinum of the wires sent by HERAEUS, either due to their being less pure by nature or to the way of drawing, were less with the platinum sent later than with that sent earlier. We come back to this in Comm. N<sup>o</sup>. 99<sup>c</sup>. Here we may still mention that DEWAR's wire gave 0,30521 to ours 0,25344 at  $-182^\circ$ , and that only the thickest (0,2 m.M.) of HOLBORN's wires gave a smaller value than ours, viz. 0,21253 to ours 0,21786 at  $-191^\circ$ .

§ 5. *Calibration formulae for the new wires.* Just as for  $Pt_I$  we have also calculated the constants for each of the wires  $Pt_{III}$  and  $Pt_V$  in a calibration formula which is adjusted down to  $-217^\circ$  and does not give to great deviations at the hydrogen temperatures. To be adjusted to the hydrogen temperatures too formulae of another form are required. The above mentioned formulae of the form (A):

$$\frac{W_t}{W_0} = 1 + a.t.10^{-2} + b.t.10^{-4} + c.t.10^{-6} + d \left( \frac{10^3}{T} - \frac{10^3}{(273.09)^2} \right)$$

give for the adjustment which we distinguish by  $A_I$ :

$A_I$	$a$	$b$	$c$	$d$
$Pt_V$	+0.401819	+0.0007403	+0.0052641	+0.020666
$Pt_{III}$	+0.398291	-0.0026645	+0.0039442	+0.016843

The mean error proved to be greater, for  $Pt_V$  even considerably greater than in the calibration in Comm. 95<sup>c</sup>, which can be ascribed only partly to the indirect method of the determination of the resistance.

**Physics.** — “*Isotherms of diatomic gases and their binary mixtures.*  
*VI. Isotherms of hydrogen between —104° C. and —217° C.*”  
 (Continued). By Prof. H. KAMERLINGH ONNES and C. BRAAK.  
 Communication N°. 99<sup>a</sup> from the Physical Laboratory at Leiden.

(Communicated in the Meeting of June 29, 1907).

§ 14. *Survey of the determinations.*

The determinations mentioned in this Communication constitute one whole with those of Communication N°. 97<sup>a</sup>. They may partly serve to control the earlier determinations at —104° and —136°, which, being the oldest observations, are not quite so reliable as the others. For the determinations of isotherms at lower temperatures they are a valuable supplement for the smaller densities from 70 to 100 times the normal one. With the exception of the isotherm of —217° the determinations communicated now may also be considered as a whole in themselves. To complete this set of determinations a part of the isotherm mentioned for the density at about 170 times the normal one is still wanting. We hope soon to publish the additional determinations referring to this. To the standard-temperatures at which we determined the isotherms, we have still added —164° C. From the data mentioned in Comm. N°. 97<sup>a</sup> may be derived (see § 13 of the communication mentioned) that the point where the inclination of the *pv*-curve for exceedingly small densities becomes zero, lies at about this temperature. The purpose of the determinations at —164° is to determine this point, which we shall call the *Boyle-point*, more definitely.

The determinations, with the exception of that at —140°, were made at temperatures which differed little from the standard-temperatures of Comm. N°. 97<sup>a</sup>. They may be reduced to these standard-temperatures by a simple correction (See Comm. 97<sup>a</sup> § 6). This reduction has not yet been carried out for the isotherms mentioned below. In Table XIX the temperatures are given at which the measurements were made. They were determined and calculated in exactly the same way as those of Comm. N°. 97<sup>a</sup>; just as to these latter temperatures the correction of Table XVIII Comm. N°. 97<sup>b</sup> is still to be applied to them.

We may still remark about the measurement of the pressure (cf. § 3), that for the lowest pressures a direct connection with the open manometer was required, because the closed auxiliary manometer cannot be used below 20 atms.

§ 15. *Remarks about the manometers and the piezometers.*

When the determinations were finished, the auxiliary manometer

was once more compared with the open standard-manometer. It proved that the normal volume had again undergone a slight diminution, i.e. of 0.00026 of the original value. This comparison was made at about 22, 28 and 55 atmospheres. If the calculations of the pressure are carried out with the corrected normal volume, the remaining differences between the indications of the open and the closed manometer are smaller than  $\frac{1}{10000}$  of the total pressure.

The steeltube  $f_4$  with hexagonal portion  $f_5$  on the stem of the piezometer  $b_5$  (cf. fig. 2 Pl. II Comm. N<sup>o</sup>. 69, for the details at the top of the tube compare fig. 4 *ibid*  $f_1, f_2, f_4$ ) was soldered to the glass stem  $b_5$  in the way described in Comm. N<sup>o</sup>. 94<sup>b</sup>. Now the packing could be pressed down more tightly (cf. § 4 Comm. N<sup>o</sup>. 97<sup>a</sup>) without danger of the block sliding from the stem.

The dimensions of the different parts of the piezometer were about the same as in the determinations of series I of Comm. N<sup>o</sup>. 97<sup>a</sup>. The glass stem had a greater length and a volume of about 12 cm<sup>3</sup>., which enabled us to determine a greater part of the isotherms than was possible in series I. The reservoir had the somewhat smaller volume of 5.1583 cm<sup>3</sup>.

§ 16. *Second group of values of  $pv_A$ .*

In table XIX the results of the determinations have been given in the same way as in Table XII of Comm. N<sup>o</sup>. 97<sup>a</sup>.

In conclusion we express our hearty thanks to Mr. J. CLAY for his valuable assistance in this investigation.

TABLE XIX.  $H_2$ . Series IV. Values of  $pv_A$ .

Nº.	$t$	$p$	$pv_A$	$d_A$
1	-103.71	28.423	0.63208	44.967
2		38.154	0.63648	59.944
3		48.682	0.64143	75.897
4		58.217	0.64638	90.222
5	-139.88	25.432	0.49452	51.428
6		33.774	0.49697	67.960
7		41.273	0.49967	82.600
8		48.558	0.50232	96.667
9		25.380	0.49466	51.308
10	-164.14	22.818	0.40065	56.952
11		28.688	0.40164	71.427
12		34.387	0.40253	85.427
13		39.947	0.40276	98.936
14	-183.18	20.409	0.32562	62.677
15		24.705	0.32550	75.898
16		28.374	0.32521	87.248
17		32.416	0.32522	99.673
18		20.400	0.32557	62.663
19	-195.17	18.554	0.27867	66.581
20		23.337	0.27765	84.055
21		27.879	0.27622	100.933
22	-204.69	16.752	0.24040	69.684
23		20.456	0.23880	85.658
24		24.019	0.23695	101.367
25	-212.82	15.416	0.20644	74.679
26		18.038	0.20430	88.296
27		20.643	0.20228	102.051
28	-217.40	14.638	0.18742	78.103
29		16.787	0.18495	90.766
30		18.857	0.18293	103.080

**Physics.** — “*On the change of the resistance of the metals at very low temperatures and the influence exerted on it by small amounts of admixtures*” I. By Prof. H. KAMERLINGH ONNES and J. CLAY. Communication N<sup>o</sup>. 99<sup>c</sup> from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 29, 1907).

§ 1. *Introduction.* In Comm. N<sup>o</sup>. 99<sup>b</sup> we called attention to the very large differences in the change of the galvanic resistance with the temperature, which different platinum wires show when we descend to the low temperatures which are to be reached with liquid hydrogen. Such differences were still more pronounced for different gold wires which we investigated. With this metal (see Comm. N<sup>o</sup>. 95<sup>d</sup> These Proc. Sept. 1906) we had taken in hand the investigation of the influence of small amounts of admixture announced in Comm. N<sup>o</sup>. 77, because the influence of admixing silver would probably be important and the percentage of silver could be determined very accurately, the possibility of drawing out wires of the different kinds of gold and its high melting point moreover rendering this metal preferable to the for the rest very suitable mercury.

Besides, the inquiry into the influence of small amounts of admixture on the change of the resistance of gold with the temperature proved at once useful as we thought that the gold resistance thermometer would be preferable to the platinum resistance thermometer. Dr. C. HOITSEMA, who already obliged us before (see Comm. N<sup>o</sup>. 95<sup>d</sup>) by putting pure gold at our disposal, has had the kindness of supplying us again with different samples of gold of high purity, further of preparing for us different alloys with accurately known small percentages of admixture, and of determining the impurity which was finally left in the wires after they had been melted down. For all this valuable help and for the information which Mr. HOITSEMA was enabled to give us by his wide experience we express our hearty thanks.

The investigation of the different gold wires with very small amounts of admixture may of course also be considered as the calibration of different gold resistance thermometers. (Comp. Comm. N<sup>o</sup>. 99<sup>b</sup> § 1). We prefer, however, to consider it as a part of our more general investigation (Comm. N<sup>o</sup>. 77) on the change of the resistance with the temperature for pure metals, and on the influence which small amounts of admixture exert on it.

As to the change of the specific resistance for the pure metals reduced to the most normal state, attention is drawn to the temperature of the

point of inflection  $\frac{d^2r}{dT^2} = 0$  the temperature of the point of proportionality

$\frac{dr}{dT} = \frac{r}{T}$  and the temperature of the minimum  $\frac{dr}{dT} = 0$ . It is clear that

the situation of these points, and the correspondence<sup>1)</sup> and difference of their situation and of the coefficient of variability of the resistance with the temperature in general for different metals of different classes must furnish important data for the theory of electrons.

The investigation of these points is only possible by the aid of liquid hydrogen. Only in some cases — and even then the purity of the metal is open to doubt — the point of inflection, whose existence was indicated by DEWAR, was found high enough to be ascertained without measurements for hydrogen temperatures. For metals in the purest and normal state the point of proportionality lies probably still below the temperatures which are to be reached with liquid hydrogen. It is true that DEWAR derived from his measurements at two hydrogen temperatures that it was surpassed for some of his metal wires. Our measurements, however, point to this that as a metal is brought to a purer and more normal state, the point of proportionality is found to be lower. The metal wire which came nearest to this *ideal* state, was one of our gold wires. Even at the lowest temperature the point of proportionality was not yet reached for that wire. Probably DEWAR'S wires were further removed from this ideal state.

With the low situation which we find for the point of proportionality measurements at two hydrogen temperatures do not suffice, but we have made determinations at at least three hydrogen temperatures, because they were necessary to determine the probable situation of the point of proportionality by the aid of  $\frac{d^2r}{dt^2}$ . Until we have reached the proportional point, we need not discuss the question of the minimum point.

In the inquiry into the properties of the metals in the ideal state we must know first of all in how far the metal is in this state, and else how we can derive what would be found in this state. The influence of small deviations in the nature of the metals on the change of the resistance with the temperature, becomes so exceedingly great for the hydrogen temperatures, that a special investigation is necessary for them. Here two things have to be paid attention to: to small amounts of admixture, and to differences in

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<sup>1)</sup> In this respect something is to be derived from the formulae given by us in this and in the preceding communications.

hardness etc. For the present we have left the latter out of account; in the investigation of the influence of the admixtures, however, the influence of the hardness was as much as possible eliminated by our treating the different samples of metals exactly in the same way when comparing them, and by reducing them to the same state of softness.

The most natural explanation of the whole of the results obtained as yet (in this and the preceding Communication) is to ascribe the deviations for the different wires of one and the same metal to impurities in the metal, which may also come in during the drawing if efficient precautions do not prevent it, and which even in very small quantities exert a very great influence on the changes of the resistance with the temperature.

The influence of the drawing is altogether lost for mercury, in which it is also easy to ensure uniform distribution of small quantities of admixture. This enhances the importance of the study of this metal for the investigation of the influence of admixture. In the first place we have measured its resistance at hydrogen temperatures which had not yet been determined; it is given in § 4. It proved that for pure mercury <sup>1)</sup> the inflection point falls in the region of liquid hydrogen temperatures. This is a drawback for the inquiry into the change of the resistance with the temperature for pure metals.

Just as the gold wire *Au<sub>V</sub>* (see § 2), also the silver wire *Ag<sub>I</sub>* and the platinum wires of the preceding Communication are probably purer than DEWAR's wires of the same metals. For bismuth, on the other hand, DEWAR has most likely had a purer sample than we. The change of the resistance at hydrogen temperatures for this metal, which had not yet been measured by him, has been given in § 5. The observations for lead for those temperatures, which were still wanting up to now, have been given in § 6.

The high degree of purity for some of the metals which were at our disposal, and the lower temperatures to which we descended (solid hydrogen evaporating at 2,5 m.m. pressure) render the decrease of the resistance in some cases many times larger than was observed by DEWAR. To this it is also owing that we have observed the great influence, which very small changes in the nature of the metal obtain on the change of the resistance at hydrogen temperatures. We may account for this by paying attention to the difference of the resistance of a wire of pure metal at the temperature  $T$ ,  $r_T$ , with

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<sup>1)</sup> Perhaps in connection with the low melting point. Possibly the point of proportionality is first reached for osmium.

that of a wire of the same metal with a proportion of admixture  $x$  at the same temperature,  $r_{xT}$ . According to a theorem of MATTHIESSEN<sup>1)</sup> derived from observations between 0° and 100°, this difference (the theorem refers to a difference that is about the same as that considered here) is constant for different temperatures. FLEMING<sup>2)</sup> found this theorem about confirmed down to -200°. As we have found, this theorem no longer holds for hydrogen temperatures. But the deviation is not of such a nature as to affect our conclusions. So if to form an idea of the influence of the admixtures, we put  $r_T = r_{iT} + px$ , further  $p$  constant and large, then it is clear that — when  $r_{iT}$  becomes as small as is the case (see Table I *AuV*) for pure metals and hydrogen temperatures — the resistance of a metal for the case that  $x$  gets an appreciable amount, will be owing almost exclusively to the admixture. The small amounts of admixture obtain a remarkable influence<sup>3)</sup>.

Analogues are easily found in the important influence of small amounts of admixture on the density in the neighbourhood of the critical temperature of a substance, in a space becoming opaque by a cloud depositing on a minimum quantity of dust. But for a further discussion the systematic investigation of the influence of small amounts of admixture should be more advanced. At all events the changes of the resistance with temperature at hydrogen temperatures proves to be a highly sensitive criterion to decide about the nature of a metal.

§ 2. *Gold.* The different samples of pure gold were all supplied by Dr. C. HOITSEMA. With the exception of two the wires were all treated in exactly the same way, drawn out by HERÆUS to 0,1 mm. diameter, and treated at every pull with diluted sulphuric acid and nitric acid. The gold wire *AuVI* was drawn in a different way and made strongly impure. The exact amount has not yet been ascertained.

1) Pogg. Ann. Bd. CXXII.

2) Proc. Royal Institution June 1896 p. 9.

3) To a less degree of purity of the examined metal wires it is perhaps to be ascribed that NICCOLAI, Att. Linc. 16, 1<sup>st</sup> sem. p. 906 finds a smaller decrease of resistance at -189° than we do, as appears by comparison with Tables I, III, V of this communication and V of Comm. N<sup>o</sup>. 96<sup>b</sup>. Indeed NICCOLAI finds:

	silver	gold	lead	platinum
0°	1	1	1	1
- 189°	0.2784	0.3068	0.3357	0.3198

[Added in the translation].

$Au_0$  is the wire which was calibrated in Comm. N°. 95<sup>d</sup>. After melting it down Dr. HOITSEMA found 0,03% impurities. As to the wires  $Au_{III}$ ,  $Au_{IV}$  and  $Au_V$ , Dr. HOITSEMA found about 0.015% admixture for  $Au_{III}$ , about 0.005% admixture for  $Au_{IV}$  and  $Au_V$ .  $Au_{AgI}$  was made of an alloy which after the wire had been remelted, contained 0.4% admixture (probably chiefly silver). Wound round the same glass cylinder all wires except  $Au_0$  and  $Au_{AgI}$  were heated at the same time in an annealing furnace for a long time, and slowly cooled, as had also been done with  $Au_0$  and  $Au_{AgI}$ , so that they were perfectly malleable.

In table I the resistances have been given expressed in that at 0° as unity. These were about  $9\Omega$ .

Temperature	$Au_{III}$	$Au_{IV}$	$Au_V$	$Au_{VI}$	$Au_0$	$Au_{AgI}$
0°	1	1	1	1	1	1
—103.83	0.59601	0.59389	0.59306	0.64827	0.60545	0.64549
—183.00	0.27653	0.27177	0.27096	0.37053	0.30070	0.37099
—197.87	0.21456	0.20963	0.20871	0.31659	0.23908	
—205.01			0.17897		0.20992	
—215.34	0.14058	0.13407	0.13337	0.16822	0.16681	
—252.93	0.01602	0.008743	0.008103	0.13669	0.04554	0.13942
—255.13			0.005691			
—258.81	0.01095	0.004265	0.003601	0.13241	0.03982	0.13288
[—261]			0.002713			
[—262]		0.003257	0.002526			

To facilitate comparison we may observe that DEWAR found 0.03290, whereas we found 0.008103 at —252°.93 for  $Au_V$ .

§ 3. *Mercury.* It was doubly distilled and brought into a glass spiral. The latter was protected by a bath of pentane, which was slowly cooled from the bottom upwards before it was immersed into the bath of the cryostat. We found:

TABLE II.	
Change of the resistance of pure mercury with the temperature	
Temp.	Resistance
0°	97 126
— 183 00	7 2650
— 197 87	6 0103
— 205 01	5 3900
— 215 34	4.5057
— 252.93	1 2613
— 258.81	0 7534

§ 4. *Silver*. This was also supplied by Dr. C. HOITSEMA and drawn to a wire of 0.1 m.m. by HERAEUS, during which operation it was treated in exactly the same way as the gold and the platinum. After the resistance had been determined, the composition was controlled; the silver contained then 0.18% impurity. The zero point

TABLE III.			
Change of the resistance of silver with the temperature.			
Temperature	Resistance $R_{g_1}$	$O-C_D$	$O-C_{AIV}$
99°.76	1.41089	0	0
0 before	1	0	0
0 after	1 00037		
— 103.81	0.58087	— 0 00042	— 0.00042
— 139.87	0 43282	+ 42	+ 42
— 183.57	0 24679	— 17	0
— 195.17	0 19703	+ 29	— 2
— 204.67	0 15528	— 31	
— 252.92	0.008913	0	
— 259.22	0.006 142	0	

of the silver wire (resistance at 0°) changes slightly by being drawn out in consequence of the difference in expansion of silver and glass. The preceding table gives the resistance expressed in that at 0° as unity. (The resistance at 0° was 21.519  $\Omega$ ).

Column  $O-C_D$  contains the deviations from a formula adjusted from +100° to -259° of the new form:

$$\frac{W_t}{W_0} = 1 + a \cdot 10^{-2} \cdot t + b \cdot 10^{-4} t^2 + c \cdot 10^{-6} t^3 + d \left( \frac{10^6}{T^3} - \frac{10^6}{(273.09)^3} \right) + e \left( \frac{10^{10}}{T^5} - \frac{10^{10}}{(273.09)^5} \right) \quad (D)$$

which agreed best with the values:

$D$	$a$	$b$	$c$	$d$	$e$
$Ag_I$	+0.402746	+0.004355	+0.004806	+0.00955	-0.000013

For a comparison with platinum and gold the column  $O-C_{A_{IV}}$  gives the deviations from a formula of the form  $A$  (see Comm. N° 95<sup>c</sup> and 95<sup>d</sup>):

$$\frac{W_t}{W_0} = 1 + a \cdot t \cdot 10^{-2} + b \cdot t^2 \cdot 10^{-4} + c \cdot t^3 \cdot 10^{-6} + d \left( \frac{10^2}{T} - \frac{10^2}{273.09} \right)$$

with values which we distinguish by  $A_{IV}$  on account of the other way of adjusting the coefficients.

$A_{IV}$	$a$	$b$	$c$	$d$
$Ag_I$	+0.40355	+0.03968	+0.005232	+0.008662

§ 5. *Bismuth.* The measured resistance, which we shall also investigate in the magnetic field, was that of a bismuth spiral of HARTMAN and BRAUN N°. 301. The resistance expressed in that at 0° as unity (the resistance at 0° was 17.3138  $\Omega$ ) was:

TABLE IV. Change of the resistance of Bismuth with the temperature.		
Temperature	Resistance $Bi_I$	$O - C_{A_{III}}$
12°64	1.05148	0
12°70	1.05165	
0	1	
- 103.71	0.63649	+ 0.00952
- 139.88	0.52865	- 127
- 164.05	0.46246	- 144
- 182.73	0.41435	- 69
- 195.17	0.38478	+ 144
- 204.68	0.36064	+ 127
- 216.01	0.33014	- 69
- 253.01	0.22329	- 92
- 255.34	0.21388	- 2
- 258.86	0.19574	0

This column  $O - C_{A_{III}}$  gives the differences with a formula of the form  $A$  (see § 4), with values which we shall indicate by  $\Delta_{III}$  on account of the adjustment at two hydrogen temperatures and over the region to  $0^\circ$ :

$A_{III}$	$a$	$b$	$c$	$d$
$Bi_I$	+0.390037	+0.051928	+0.0038155	-0.0079700

§ 6. *Lead.* The knowledge of the resistance of lead is of particular importance on account of the fact that this metal does not show the THOMSON-effect. Probably the lead used by us, contained no more than 0.015 % admixture.

The resistance of a narrow strip cut out from the flatted lead and protected against chemical action by paraffine expressed in the resistance at  $0^\circ$  (3.18114  $\Omega$ ) as unity was found to be:

TABLE V.	
Change of the resistance of lead with the temperature.	
Temperature	Resistance
+ 16.33	1 0652
0°	1
-103.63	0 59548
-183.65	0.29439
-195.15	0.25257
-204.52	0.21742
-216.61	0.17129
-252.78	0.03032
-255.07	0.02314
-258.70	0.01311

**Physics.** — *Repetition of DE HEEN's and TEICHNER's experiments on the critical state*", by Prof. H. KAMERLINGH ONNES and G. H. FABIVS. Communication N°. 98 from the Physical Laboratory at Leiden.

(Communicated in the meeting of April 26, 1907).

§ 1. *Introduction.* Experiments have been repeatedly made from which the conclusion was drawn, that a substance can assume different densities above its critical temperature with the same pressure and the same temperature, which densities it can retain for hours according to some investigators<sup>1)</sup>. That in reality this is not the case, and that the

<sup>1)</sup> TRAUBE *Ztschr. f. phys. Chem* 58 p. 477. 1907, cf. also MATHIAS, *Le point critique des corps purs* p. 250.

When with change of density dissociations or variations of volume of the molecules themselves should made their appearance which clearly require more time than the establishment of temperature equilibrium through conduction of heat and convection, we should when a phase was kept at constant volume after having suffered variation of density, have to find an increase of the pressure both for liquid and vapour phases and for phases above the critical temperature; thermodynamically it follows from this that the density of liquid in equilibrium with vapour would then have to be a function of the time.

Cf. TRAVERS and USHER on variations of density in consequence of false equilibria.

differences found are to be ascribed to admixtures or to differences in the pressure or the temperature of the phases compared appeared already when KUENEN (Comm. n<sup>o</sup>. 11, Verslag Kon. Ak. v. Wet. May and June 1894) repeated GALITZINE's experiments (Wied. Ann. 50, 1893), and found but trifling differences remaining. Afterwards when DE HEEN (Bull. Ac. Belg. 3e S. t. XXXI '96) had again found the differences of density in question by another way, it was shown by repetition of his experiments at Leiden (Comm. N<sup>o</sup>. 68, These Proc. April 1901 p. 628 and p. 691), that also these differences of density vanish almost entirely for pure CO<sub>2</sub> when attention is paid to the differences of temperature. In the last few years, however, it has been particularly TEICHNER's<sup>1)</sup> experiments that have given new support to the opinion that after all these differences of density really exist (Drudes Ann. 13, 1904).

In the first place we have repeated DE HEEN's experiment in different ways. Already with the earlier repetition (1901) thermo-elements had been introduced for the determination of the difference in temperature of the two metal reservoirs of the apparatus, which were separated by a cock, the apparatus for the rest resembling that of DE HEEN as closely as possible. One of the thermo-elements, however, was damaged during the experiments. Though it could be ascertained that the differences in density even without correction for the temperature were considerably smaller than those found by DE HEEN, probably on account of the greater purity of the CO<sub>2</sub>, the exact amount of the difference remaining after temperature correction could not be determined. To replace these measurements by better ones a new, improved apparatus with thermo-elements was built, resembling for the rest DE HEEN's apparatus as closely as possible, and with this apparatus we made the observations communicated in § 3. They confirm that the differences in density derived by DE HEEN from his experiments do not exist for a pure substance when temperature and pressure are uniform<sup>2)</sup>.

<sup>1)</sup> In the TEICHNER's tube the same differences of density which GALITZINE and WILP (Congr. Intern. de Physique I 668, 1900) had found were shown by GILBERT-FARADAY's density-bulbs. What holds for TEICHNER's experiments applies therefore also to those of GALITZINE and WILP.

<sup>2)</sup> So if there exist processes as meant in p. 215 note 1, they pass so quickly that it is not possible to demonstrate them by methods which require that the equilibrium of pressure and temperature has first been established. As yet nothing has been found that points to the fact that the establishment of the temperature equilibrium is retarded an appreciable time on account of changes of energy which increase in course of time to a definite limiting value, the volume remaining constant.

It was demonstrated in Comm. N<sup>o</sup>. 68 that admixtures and differences of tem-

Further we have repeated TEICHNER's experiment<sup>1)</sup> with more precautions than had been taken by this observer. Especially a thermoelement (platinum-platinum-iridium not to sacrifice the security which the glass apparatus offers for the preservation of the purity of the substance) was adjusted in the upper and in the lower end of the TEICHNER tube, just as in DE HEEN's modified apparatus, to enable us to follow the differences of temperature in the tube.<sup>2)</sup> By using CO<sub>2</sub> for the experiment, a high degree of purity could be reached, and we came into a region where the temperature could be kept constant up to a very small amount.

If we wish to prevent diffusion between the higher phases and the lower ones, the modified TEICHNER tube (at least when not a capillary constriction has been made in it<sup>3)</sup>) is inferior to the modified apparatus of DE HEEN. Moreover when we wish to reach the equilibrium of temperature quickly, the bad conductivity of heat of the glass is a drawback, but it has the great advantage, that the changes of density can be observed at the same time with the other phenomena for the critical state. With regard to these phenomena TRAVERS and USHER (*Ztschr. f. phys. Chem.* 57, p. 365, 1906) and YOUNG (*ibid* p. 262) published important papers, after we had made the experiments mentioned in § 7. In the main points our observations agree with the descriptions given by TRAVERS and

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perature lead to systematic disturbances as in DE HEEN's experiments. Both give rise to disturbances of the same character. In the discussion of the influence of the differences of temperature the valuable paper by VILLARD *Ann. d. Ch. et d. Phys* (7) 10. 1897 has been overlooked there. That TEICHNER's results might be ascribed to small admixtures has appeared in details from the calculations by VERSCHAFFELT (*Comm. Suppl. n<sup>o</sup>. 10, (Dec. 1904).*

To the influence of admixtures on phenomena in the neighbourhood of the critical point attention has also been drawn by YOUNG *Journ. de Chim. Phys.* 4 (1906) p. 475. To this may be added that KEESOM, *Comm. No. 88, These Proc. Jan. 1904* p. 593 did not only consider the increase of the pressure during condensation with constant temperature as a proof of the presence of admixtures, but that it served him further to arrive at an opinion on the quantity of the admixture.

<sup>1)</sup> This was already mentioned *Comm. Suppl. No. 10 These Proc. Dec. 1904.* Lately TRAUBE strongly urged the advisability of a repetition.

<sup>2)</sup> In a CAGNIARD-LATOUR tube thermometers were fused by VILLARD. Our tube may just as well be called a VILLARD tube with density-bulbs as a TEICHNER tube with thermo-elements.

<sup>3)</sup> Such an apparatus, if necessary provided with a valve which is worked magnetically might be serviceable in the investigation of the variation of density with temperature. [After this was printed we noticed that the device of a capillary constriction was used by RAMSAY, *Proc. Roy. Soc.* 30 (1880) p. 327. Note added in the translation].

USHER and by YOUNG, and supplement them by giving the variations of the densities.

After what the repetitions of DE HEEN's experiments had taught us again about the asserted differences of density at the same pressure and the same temperature above the critical temperature, our repetition of TEICHNER's experiments has become rather a first contribution to the study of the variations of density with temperature and pressure by this way, than a refutation of the conclusions derived from TEICHNER's experiments. We have, however, been able to show sufficiently by our experiments that these conclusions are erroneous.

§ 2. *Repetition of one of DE HEEN's experiments.* As we can refer to Comm. n°. 68 with regard to the choice of the experiment which is to be repeated (on account of the systematic character of the deviations only one need be repeated), and as on another occasion a full description of the apparatus used and the different operations will be given, we think that the following remarks on the arrangement of the experiments will suffice here.

1. The pure carbonic acid was prepared by distillation. The admixtures are to be estimated at no more than 0,00027 ( cf. KEESOM Comm. N°. 88 II, § 2 and V § 10 These Proc. Jan. 1904). In the apparatus it comes into contact only with metal, glass, and cork (packings of this gave a perfect closure after having been repeatedly tightened during a week.).

2. The apparatus, the conduits, and the further auxiliary arrangements, among which also two metal bottles with the purified CO<sub>2</sub>, are all in connection with a mercury airpump. One of the bottles with pure CO<sub>2</sub> serves for rinsing. From the second the desired quantity is conveyed into the apparatus by distillation.

3. The density in every reservoir is determined by making the carbonic acid flow from it into a large reservoir with mercury manometer kept at constant temperature. In the volumetric calculations the corrections are applied according to the empiric equation of state V s. 1 of Comm. n°. 74 (Arch. Néerl. (2) 6, 1901). Errors in the density caused by leakages in the reservoirs at high pressure are excluded. It was ascertained by separate control experiments that the total amount of CO<sub>2</sub> in the apparatus remained unchanged during the experiments.

4. The apparatus was kept at uniform constant temperature by means of flowing water, a xylene thermoregulator (see Comm. N°. 70 III § 3 These Proc. May 1901) and a valve stirrer (see Comm.

N<sup>o</sup>. 83 III § 4 These Proc. Febr. 1903). Sufficient precautions were taken to prevent conduction of heat from outside to parts of the apparatus.

§ 3. *Variations of density found in the repetition of the experiment of DE HEEN after correction of the difference in temperature of the reservoirs.*

DE HEEN brings the temperature of the two reservoirs (see § 2 beginning) from 28° to about 35° C, and opens the cock between them 6 times four seconds during the heating; then when the temperature has become constant at about 35°, he opens the cock once more 6 times 4 seconds. Then he assumes that temperature and pressure are the same in the two reservoirs.

When repeating the experiment (being very careful to prevent drops from being scattered from one reservoir into the other) we found confirmed by reading the thermo-elements (nickel-iron), what was observed in Comm. N<sup>o</sup>. 68 viz. that every time when the cock between is opened for adjustment of pressure, a difference of temperature arises between the two reservoirs, and that when closing the cock at the end of the experiment a difference of temperature remains, which must be taken into account.

In order to find out in how far the equilibrium of temperature and pressure has been reached, we have in the first place made three determinations, in which the cock was opened respectively 2, 4, and 6 seconds every time (probably our cock allowed comparatively less substance to pass than that of DE HEEN). The results have been given in the following table:  $v$  denotes the upper,  $l$  the lower reservoir, so  $\rho_l$  is the density in the lower reservoir; the numbers of times the cock was opened during the heating (distributed over 15 minutes) and then at constant temperature (distributed over half an hour) have been separately given;  $\rho'_l$  is  $\rho_l$  corrected for  $t_v - t_l$ .

SERIES I.

Establishment of the equilibrium by opening the cock	$\rho_v$	$\rho_l$	$\rho_l/\rho_v$	$t_v$	$t_v - t_l$	Corrected for difference of temperature	
						$\rho'_l$	$\rho'_l/\rho_v$
6 times 2 + 6 times 2 sec.	0.418	0.506	1.21	34.25	0.27	0.456	1.09
6 times 4 + 6 times 4 sec.	0.424	0.495	1.17	34.40	0.22	0.454	1.08
6 times 6 + 6 times 6 sec.	0.427	0.489	1.15	34.20	0.16	0.456	1.07
6 times 6 + 6 times 6 sec.	0.437	0.501	1.15	34.30	0.20	0.466	1.07

The temperature corrections have been borrowed from the graphical representation derived in Comm. N<sup>o</sup>. 68 from AMAGAT's determinations. The uncertainty which still prevails with respect to the correct course of the isotherms in the neighbourhood of the critical state is, of course, also found in these corrections.

The rather rapid process of the heating from 28° to 35° prevents further that the whole apparatus has already assumed the temperature of the waterbath, so that also the observed differences of temperature themselves are not quite certain.

In the following series of determinations we proceeded in the same way till the 12<sup>th</sup> opening (the 6<sup>th</sup> at constant temperature). It was put off for 3 hours. When the cock was opened the course of the deviations of the galvanometer appeared to be the same as in the preceding series; the remaining temperature corrections, however, were somewhat smaller than in the 1<sup>st</sup> series, which we ascribe to this that all parts of the apparatus have had time to assume the temperature of the waterbath. An increase of pressure in the lower reservoir, which should have been found when e. g. in this lower reservoir molecules were dissociated during these three hours (see § 1, p. 216 footnote 2), and which should have given rise to a greater galvanometer deviation when the cock was opened for the last time, could not be traced. We found:

## SERIES II.

Establishment of the equilibrium by opening the cock	$p_v$	$p_l$	$p_l/p_v$	$t_v$	$t_v - t_l$	Corrected for difference of temperature	
						$p'_l$	$p'_l/p_v$
6 + 5 + 1 time 2 sec.	0 430	0 497	1.16	34° 55	0° 20	0.466	1 08
6 + 5 + 1 „ 4 sec.	0 440	0.489	1 11	34 85	0 16	0 456	1 04
6 + 5 + 1 „ 6 sec.	0 439	0.485	1.10	34 40	0.15	0.452	1 03

In virtue of what the preceding determinations had taught us as to the reaching of equilibrium of temperature and pressure the cock was opened 12 times 12 seconds in a following determination, and finally two more determinations were made in which the cock was opened 12 times 4 seconds and at last once five minutes. We found:

## SERIES III.

Establishment of the equilibrium by opening the cock	$p_v$	$p_l$	$p_l/p_v$	$t_v$	$t_v - t_l$	Corrected for differences of the temperature	
						$p'_l$	$p'_l/p_v$
6 + 6 times 12 seconds	0.446	0.488	1.09	34.70	0.20	0.456	1.02
6 + 6 times 4 sec. } at last 5 minutes }	0.427	0.445	1.04	34.05	0.06	0.422	1.01
	0.462	0.478	1.03	34.00	0.06	0.467	1.01

From this follows that as the equilibrium of pressure and temperature is obtained better, the densities of the phases become more and more equal, and that at last after the application of the temperature correction only very small differences remain.

The much more considerable deviations found by DE HEEN ( $\rho_l/\rho_v = 1.19$ , see Comm. No. 68) must, therefore, be attributed to admixtures and differences of temperature. <sup>1) 2)</sup>

§ 4. *Example of differences of density as found by DE HEEN, caused by a slight impurity of the CO<sub>2</sub>.*

The great influence of small quantities of admixture is very convincingly shown by the following results.

In a group of determinations ending with a repetition of experiment 2 Series I we found:

Establishment of the equilibrium by opening the cock	$p_v$	$p_l$	$p_l/p_v$
6 + 6 times 4 sec.	0.392	0.531	1.35

It appeared that in consequence of carelessness in the cleaning after it had been repaired, in the metal bottle in which the pure

<sup>1)</sup> That during the opening of the cock no important exchange of liquidogeneous and gasogeneous molecules between the upper and the lower reservoir can have taken place (to use the terminology of DE HEEN), appears from this, that when the upper reservoir was filled with air and the lower reservoir with air with 31 pCt. CO<sub>2</sub>, and the equilibrium was established without the cock being opened, after the cock had been opened for 5 minutes, only 0,33 percent of CO<sub>2</sub> had passed into the upper reservoir.

<sup>2)</sup> They give both systematic errors of the same character (cf. § 1 p. 2 note 1 above).

carbonic acid was kept, a trace of oil had been left which had diffused in the carbonic acid. When we thought that the whole apparatus had been sufficiently cleaned by blowing pure carbonic acid through it, we found:

Establishment of the equilibrium by opening the cock	$p_v$	$p_l$	$p_l/p_v$
Only 6 times 4 sec. during the rise of the temperature.	0.385	0.555	
6 + 3 times 4 sec.	0.399	0.521	1.30
6 + 6 times 4 sec.	0.417	0.505	1.21

which by the side of Series I and II gives at the same time an idea with what degree of approximation equilibrium of pressure is reached by the repeated opening of the cock. Repeating the last determination after continued blowing we found:

$$6 + 6 \text{ times } 4 \text{ sec.} \quad | \quad 0.426 \quad | \quad 0.496 \quad | \quad 1.19$$

The last observation harmonizes pretty well with Series 1 N<sup>o</sup>. 2, of which it is a repetition, the same deflections of the galvanometer being moreover found. It leads to the same  $p_l/p_v$ .

It appears how misleading even the presence of slight impurities may be, and that in Comm. N<sup>o</sup>. 68 the leather packings have been justly called a fundamental defect of DE HEEN's apparatus (cf. 1 § 2 above).

§ 5 *Correction for gravity and for slight admixtures in the experiment of DE HEEN. Result.*

In order to be able to calculate the correction which is to be applied to  $p_l/p_v$  for gravity, we must know the density as function of the level in a column of pure CO<sub>2</sub>. The accurate shape of the isotherms in the critical state being very uncertain <sup>1)</sup>, this function is not accurately known. GOUY has taken SARRAU's equation of state as basis for his calculation. We have started from the equation of state V s. 1 of Comm. N<sup>o</sup>. 74. Only 0,0002 was found for the correction at 34° and 8 c.M. difference of level, so that it may be neglected. As to the correction for the admixtures for the CO<sub>2</sub>, when we put their amount as given in § 2, at 0,00027, it becomes

<sup>1)</sup> It is just to the knowledge of this shape that observations as made in § 3 and § 7 may contribute.

1 % à 1,5 % at 34°.5 according to the calculations of VERSCHAFFELT, Comm. Suppl. N°. 10. If the uncertainty of this correction is taken into account, we must come to the conclusion, the limit of accuracy of our experiments not being higher than 1 % either, that the differences of density derived by DE HEEN from his experiments do not exist for pure CO<sub>2</sub> when sufficient care is taken to ensure equilibrium of pressure and temperature.

§ 6. *Repetition of TEICHNER's experiment.* An elaborate description of the apparatus and the operations will be given on another occasion. Here the following remarks may suffice:

1. Repetition with CO<sub>2</sub> was considered to be desirable also by TEICHNER because it gives more warrants for purity.

2. A platinum-platinum-iridium thermo-element (used with a magnetically protected galvanometer of DUBOIS) was successfully fused into TEICHNER's tube at the top and at the lower end, so that the tube remained proof against a pressure of 150 atmospheres. However we did not succeed in making the thermo-elements free from disturbing electromotive forces, nor did they give with certainty the accuracy of 0°.01 we wished. The places of contact were found at  $\frac{1}{4}$  and  $\frac{3}{4}$  of the height of the tube. A third thermo-element to compare the temperature in the tube with that in the bath would be desirable.

3. The critical density of CO<sub>2</sub>, 0.469 <sup>1)</sup>, being smaller than that of CCl<sub>4</sub>, with which substance TEICHNER worked, it was much more difficult to obtain the required density-bulbs (small glass bulbs) of 0.365, 0.390 and 0.405. We owe them as well as the fusion of the thermo-elements to the skill of Mr. O. KESSELRING, chief of the glass-blowing department of the laboratory. By means of CLEBSCH's formula it was found that the decrease of volume of the bulbs at the highest pressures can only amount to from  $\frac{1}{600}$  to  $\frac{1}{400}$ .

4. Still greater care was devoted to the purification of the CO<sub>2</sub> than in the repetition of DE HEEN's experiment. From a metal bottle of CO<sub>2</sub> as used for the latter,  $\frac{1}{3}$  is once more blown off, and then  $\frac{1}{3}$  distilled over into a second bottle from which under weighing, so much is suffered to escape that a fixed quantity remains. This second bottle is connected by glass tubes with the experimental tube, a mercury manometer, a mercury airpump and an auxiliary bottle (also of metal) with pure CO<sub>2</sub> for rinsing the conduits, after which the fixed quantity which it contains, is quite distilled over into the

<sup>1)</sup> Derived by KEESOM Comm. N°. 88 These Proc. Jan. 1904, p. 574, from his observations by means of the rule of the rectilinear diameter.

experimental tube, the latter being immersed in liquid air; at last the experimental tube, still immersed in liquid air, is connected with the mercury airpump, and fused off. By weighing it is ascertained that the desired quantity has been transferred to the experimental tube.

5. A mode of heating which does not give rise to convection currents inside the tube, is considered of great importance also by TEICHNER and TRAUBE, to prevent mixing of what is at the upper end and what is at the lower end of the tube. TEICHNER does not accept YOUNG's refutation of his experiments (see TEICHNER, loc. cit.) because in YOUNG's apparatus convection currents are not so well prevented as in that of himself. The thermostat used by us, however, satisfies much higher demands than that of TEICHNER. The tube is immersed in a liquid bath in a double walled non-silvered vacuum-glass which is hermetically closed with a badly conducting lid. The glass is provided with a valve-stirrer and an arrangement to heat the bath electrically from above, and is itself again immersed in a bath with double glass walls, which is likewise provided with a valve-stirrer. With the exception of two windows, the space between these two walls is filled with cotton wool, by which the outer wall too is surrounded. Like the bath in which the improved apparatus of DE HEEN (§ 2) was placed, the outer bath was kept at constant temperature (up to  $0^{\circ},02$ ) by flowing water with the aid of a xylene thermoregulator (§ 2). In this way the temperature of the bath in which the experimental tube is, can be kept constant up to  $0^{\circ},002$ . The heating takes place according to the indication of thermometers divided into  $50^{\text{th}}$  of a degree, which are placed in the inner and in the outer bath, and is regulated in such a way that everything that might give rise to convection currents is as much as possible avoided.

6. When manipulated the tube was always efficiently shielded for the protection of the observer.

§ 7. *Observations.* The bulbs correspond with the densities 0.365, 0.390, 0.405, 0.421, 0.443, 0.450, 0.466, 0.483, and 0.510.

The position of the bulbs and that of the meniscus (indicated in what follows by the read number of the mark of division between [ ]) was read on a millimeter scale etched on the tube; in the middle of the tube the mark 30 is found, the zero point is 20 mm. above the bottom.

In the *first experiment* the heating took place very slowly; at first also the inner bath was (electrically) heated,  $t$  refers to the outer bath,  $t_i$  to the inner one. After three hours small gas bubbles were seen to rise from the downmost thermo-element, probably

caused by conduction of heat along the threads, in consequence of  $t_e$  having increased too much. We observed:

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time	$t_e$	$t_i$	men.
11 <sup>h</sup>	27° 8	27° 15	[31]
11 30		27.92	
12 20		30.00	
12 25	30.4	30.39	the rising of the gas bubbles has finished, the bulbs begin to show a tendency to divide
12 30		30.69	0.365 rises
12 33		30.83	0.365 at 33
12 36		30.88	[33] 0.510 begins to descend slowly to 25
		30.94	0.510 at 5
		30.99	0.510 on the bottom
			the separate (electrical) heating of the inner bath is stopped,
12 40	31.00	31.00	0.365 at 36
			0.483 begins to descend
12 44		31.00	[34] 0.365 between 38 and 39
			0.483 ,, 21 and 22
			$t_i$ rises very slowly whereas $t_e$ was all the time kept somewhat higher to 2 <sup>h</sup> .50
12 48			0.483 between 10 and 11
			0.365 rises to the top with accelerated motion
			0.483 continues to descend very slowly
12 52			[34.5] 0.483 has arrived at the bottom
			all except 0.510, 0.483, and 0.365 in meniscus
1			[35] 0.390 begins to rise
1 3			0.390 between 37 and 38 with 0.405 by its side somewhat lower
1 10			0.390 between 38 and 39 with 0.421 below it in a slanting direction
1 15			[35] 0.421 begins to rise, for the rest like 1 <sup>h</sup> 10'.

Looking from the top downward in a slanting direction through the tube we observe a slight grey mist which is denser in the part below the meniscus. When we look straight through the tube, with a light behind the tube, the whole shows a light brown colour, which is somewhat darker under the meniscus.

The bulbs continue to move slowly apart, the rising ones

moving faster than the descending ones, and the velocity of the rising bulbs increasing as they get higher, the same thing taking place though in a smaller degree with the descending ones.

- 2<sup>h</sup>15 31.032 the meniscus has gradually got fainter and is hardly to be distinguished, only a slight constriction of the light band is to be perceived at 35.
- 2 20 31.036 0.421 between 42 and 43  
0.443 „ 36 and 37  
0.450 „ 34 and 35  
0.466 „ 32 and 33
- 2 50 31.22 the outer bath is further kept at this temperature
- 2 50 31.050 the rise of the temperature of the inner bath is now exceedingly regular
- 4 30 31.096 0.443 in the middle of 53  
0.450 between 32 and 33  
0.466 „ 24 and 25

The mist in the tube is now equally dense everywhere, and becomes gradually less, the moving apart of the three still descending bulbs continues slowly and regularly

- 8 7 31.210 0.466 lies just on the bottom  
0.450 between 36 and 37; has risen 4 mm in 2<sup>h</sup>15' and so shows a tendency to move to the top.
- 8 10 The cooling takes place by reducing the outer bath to a lower temperature
- 8 30 31.133 0.466 begins to rise from the bottom  
0.450 at the same place
- 8 35 Throughout the tube a bluish mist appears
- 8 40 This mist gets denser
- 8 50 At [15] a thick milky white mist is formed, which spreads rapidly upwards and downwards.

30.984 At [10] the meniscus appears. From the upper place of contact of the thermo-elements drops fall down, from the lower place of contact smaller gas bubbles rise upwards. (The cooling proceeds too rapidly). The meniscus rises, 3 bulbs fall quickly into it from above, and 1 rises towards it from the bottom.

The differences of temperature within the tube were found to be between 0°.02 and 0°.03, but in consequence of disturbances they were often not to be observed. In the observation of 8<sup>h</sup>7 they were no more than 0°.01.

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In the *second experiment* the heating took place somewhat more rapidly. In 1<sup>h</sup>10' the inner bath was brought at  
 9<sup>h</sup> 10' 29°.99 The separation of the bulbs has, of course, not advanced so far as in the first observation, and the deflections of the galvanometer were larger. The tube remained now farther behind the temperature of the waterbath.  
 9 40 31.60 [36] The meniscus is still dimly to be distinguished here, and a thin light mist is visible through the whole tube. Under the meniscus a somewhat darker band of a light brown colour is seen.

The position of the bulbs is now

0.365 at the top

0.390 between 43 and 44

0.405 „ 42 and 43

0.421 in the middle 41

0.443 „ „ „ 40

0.450 „ „ „ 39

0.466 between 37 and 38

0.483 and 0.510 on the bottom.

31.7 0.390 and 0.405 now go very rapidly to the top followed by 0.421.

At the place of the meniscus now only a slight constriction and a light brown mist band are to be perceived.

10 45 31.900 The temperature is then kept constant till 11<sup>h</sup>37 with no greater deviation than 0°.004 and then from

11 37 31.888 till 2<sup>h</sup>15 with no more deviation than 0°.002.

2 15 The mist has now entirely vanished and the bulbs are all apart.

0.510, 0.483, 0.466 on the bottom

0.450 and further ones in the top, none

of the bulbs remain suspended in the body

of the tube; the bulb 0.450 was the

last to go to the top, whereas 0.466 had

already been on the bottom for some time.

A difference of temperature is no longer to be perceived.

At first the cooling took place more slowly.

3 31.550 A slight mist is perceived

3 45 31.040 the mist has become distinctly denser.

5 10 30.985 [5]. In this position the meniscus originates in a milky cloud in the lower part of the tube. Further the lowering of the temperature proceeds too rapidly.



TRAVERS and USHER and YOUNG <sup>1)</sup>, must be deferred to a later occasion. However, some conclusions are obvious.

As the temperature rises more slowly and the equilibrium in the tube is better reached, we can get nearer to equality of density of the vapour and liquid phases. We think we found a smaller difference in density in our measurements than any of the observers before us <sup>2)</sup>.

We did so in the third experiment. The critical temperature was then fixed between 30°.984 and 30°.986 <sup>3)</sup>. That at 30°.984 only a small difference in density existed between liquid and vapour appears as follows: When the meniscus appeared we found 0.443 for the density of the vapour at the height 35. So we estimate the density at 0.452 at the height of the meniscus (25) according to the correction of § 5 (doubtful); bulb 0.450, however, floats on the meniscus. The density on the bottom is < 0.483 (height (see § 7 beginning) 5 cm. under 30), so we estimate the density of the liquid at 0.468 at the height of the meniscus; bulb 0.466 floats. Vapour and liquid differ, therefore, certainly less than  $\frac{1}{10}$ , and probably no more than  $\frac{1}{20}$  in density. In the first experiment we found  $\rho_v > 0.421$ ,  $\rho_l < 0.483$  from which  $\rho_v > 0.430$ ,  $\rho_l < 0.468$  follow with the estimated correction for gravity; so under these less favourable circumstances a difference of less than  $\frac{1}{10}$  is most likely realized. These results concerning the closer and closer approach of the density of liquid and vapour, which quite agree with the views of ANDREWS-VAN DER WAALS, deprive the much larger differences of phases at the same temperature and pressure above the critical temperature, which TEICHNER derives from his experiments, of all importance <sup>4)</sup>.

<sup>1)</sup> This includes the discussion of the mist stage of von WESENDONCK, which would constitute the transition stage in the neighbourhood of the critical state, and which in any case can only extend over a small part of the region of density and temperature where a mist can be seen.

<sup>2)</sup> YOUNG, Journ. Chem. Soc. 71 (1897) p. 455 stated at 0°.05 below the critical temperature a difference of 14% between the liquid and vapour densities. [Note added in the translation].

<sup>3)</sup> The readings of the temperature have been reduced to those on a thermometer which had been controlled with an air thermometer accurate up to 0°.01 by the Phys. Tech. Reichsanstalt. Our result agrees with that of KEESOM, 30°.98 (Comm. N°. 88 see above), made with the same thermometer. Moreover, besides and after the determinations of the critical temperature of CO<sub>2</sub> cited in LANDOLT-BORNSTEIN-MEYERHOFFER's Phys. Chem. Tables are to be mentioned: VERSCHAFFELT Zitt. Versl Juni '96 (31°.0), von WESENDONCK Verh. d. Deutsch. Phys. Ges. 5 p. 238 (30°.95), BRINKMAN Diss. Amsterdam 1904 (31°.12).

<sup>4)</sup> It is true we might assume that the equilibrium of liquid and vapour with so slight a difference of density as we observed, is only reached after so long a time as was allowed in this experiment to obtain equilibrium of temperature and that at first states with greater difference of density of liquid and vapour (cf. note 1 p. 1 § 1) appear at the same temperature, which gradually pass into the final

It is in harmony with this that a tolerably sharply defined critical density can be assigned. We derive 0.460 from the density of vapour and liquid in the third experiment for it, which agrees with the mean which would follow from experiment 1 at  $2^{\text{h}}15$ , i.e. 0.450, and 0.470, derived from experiment 3 on account of the appearance of the meniscus at 25 (cf. further § 6 p. 223 footnote 1).

Differences of density as TEICHNER finds, were also found by us; it was in the second experiment at the moment that the meniscus disappears with comparatively rapidly rising temperature. However, after the tube has been kept at the same temperature above the critical temperature for 3 hours, and the temperature in the tube has become uniform probably up to less than  $0^{\circ},01$   $0^{\circ},9$  above the critical temperature, they have been reduced to less than 0,466 -- 0,450, or less than 3,5 %, i. e. after correction for gravity  $< 3,3$  % over 10 cm.

The remaining difference in the first experiment  $0^{\circ},23$  above the critical temperature after 6 hours' heating above the critical temperature can be derived from the fact that bulb 0.450 floats 5.6 cm. above 0,466. This difference is no more than 3,5 %, and corrected for gravity 2,9 %.

From VERSCHAFFELT's calculations follows that at  $0^{\circ},23$  above the critical temperature 0,0001 molecule of admixture may cause about 12 % difference of density. Differences of temperature and admixtures which may account for remaining differences such as those just treated are scarcely to be avoided even with the precautions taken by us.

Nothing has been observed of an "Entmischung" by cooling when the critical temperature is approached, as TRAUBE l.c. p. 477 mentions.

TEICHNER observed that, after the disappearance of the meniscus, at the place where it was found last a transition zone exists towards which the differences of density concentrate, whereas outside it the changes are only insignificant. In our observations the contrary appeared, and the changes in density continue regularly with increase of temperature, only the motion of the bulbs was slightly accelerated as they approach the top of the tube, and they cover the last 1 or 2 cm. very rapidly. In a less degree but in the same way this takes place with the bulbs which descended. We consider these phenomena to be connected with heating and cooling of phases by compression and expansion <sup>1)</sup>.

state with simultaneous change of the pressure of coexistence (cf. note 1 p. 1 § 1). But the absence of subsequent rise of pressure in the repetition of DE HEEN's experiment (see § 3) has taught us, that already after a very short time after-changes of the density no longer occur.

<sup>1)</sup> They just as the "Entmischung" assign that the temperature differences within the tube in the experiments of TEICHNER were probably greater than in ours. [Note added in the English translation].

**Physics.** — “Contributions to the knowledge of the  $\psi$ -surface of VAN DER WAALS. XV. The case that one component is a gas without cohesion with molecules which have extension. Limited miscibility of two gases.” (Continuation). By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Supplement N<sup>o</sup>. 15 to the Communications from the Physical Laboratory at Leiden.

(Communicated in the meeting of May 24, 1907).

§ 8. *On the temperatures and the pressures on the gas-gasplait.* In order to form a provisional opinion as to the experimental conditions which must be satisfied that limited miscibility in the gas state may be observed, and to be able to derive what pairs of substances must be considered suitable for this purpose, it is desirable to examine for some cases what temperatures and pressures occur on the gas-gasplait<sup>1)</sup>. In the case (§ 2, March '07) of a component without cohesion<sup>2)</sup> or almost without cohesion ( $m < m_1$ , see § 7), the gas-gasplait will occur for all temperatures between the critical temperature of the less volatile component and the critical temperature of complete miscibility<sup>3)</sup>. Its pressures will then be larger than

<sup>1)</sup> In our opinion Mr. VAN LAAR (These Proc. May '07, p. 35, note 2) is wrong in thinking that in the case of a three-phase-equilibrium, as e.g. in the system water ether, our terminology with regard to the distinction between gas and liquid does not agree with that used by VAN DER WAALS. According to what has been said about this distinction in § 4, for a three phase equilibrium of a system of the type water-ether the denser phase which is rich in water, *must* be called liquid as belonging to the liquid branch of the connode, just as the less dense phase which is rich in ether, *must* be called gas phase; whether the denser phase which is rich in ether is to be called liquid or gas, is not determined by the principle of the continuity of the phase along the connode; if the reduced temperatures at which this phase appears, are taken into account, also the last mentioned phase will be called liquid for the system ether-water in accordance with what has been said in § 4.

<sup>2)</sup> The second branch of the plaitpoint curve in Fig. 1 § 2 (These Proc. March '07, p. 787), about which VAN LAAR speaks in These Proc. May '07, p. 36, has there ( $a_{32} = 0$ ) contracted to a point  $x = 1$ ,  $v = b_{32}$ . It is true that in the case of our § 7 (Plate II, These Proc. March '07) a second branch of the plaitpoint curve occurs, but it has been explicitly stated there (p. 795 at the bottom and p. 797) that we did not discuss the spinodal curves at the lower temperatures at which this branch of the plaitpoint curve makes its influence felt, referring inter alia with a view to these temperatures to VAN LAAR's papers.

<sup>3)</sup> As mentioned in § 1 this idea was introduced by VAN DER WAALS, who also gave the formulae for the calculation of this temperature (VAN LAAR calls it “third critical temperature”).

the critical pressure of the least volatile component. If the suppositions mentioned in § 2 might be applied for this, and the values of  $a_M$  and  $b_M$  for He might be borrowed from Comm. N°. 96<sup>c</sup>, Febr.-'07, p. 660 footnote 2, so that  $a_{MHe} = 1/176 a_{MH_2} = 0.000024$  and  $b_{MHe} = 1/2 b_{MH_2} = 0.00044$ , this case would be realized for mixtures of He and water<sup>1)</sup>. Then we should find  $T_{km} = 1.056 T_{k1}$ , so that the gas-gasplait would occur over a range of temperature of 36° above 365° C., and at pressures above 195 à 200 atms.

In the case that the molecules of the least volatile component act on each other feebly, but still exert such an attraction that a double plaitpoint<sup>2)</sup> occurs in the net of the spinodal curves, the pressure in this plaitpoint and its temperature in connection with the critical temperature of complete miscibility give important indications as to the pressures and temperatures of the gas-gasplait.

In table II these data, calculated for the case that the suppositions

T A B L E II.

Pair of substances	$T_{km}/T_{k1}$	$T_{dpl}/T_{k1}$	$T_{dpl}/T_{kx}$	$p_{dpl}/p_{k1}$
Hydrogen-helium	0.933	0.915	4.44	41.6
Oxygen-helium	0.962	0.957	8.64	61.3
Argon-helium	0.970	0.962	7.90	64.5
Neon-helium	1.007	0.961	3.72	18.8
NO-helium	1.031	0.991	3.76	13.1
NH <sub>3</sub> -helium	1.009	0.969	6.20	25.2
H <sub>2</sub> S-helium	0.972	0.970	13.79	171
CO <sub>2</sub> -helium	0.9540	0.9536	15.89	1045

<sup>1)</sup> The  $a_M$  and  $b_M$  for water have been borrowed from LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen.

<sup>2)</sup> The appearance of a double plaitpoint near  $K_m$  was already observed by VAN LAAR (These Proc. May 1905 p. 42). The conditions for its appearance, however, were not correctly defined by him (cf. § 9 II). In view of this latter fact we thought that we drew sufficient attention to this result of VAN LAAR by referring the reader to VAN LAAR's papers. (see p. 797 footnote 1). The detaching of a longitudinal plait at high temperatures, which leaves the  $\psi$ -surface with its open side turned to  $v = b$ , follows immediately (see These Proc. April '07 p. 848 footnote) from the general considerations and calculations of VAN DER WAALS Cont. II § 19 sqq. and VAN DER WAALS' diagram in Zittingsverslag Kon. Akad. Nov. 1894 p. 133, when the case  $\alpha$ ) cf. § 9. I, a case which VAN LAAR has not included in his considerations, does not occur.

mentioned in § 2 might be applied, have been given for some helium mixtures.  $T_{km}$  has here been calculated according to VAN DER WAALS Cont. II, p. 43 (cf. § 6),  $T_{dpl}$  according to the formula mentioned in § 7,  $p_{dpl}$  from the equation of state with the just mentioned  $T_{dpl}$  and the  $v_{dpl}$  also represented in formula in § 7<sup>1)</sup>.

The reduced temperature of the double plaitpoint  $T_{dpl}/T_{cx}$ , mentioned in this table, gives an idea in how far the phases in its neighbourhood behave as compressed gas-phases.

The values of  $a$  and  $b$  of the different components have been borrowed from KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOFFER'S Physik. Chem. Tabellen; for those of helium see above; for neon we have made use of the ratio of its refractive power<sup>2)</sup> to that of helium according to the determinations of RAMSAY and TRAVERS<sup>3)</sup>, and of the estimation concerning the critical temperature by TRAVERS, SENTER and JAQUEROD<sup>4)</sup>.

It appears from table II that when the gas-gasplait can make its appearance, the range of temperature within which this is the case (between  $T_{km}$  and  $T_{dpl}$ ), on the mentioned suppositions is small for most of these pairs of substances, for some even exceedingly narrow.

For the pressures on the gasplait higher values than  $p_{dpl}$  will have

<sup>1)</sup> Though originally we did not consider the developments which led us to the explicit expressions for the double plaitpoint mentioned These Proc. March '07 pp. 796 and 798 of sufficient importance, now that VAN LAAR (see These Proc. May '07 p. 41) thinks the derivation of such like expressions impossible there is a reason for communicating them on a following occasion.

<sup>2)</sup> HAPPEL, Habilitationsschrift Tübingen 1906, p. 30, found that the refractive power for argon, krypton and xenon would yield values for  $b$  which greatly deviate from the  $b$ 's derived from the critical data. When according to the principle of the corresponding states (cf. HAPPEL loc. cit. p. 31, note 1) we compare the ratios of the refractive powers for these gases with those of their critical volumes (derived from  $p_k$  and  $T_k$ ) the deviations are far less considerable. So with regard to this property, these one-atomic gases form a group, just as is the case with the bi-atomic and with a great many more-atomic substances (GUYE, Journ. de phys. (2) 9 (1890) p. 312).

<sup>3)</sup> RAMSAY and TRAVERS, Phil. Trans. A197 (1900) p. 81. Yet we must remark that when comparing this ratio for helium and argon according to RAMSAY and TRAVERS with the ratio of  $b_{He}$  according to our estimation and  $b_A$  derived from  $p_k$  and  $T_k$ , we should find an important deviation (cf. note 1). Also in view of this the data concerning mixtures of helium and neon are very uncertain.

<sup>4)</sup> TRAVERS, SENTER and JAQUEROD, Phil. Trans. A 200 (1902) p. 177. Their views, however, on a connection between atomic weight and critical temperature lead to an unlikely result for the critical temperature of helium.

The determinations of isotherms of neon by RAMSAY and TRAVERS, loc. cit. have been of as little use to us as those of helium for the determination of  $a$  and  $b$  (different particulars in the course of the isotherms of the one-atomic gases given by these scientists in plate 2 loc. cit. do not seem very probable to us).

to be expected as a rule. Thus it appears from table II that these pressures become very high, if the circumstances are not very favourable.

It would have a very favourable influence on the circumstances of temperature and pressure at which limited miscibility in the gas state might be observed, if it should prove that for mixtures of helium with another gas  $a_{12M}$  is smaller than is expressed by  $\sqrt{a_{11M} a_{22M}}$ <sup>1)</sup>.

§ 9. *Mr. VAN LAAR's remarks*, (These Proc. May '07 p. 34—46) which imply that we have set forth some of our results as new, whereas they had been already derived and published by him before, compel us to the following explanations in order to show the incorrectness of these assertions.

I. As to part of these observations, they are best refuted by shortly repeating the train of thought followed by us.

When we applied the equations laid down by VAN DER WAALS with regard to the spinodal curve<sup>2)</sup> in Cont. II, § 19 sqq., transferred to the  $\psi$ -surface for the unity of weight, to the case that one of the components is a gas without cohesion<sup>3)</sup> with molecules which have extension, we arrived on the suppositions<sup>4)</sup> mentioned in § 2 at a *plait which starts from the side of the small volumes, comes*

1) These Proc. March '07 p. 796 note 1, and VAN DER WAALS These Proc. April '07 p. 831.

2) The equation for the spinodal curve of the molecular  $\psi$ -surface (cf. VAN LAAR These Proc. May '07 p. 37 at the top) was given by VAN DER WAALS in Cont. II. p. 45, equation (1) in a form which after substitution of  $\frac{da}{dx}$ ,  $\frac{db}{dx}$  and  $\frac{d^2a}{dx^2}$  passes immediately into that used by VAN LAAR. (See VAN LAAR, These Proc. May '05 p. 33 at the bottom). The equation given by us p. 788 referred to and was derived from the equation for the  $\psi$ -surface for the unity of weight (These Proc. Dec. '06 p. 510). For the rest we differ from the opinion repeatedly expressed by VAN LAAR (inter alia These Proc. May '05 p. 34), that it would be more difficult and more elaborate to derive the equation of the spinodal curve and also that of the plaitpoint curve from the  $\psi$ -function than to do the same from the  $Z$ -function.

3) This investigation was announced in Comm. No. 96b, Dec. '06 p. 502.

4) When we were not allowed to put  $\frac{\partial^2 b}{\partial x^2} = 0$  for and in the immediate neighbourhood of  $v = b$ , as we did (cf. VAN DER WAALS Cont. II p. 42), the spinodal curve will always be closed towards the side  $v = b$  as VAN DER WAALS observes l.c. and These Proc. April '07 p. 848. It is then to be expected, at least for small  $\frac{\partial^2 b}{\partial x^2}$ , that the plait in question makes its appearance for the first time at a maximum plaitpoint temperature, and for the rest extends to the large  $v$ 's in the same way as the plait described here.

into contact with the line  $x = 0$  at a certain temperature, and crosses in a slanting direction from  $v = b$  to the side  $x = 0$  at lower temperature (§ 2 These Proc. March '07 p. 787). Comparison of this result with VAN LAAR's papers induced us then to cite (p. 786 footnote 1) that the latter already treated the projection of the plaitpoint curve on the  $v, x$ -plane for the case of a gas without cohesion, but without further investigating the shape of the spinodal curve and of the plait for this case. Now that VAN LAAR (These Proc. May '07 p. 35) says: "The case that a plait starts from  $C_0$ <sup>1)</sup> to  $C_2$ <sup>2)</sup>, or also at the same time from  $C_2$  to  $C_0$  (when there is a minimum temperature in the plaitpoint line) is not new (see KAMERLINGH ONNES and KEESOM, p. 788 below), but has been before described and calculated by me in all particulars", we have once more looked through his papers.

It would have been good if Mr. VAN LAAR had indicated the place where we had to look for this description of the plait treated in § 2 and indicated by VAN LAAR in the italicized words (the italics are ours); we have not been able to find this description in his preceding papers even on this renewed careful perusal<sup>3)</sup>.

That the shape of the plait described by us occurs for temperatures above the critical temperature of the least volatile component led us to the considerations on limited miscibility in the gas state mentioned in § 3 sqq.

Always availing ourselves of the above mentioned equations of VAN DER WAALS, we examined then if also with  $a_{22} > 0$  such a plait may occur for values as they are to be expected for mixtures with helium. We saw in § 7 (These Proc. March '07 p. 795) that for the case of the plaitpoint curve running from  $K_1$  to  $K_m$  (called type I by VAN LAAR) 3 cases are to be distinguished: *a*) that with falling temperature the plaitpoint gets from  $K_m$  on the  $\psi$ -surface, and proceeds regularly towards  $K_1$ ; *b*) that with falling temperature a plaitpoint coming from  $K_m$  and one coming from  $K_1$  unite to a double plaitpoint; *c*) that the plaitpoint gets from  $K_1$  on the  $\psi$ -surface and proceeds regularly towards  $K_m$  (without double plaitpoint with minimum

1) Our  $K_m$ .

2) Our  $K_1$ .

3) On the contrary he says in his paper These Proc. Sept. 1906 p. 231 (cf. VAN LAAR, These Proc. May 1905, p. 42 at the bottom): "In former papers it has been demonstrated that in the neighbourhood of  $C_0$  a minimum plaitpoint temperature makes its appearance both with type I in the line  $C_0C_2$  and with type II in the line  $C_0A$ , and that therefore with decrease of temperature a *separate plait* begins to detach itself starting from  $C_0$  at a definite temperature  $T'_0$  (the plaitpoint temperature in  $C_0$ ), which plait will merge into the main plait (or its branch plait) later on in an homogeneous double point.

plaitpoint temperature). The conditions for the occurrence of these cases were defined by us by means of the equations (2) and (3) there. From this appeared that with very feeble attraction the case *a*) occurs, with greater attraction the case *b*), whereas with still greater attraction case *c*) occurs (supposing the system to belong to type I).

We have found neither the case *a*) as we already observed above, nor the case *c*) in VAN LAAR. We did find the case *b*), chiefly with regard to the treatment of what takes place at lower temperatures, when three-phase-equilibria occur. For this treatment we referred to VAN LAAR (cf. These Proc. March '07 p. 797).

From the fact that VAN LAAR has declared this shape *b*) to hold universally for type I (cf. p. 235 footnote 3; see also VAN LAAR p. 36) it appears in our opinion, that VAN LAAR has not only left the cases *a*) and *c*) unmentioned, but has decidedly overlooked them.<sup>1)</sup>

II. One more remark remains to be discussed. In § 7 we put as the *two* criteria of the case *b*), the course of the plaitpoint curve being from  $K_1$  to  $K_m$  (see above), in which case a minimum plaitpoint temperature occurs (supposing  $b_{22M} < b_{11M}$ ):

$$\sqrt[4]{a_{22M}/a_{11M}} > \frac{1}{3} \left\{ -1 + \sqrt{1 + 3 b_{22M}/b_{11M}} \right\}$$

and

$$\sqrt[4]{a_{22M}/a_{11M}} < - (1 - b_{22M}/b_{11M}) + \sqrt{1 - b_{22M}/b_{11M} + (b_{22M}/b_{11M})^2}.$$

Mr. VAN LAAR points out (These Proc. May '07, p. 45, appendix), that the first-mentioned condition corresponds with a condition for the occurrence of a minimum plaitpoint temperature, derived by him These Proc. Dec. '05, p. 581 (and VERSCHAFFELT These Proc. March. '06 p. 751). In our opinion, however, Mr. VAN LAAR is mistaken when he thinks that the *one* condition stated by him is sufficient in all cases to decide as to the occurrence of a minimum plaitpoint tem-

<sup>1)</sup> We might consider the course of the spinodal curves in case *b*), if this is also extended to values of  $x > 1$  and  $< 0$ , and of  $v < b$ , as a more general case, from which the cases *a*) and *c*) might be obtained, at least qualitatively and when we restrict ourselves to the region of the  $\psi$ -surface ( $1 > x > 0$  and  $v < b$ ) that is of importance for the treatment of mixtures. This might be done by cutting out a region bounded by  $x = 0$  and  $x = 1$ , and a suitable line  $v = b$  in the same way as VAN DER WAALS These Proc. Feb. '07, p. 621 sqq. treats the course of the isobars (cf. § 7 p. 796 of this Communication). We have not found a single indication that VAN LAAR's description of case *b*) is to be interpreted in this way; from the phrase, quoted p. 235 footnote 3 e.g. we should much sooner conclude to the contrary.

At any rate the distinctions which are of physical importance, have not been made.

perature. Nor can his considerations of Dec. 1905 give an indication to conclude to the occurrence of a minimum plaitpoint temperature in the branch  $K_1 K_m$  of the plaitpoint curve. For there VAN LAAR starts from the value of  $dT_{xpl}/dx$  at the critical temperature of the most volatile component called  $T_{k_2}$  by us. The condition that at  $T_{k_2}$ , the *lower* of the critical temperatures of the components,  $dT_{xpl}/dx < 0$ , implies that *if the plaitpoint curve crosses from  $K_2$  to  $K_1$ , a minimum temperature must occur in it*<sup>1)</sup> VAN LAAR (These Proc. May '07 p. 43), considers now the value of  $dT_{xpl}/dx$  for the least volatile component (for  $K_1$ ). It is clear in our opinion, that at the *highest* critical temperature the condition  $dT_{xpl}/dx < 0$ , which coincides with the first of the inequalities mentioned (cf. p. 797 last sentence of the alinea at the top), does not give any indication to conclude to the occurrence of a minimum plaitpoint temperature. That if for  $K_1$   $dT_{xpl}/dx < 0$ , really *one* of the conditions for the occurrence of a minimum plaitpoint temperature in the branch  $K_1 K_m$  of the plaitpoint curve has been fulfilled, VAN LAAR has, in our opinion, only shown by his considerations on the situation of the double plaitpoint, not given until April (translated in These Proc. of May) at the same time with his remarks, which considerations agree with those which had led us a month before to the statement of the two conditions mentioned.

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1) Only if the plaitpoint curve crosses from  $K_1$  to  $K_2$ , this condition is sufficient to conclude to the occurrence of the minimum plaitpoint temperature (cf. VAN LAAR p. 46); for if the branch of the plaitpoint curve starting from  $K_2$  bends round to VAN LAAR's point  $A$  ( $x=1$ ,  $v=b_{22}$  in our notation), we cannot speak of a minimum plaitpoint temperature in the sense which is generally attached to this word.

A similar consideration gave rise to our remark in note 2 p. 795, which remark we are obliged to maintain in spite of Mr. VAN LAAR's contradiction, p. 46. (Wrongly Mr. VAN LAAR thinks there, note 1, that in our note instead of "maximum-temp." "minimum-temp." should be read, which might also immediately appear by comparison with the cited text of VERSCHAFFELT).

**Physics.** — “Some remarks on the last observations of Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM.” By Mr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

In the Proceedings of May 24 (1907) Prof. KAMERLINGH ONNES and Dr. KEESOM answered some remarks which I published in the Proceedings of April 26 (1907) (in reference to their last papers).

I may be allowed to revert briefly to the chief points of this answer.

*a.* P. 235, line 14—18: “It would have been good”, etc.

In fact the course of the *plait* in the case referred to by Prof. KAMERLINGH ONNES and Dr. KEESOM has not been given by me. I confined myself to investigating the course of the *plaitpoint line* in general. The results which I obtained on this point harmonize fully with what was found by KAMERLINGH ONNES and KEESOM.<sup>1)</sup>

*b.* P. 236, line 7—15.

In my papers published in These Proceedings only the case *b* has been mentioned (in which a minimum temperature occurs on the branch  $C_0C_2$  of the *plaitpoint line*). The reason of this is, that I then (7 June 1905 and 10 January 1906) only worked out the case  $b_1 = b_2$ , in which such a minimum always occurs.<sup>2)</sup> The formulae which I developed afterwards for the general case  $b_1 \begin{cases} < \\ > \end{cases} b_2$  (see TEYLER I, II and III), [which last publication (viz. III) was delayed by circumstances independent of my will], contained the *possibility* of the three cases *a*, *b* and *c*. As a matter of course Prof. KAMERLINGH ONNES and Dr. KEESOM could not take this yet unpublished investigation into account, and I only mention the fact to prove that the *possibility* of the cases *a* and *c* had not escaped my notice.

*c.* P. 236. “In our opinion, however, Mr. VAN LAAR is mistaken, when he thinks that the one condition stated by him is sufficient in all cases to decide as to the occurrence of a minimum *plaitpoint* temperature.”

<sup>1)</sup> At the same time I am glad to declare that I completely acknowledge the priority of Prof. KAMERLINGH ONNES and Dr. KEESOM in bringing to light the possibility of *plaits* which proceed without minimum from  $C_1$  to  $C_2$  and inversely (cases *a*. and *c*. of KAMERLINGH ONNES and KEESOM), the knowledge of which is necessary for understanding the behaviour of binary mixtures, containing as one component a substance with weak attraction.

(Note added in the English translation).

<sup>2)</sup> Afterwards I have seen that also for  $b_1 = b_2$  the case *a*. does occur, when it is not supposed that  $T_0 < T_2$ .

(Note added in the English translation).

I may remark about this that I have meant nothing else — which it seems, I ought to have set forth more clearly — but to conclude to the existence of the minimum temperature, when the plaitpoint temperature at the extremity of the branch of the plaitpoint line where the condition in question is fulfilled, is *lower* than at the other end of that branch, in which case this one condition is really sufficient.<sup>1)</sup>

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E R R A T A.

In the Proceedings of the meeting of February 1907:

- p. 660 l. 5 from the bottom: for "least" read: "most"  
 p. 662 table II in the heading read  $M_2/M_1 = 2$

In the Proceedings of the meeting of March 1907;

- p. 765 l. 13 from the top: read:

$$\left[ \frac{(pv_A)_{t''} - (pv_A)_{t'}}{t'' - t'} \right]_{v_A} = \left( \frac{d(pv_A)}{dt} \right)_{t'}$$

table VII, for:  $\alpha_p$  read:  $\frac{d(pv_A)}{dt}$

- p. 778 l. 13 and 14 from the top: for  $\alpha_p$  read:  $\alpha_v$

- p. 785 l. 17 from the bottom: Insert:

For the temperatures in liquid hydrogen first the correction is to be applied which will prove to be necessary according to Comm. N<sup>o</sup>. 95<sup>e</sup> § 3b and § 8.

- p. 796 the value for  $\frac{\alpha_M}{1-\alpha_M}$  given in equation (1) is to be multiplied  
 by  $\sqrt{\alpha_{1M}/\alpha_{22M}}$ .

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<sup>1)</sup> But I readily concede that Prof. KAMERLINGH ONNES and Dr. KEESOM have been the first to deduce both conditions for the minimum and to take in consideration the cases *a* and *c*. (Note added in the English translation).

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(October 31, 1907).

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

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PROCEEDINGS OF THE MEETING  
of Saturday October 26, 1907.

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(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 26 October 1907, Dl. XVI).

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**Physiology.** — “*About Odour-affinities*”. By Prof. H. ZWAARDEMAKER.

(Communicated in the meeting of September 28, 1907).

The great number of odours occurring in nature and in technics may, by virtue of the current opinions in literature, be divided into 9 classes, which may be indicated by historical names<sup>1)</sup>, chiefly borrowed from Linnaeus. These classes are · etherial odours, aromatic odours, odores fragrantes, moschus odours, allyl odours, empyreumatic odours, capryl odours, narcotic odours, odores nauseosi. I have selected from each class a representative which, chemically well characterized, can in a very simple way be made fit for olfactometric investigation (by dissolving the chemically pure odoriferous material in paraffinum liquidum<sup>2)</sup>), with one exception, viz. muscon, which is odourless in by itself odourless paraffine, and which therefore has been used mixed with myristine acid. They are:

isoamylacetate	0.5%
nitrobenzol	5%
terpineol	2.5%
muscon	0.627%
aethylbisulfide	1 <sup>o</sup> / <sub>1000</sub>
guajacol	1 <sup>o</sup> / <sub>100</sub>
valerian acid	1 <sup>o</sup> / <sub>1000</sub>
pyridine	1%
scatol	1 <sup>o</sup> / <sub>100</sub>

If in the double olfactometer two of these materials are joined together, there occur among the 36 combinations thus obtained no real mixed odours, but because they are counterbalancing each other, either an odourless mixture or rivalry is obtained. Odourlessness, respectively indefiniteness of odour, with change into odourlessness by rarefaction of the airmixture, is met with, when the stimuli are weak; rivalry, i. e. the alternate preponderance of one or the other of the two mixed odours is met with, when the stimuli are strong. However, also in the last case the impression, made by the mixture, is considerably weaker than the impression that every odour by itself brings about.

As unit of smelling-power I take the olfaction, i. e. the smallest quantity of odour of a definite quality, which can be recognized

<sup>1)</sup> H. ZWAARDEMAKER, Physiologie des Geruchs Leipzig 1895 p. 207.

<sup>2)</sup> Not water, but paraffinum liquidum has been chosen as a solvent because it is desirable to work for months at a stretch with the same cylinders without alteration of the solution.

by a normal organ of smelling ("Erkennungsschwelle", "recognizing-limit").

If the above mentioned paraffinic solutions are evaporated at a temperature of 15° C. and give off smelling material to a current of air brushing past with a velocity of 75 cub. cm. per sec., one olfaction will be communicated to the latter per 50 à 100 cub. cm. of air by shoving out the cylindric evaporating surface to a definite cylinderlength. This cylinderlength amounted on an average:

for the isoamylacetate-solution	to	0.2	cm.
„ „ nitrobenzol-solution	„	0.03	„
„ „ terpineol-solution	„	1.1	„
„ „ muscon-mixture	„	0.15	„
„ „ aethylbisulfide-solution	„	0.015	„
„ „ guajacol-solution	„	0.3	„
„ „ valerian acid-solution	„	0.03	„
„ „ pyridine-solution	„	0.02	„
„ „ scatol-solution	„	0.003	„

In judging of this table, it should be taken into consideration that the numbers have sometimes been obtained by taking the cylinderlengths during the experiment actually 10 or 12 times longer and by rarefying the air in the reservoir that is smelled at, 10 or 100 times. Thus the objection was obviated, on the one hand that small cylinderlengths should not be capable of being read with precision, on the other hand that the evaporation should not regularly take place from very narrow strips.

The mixing of the odours, which are to be joined together two by two, took place in a common reservoir, which, provided with two stop-cocks had been placed downstream the double olfactometer. The symmetry of the latter, in view of the resistance offered to the current of air, was previously examined by means of a bridge of Wheatstone applied to air-streams, while the purification of odours adhering by absorption between each number of two experiments has taken place by a permanent stream of air and electric warming of the wall of the reservoir. The reservoir in which the mixture takes place was smelled at by means of a separate tube, the downstream cock being opened.

The 36 combinations procured indefiniteness of odour or rivalry, if  $p$  olfactions of one odour and 9 olfactions of the other showed a proportion of  $p/q$ , of the following amount:

16<sup>2</sup>

T A B L E.

Mixture	$p$ $q$ <sup>1)</sup>	Degree of completeness <sup>2)</sup> of the compensation
isoamylacetate and nitrobenzol	0.44	indefiniteness*
" " terpeneol	1.32	moderately acid additional odour
" " muscon	0.0625	indefiniteness
" " aethylbisulfide	0.244	complete compensation*
" " guajacol	3	indefiniteness
" " valerian acid	0.01	rivalry
" " pyridine	3.6	indefiniteness*
" " scatol	0.0037	indefiniteness
nitrobenzol	1.375	indefiniteness*
" " muscon	0.434	"
" " aethylbisulfide	0.111	"
" " guajacol	0.65	"
" " valerian acid	0.03	"
" " pyridine	3.	"
" " scatol	0.012	indefiniteness*
terpeneol	0.125	"
" " aethylbisulfide	0.067	somewhat aromatic remainder
" " guajacol	1.	rivalry
" " valerian acid	0.05	almost complete compensation
" " pyridine	0.53	" " "
" " scatol	0.12	" " "
muscon	1	indefiniteness
" " guajacol	0.03	tolerably satisfactory
" " valerian acid	2.7	almost complete compensation
" " pyridine	1.2	rivalry
" " scatol	0.2	indefiniteness*
aethylbisulfide	0.056	rivalry*
" " valerian acid	1.2	indefiniteness
" " pyridine	3.2	very indefinite empyreum. odour
" " scatol	0.0075	indefiniteness
guajacol	0.03	"
" " pyridine	0.016	indefiniteness*
" " scatol	0.0007	"
valerian acid	4	"
" " scatol	1.2	"
pyridine	0.42	indefiniteness

The details of these experiments and more particularly the absolute quantities which were made to be the foundation of each combination of odours, will soon be communicated elsewhere in a more extensive treatise.

The proportional number given in the table holds good, besides for a definite average combination, also for an adjacent group of stronger, respectively weaker stimuli. For this zone holds good the rule that if  $p$  olfactions of an odour are compensated by  $q$  olfactions of another odour, this must likewise be the case for  $np$  and  $nq$  olfactions. FECHNER called the intensities of stimulus and sensation,

<sup>1)</sup>  $p < q$ .

<sup>2)</sup> Marked with an asterisk are those cases in which by an intentional experiment it has been proved that the proportional number is applicable to a certain zone of stimuli.

mutually increasing and decreasing in due proportion, the cardinal values of stimulus and sensation. By analogy we might speak here of cardinal values of the stimuli counterbalancing each other, leaving altogether out of the question whether this proportion will prove as easily explainable as that which FECHNER has in view. The zone for which the proportional number of the table holds good, may therefore be called the zone of cardinal proportions.

From the fact that at a simultaneous impression two odours can neutralize each other, it follows that the action of these stimuli on the organ may be represented by two vectors, standing as it were for two forces, which in general act more or less in opposite directions, the direction of the vector of the strongest odour (answering to  $q$  in the table) being chosen in such a way that the co-sine of the angle that it forms with the continuation of the vector of the weakest odour (answering to  $p$  in the table) is exactly equal to the proportion found for  $p/q$  in the combination concerned. For in this case the vector of the strongest odour may be thought to be replaced by the sum of two other vectors: one in a direction opposite to the vector of the weakest odour, and one at right angles to it (in the plane of the original vectors). If, moreover, the two original vectors are given equal length, each with such a unit of length as the proportional number implies, i. e. for the vector  $q$  and its components of  $q/p$  times more weight than for the vector  $p$ , the neutralization of actions that has to be symbolized by the original vectors, will have been accurately expressed. For the vector  $p$  and one of the components of vector  $q$  will represent equal, but opposite forces. We shall only have to consider the direction of the other component of vector  $q$  as direction of odourlessness, in order to have duly accounted for the complete lack of sensation.

A second set of vectors can be placed in the same system, provided the two sets have one vector in common. Starting from of a new proportional number  $p'/q'$  the new third odourvector that has been introduced, may then be given a definite direction with regard to the first odourvector; also the second and third vectors may be given their relative directions by means of a third proportional number  $p''/q''$ . The latter, it is true, can be done in two ways, according as the third vector is reached by a right- or a left-handed rotation starting from the vector answering to  $p$ , but of these two one may be chosen. To the combination  $p'/q'$  belongs a vector of odourlessness at right angles to the vector of weakest odour and to the combination  $p''/q''$  a vector of odourlessness at right angles to the vector of weakest odour. The units of length of these vectors will in general

never be the same and also differ according to the combination that one has in view. As, however, we have never mutually combined three, but always two odours at a time, it will never be necessary to occupy ourselves with the units of length of the three at the same time, nor does this change of units, depending on the case considered, raise any objection. Even in our further demonstration this does not give rise to any difficulty, as we are never going to mutually compare vectors but when they have the same direction with regard to an independent vector that is at the same time considered, in other words possess with respect to the latter about the same units of length<sup>1)</sup>).

A third set of vectors can, speaking generally, not be placed in the same system, even though it has one vector in common with the two preceding systems, for the fourth vector will in general have to be given different directions, according as it is considered in connection with the first and second, with the first and third or with the second and third. But what is in general impossible, may in special cases prove quite practicable. Let us consider this.

If we number our nine standard-odours with the figures 1 to 9 and likewise the corresponding vectors, each time two of these vectors can be fixed and the rest arranged with regard to these two vectors, which are definite in their situation. The question we put just now, comes to this: Is the mutual relation between the odours perhaps so as to make some of these last seven vectors coincide? In consequence of mistakes in the experiment a complete coincidence will no doubt be out of the question, but let us consider whether it happens within a margin of error of at most 1% of  $2\pi$  difference of direction ( $= 3.6^\circ$ ). For this purpose we have first combined 1 and 2, considering all the others with regard to these two; then 1 and 3 are fixed, the rest arranged according to this, etc. till all combinations, 36, have occurred. In each of the combinations seven vectors were met with, whose situation with regard to the two vectors previously chosen had to be traced in order to see whether they coincided or not. For each set of two previously determined vectors this gives rise to 42 judgments, so that in all 1512 judgments have

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1) The proportional numbers as they have been empirically composed and taken together in our table, form 252 possible constellations of three vectors. Among them there is only one which, also as to the units, is completely satisfactory for all three proportions at the same time. It is the constellation in which terpineol, scatol and valerian acid are combined. The length of the vectors measured by means of a joint unit of length amounts in this case to 1 for the terpineol-vector, 8 for the scatol-vector and 20 units for the valerian acid vector.

been necessary for 36 combinations. However, as each case is repeated once, there are in reality 756 separate judgments.

Just now we said it was necessary that never other vectors than those about equally directed, which accordingly possess about the same unit of length, should be mutually compared. If we keep this in view, the following constellations are identical within a limit of 1% :

isoamylacetate and nitrobenzol	}	each four times
valerian acid and scatol		
isoamylacetate and guajacol	}	each three times
nitrobenzol and guajacol		
muscon and scatol		
aethylbisulfide and valerian acid		
isoamylacetate and terpineol	}	each once
isoamylacetate and aethylbisulfide		
nitrobenzol and terpineol		
terpineol and guajacol		
muscon and aethylbisulfide		
muscon and valerian acid		
aethylbisulfide and scatol		

together 27 constellations<sup>1)</sup>.

Some of these 27 constellations give rise to reciprocity, in such a way, that the vectors which are identical to two previously determined vectors, make the latter identical, when they themselves are previously determined in their mutual situation. This occurs in :

isoamylacetate	}	←	{	muscon	→	{	isoamylacetate
and		with regard to	{	and	with regard to	{	and
terpineol		}	←	{	scatol	←	{

Though the coincidence of two odour-vectors, if considered with respect to two other odour-vectors, is already very remarkable, a coincidence of 3 vectors is still more interesting. This has been realized in the following cases, if we extend the limit of error to 2% :

<sup>1)</sup> This figure rises to 42, if besides complete coincidences also coincidences with reciprocal values are taken into consideration.

isoamylacetaat	}	with regard to muscon and scatol
terpineol		
guajacol	}	with regard to aethylbisulfide and scatol
nitrobenzol		
terpineol	}	with regard to isoamylacetate and terpineol
guajacol		
muscon	}	with regard to nitrobenzol and terpineol
valerian acid		
scatol	}	with regard to nitrobenzol and terpineol
aethylbisulfide		
valerian acid	}	with regard to nitrobenzol and terpineol
scatol		

Even a coincidence of 4 vectors, has been found once, and that for :

isoamylacetate	}	with regard to valerian acid and scatol
nitrobenzol		
terpineol		
guajacol		

The planes in which the vectors of odourlessness, belonging to these odours, meet, have the form of a cone, respectively with the vector of valerian acid and that of scatol for their axis.

If we cast a glance at the sum of the results arrived at, it is especially the coincidence of several vectors at the same time which draws our attention: 4 vectors with regard to valerian acid and scatol, 4 sets of 3 vectors each time with regard to two others. Evidently there exists between the coinciding vectors agreement in action on our consciousness for those definite cases. But some of the coinciding vectors are repeatedly found together. Their mutual agreement must therefore be of a more intimate nature, otherwise it could not reveal itself so frequently and in so many different circumstances. This closer connection exists e.g. between isoamylacetate and nitrobenzol, which in no less than 4 cases become reciprocally identical to 1% of the circumference of the circle; a connection only a little less close between nitrobenzol and terpineol, nitrobenzol and guajacol and isoamylacetate and guajacol, which do the same in 3 cases; a connection not quite wanting between isoamylacetate and terpineol and terpineol and guajacol, where also these appear to coincide to 1%. But also the vectors with regard to which the coincidence of

several vectors comes about, are closely connected with each other. Valerian acid and scatol, with regard to which no less than 4 vectors become identical, have 4 mutual coincidences, to 1% and also the vectors with regard to which the coincidence of three vectors takes place, show in 3 cases out of 4, a plurality of identity. Considered from certain definite points of view, therefore, they must have something in common in their action upon our consciousness.

- If we ask ourselves what physical importance the relations found might have, it must be this that odour-mixtures formed from the coinciding vectors possess fixants in common and these fixants will have to be found in the odour-classes to which the vectors with regard to which they are placed, belong. In perfumery are known a number of such fixants rendering useful services with regard to certain definite perfume-mixtures, which otherwise would not be durable. In my "Physiologie des Geruchs" I have given a series of such examples. Here we quote one borrowed from G. COHN's "die Riechstoffe". Artificial jasmin is obtained by joining together benzylacetate, linalylacetate, linalool and benzylalkohol, mixed with some indol, which serves "als Fixiermittel und zur Auffrischung des Geruchs", and which may be replaced by methylketol, scatol, propyldimethylindol, propylaethylindol, allylmethylindol, etc. With the aid of our table it must be possible to devise mixtures that will furnish available bouquets with fixants to be specified beforehand. Their practical fitness for the perfume-industry will depend, besides on the pure compensation-proportions, also on the velocity of evaporation and diffusion of the materials used. In a practically available perfume the latter should not differ too much.

The multidimensional character of the organ of smelling prevents, alas, projecting a clear representation of all proportions of the different qualities in their action upon consciousness. This is only partially possible, for separate vectors, isolated from the whole. Yet it appears that in general there exists a contrast between

isoamylacetate	}	with regard to	}	aethylbisulfide
nitrobenzol				valerian acid
terpineol				scatol
guajacol				

From a phylogenetic point of view the first group might be called the food-odours, the second the putrid odours, if not in many a case also muscon should be added to the last category, for which reason it is perhaps safer to refrain from any denomination. The arrangement in each group is governed by the above mentioned reciprocities.

**Physiology.** — *“A method to extract enzymes and pro-enzymes from the mucous membrane of the digestive tube and to establish the topic distribution of them.”* By Prof. H. J, HAMBURGER.

#### I. INTRODUCTION ; PRINCIPLE OF THE METHOD.

The method applied as yet to extract enzymes and pro-enzymes from the mucous membranes of the stomach and the intestines consists in preparing the mucous membrane and extracting it in a fine state of division, with or without the addition of antiseptics; by repeated precipitation and dissolution the body to be examined is finally obtained in a more or less pure state. If we wish to be informed as to the distribution of the enzyme over the various parts of the mucous membrane, in other words to establish the topic distribution of it, extracts are made of equal weights or of equal surfaces, and of these the specific action is determined quantitatively.

It need hardly be said that these methods are rather complicated and lengthy as well. A great drawback more especially is, that in extracting, the enzyme is polluted with so many other substances of the mucous membrane.

Now, we have occupied ourselves for some time with the question by what force enzymes (pro-enzymes) are brought to the surface of the mucous membrane, and more especially tried to determine whether we have to do with kataphoresis, in other words whether in normal life enzymes (pro-enzymes) are carried along by the electric current arising when the secretory nerve fibres are stimulated in the natural way.<sup>1)</sup> We will not dwell on the results of these investigations now. Let us only observe here that the method consisted in laying on the mucous membrane a small column of solidified agar-agar, into which a platinum electrode had been melted; then it was investigated whether under the influence of a weak electric current, moving from the muscular side of the mucous membrane, to the free surface of it, enzyme or pro-enzyme passed from the epithelium cells into the agar agar.

That, if the enzyme or pro-enzyme was indeed moved by kataphoresis it would also pass into the agar-agar, we had a reason to expect after the investigations of GRAHAM<sup>2)</sup>, VOIGTLANDER<sup>3)</sup> and others

<sup>1)</sup> HAMBURGER, Osmotischer Druck u. Ionenlehre. Bd. II. S. 433 ff.

<sup>2)</sup> GRAHAM, Liebig's Annalen 121, 1862 S. 1.

<sup>3)</sup> VOIGTLÄNDER, Zeitschr. f. physik. Chemie. 3, 1889 S. 316.

For the literature on this subject compare, COHEN, Vorträge für Aerzte über Physikalische Chemie 2e Aufl. 1907 S. 128.

according to which the velocity of diffusion in colloids is as great as in the water in which the colloid is dissolved.

If it should be objected that these experiments were made only with crystalloids, the investigations of C. EYKMAN<sup>4)</sup> have shown conclusively that colloids can diffuse into other colloids (gelatine into agar-agar).

But before trying to establish the influence of a constant electric current on the transition of enzyme into the agar-agar, we wished to know to what extent the ferment would diffuse into the agar-agar without the introduction of the electric current.

Evidently this transition took place. This fact seemed to suggest a means of extracting in an easy manner enzymes and perhaps pro-enzymes as well, from the mucous membrane in not too impure a state. Perfect extraction would, it is true, be unattainable in this way, but there was a likelihood that the method might be employed to determine in a simple manner the relative amounts of enzyme in the various parts of a mucous membrane.

## II. EXPERIMENTAL METHOD.

Parts of a glass tube having in our experiments an internal diameter of 22 mm. and a height of 30 mm., were ground flat at one end by means of emery and placed with that side on a glass plate, plate glass being the best for this purpose.

By means of a pipette 3 cc. of liquid agar-agar were put into each little cylinder. I shall not discuss the way to prepare this liquid: it is to be found in all handbooks on the technics of bacteriology. It must be observed, however, that it is advisable to let the agar-agar solution cool down to  $\pm 45^\circ$  before measuring it in the pipette; otherwise there is a danger of its flowing partly away from underneath the glass cylinder.

After some time the agar columns have become solid and are placed, still surrounded by the glass tube, on the spread out parts of the membrane which, if necessary, has been previously cleaned. For this cleaning which also may serve to remove the mucus, we take NaCl 0,9%. Investigations especially made for this purpose on the gastric mucous membrane have shown, however, that for this organ at least washing with water gives satisfactory results.

On the mucous membrane, which if necessary has been cleaned, the agar-agar columns remain for 8 hours or more, in order to enable enzymes and pro-enzymes to diffuse into the agar-agar.

<sup>4)</sup> C. EYKMAN, Centralbl. f. Bakteriol. 29, 1901, S 841.

If the experiment bears upon the *pepsin incl. the pepsinogen of the gastric mucous membrane*, the agar columns which have been on it, are cut fine and mixed with 3 cc. HCl of 0.4%. For this we use cylindrical bottles with close fitting glass stoppers: they have a diameter of 24 mm. and a height of 48 mm. Into these bottles we put albumen columns prepared according to MERTT's method. When these have been in contact with the agar-suspension for 10 hours or more at 37.5 C., we determine by measurement how much has been digested; then the albumen columns are placed in it again and the measurements are repeated a few hours later. In each bottle we generally had two albumen tubes. Perhaps it will be objected that the presence of solid particles of agar-agar must impede the action of the pepsin on the albumen. This proves not to be the case: in the first place we observe that on all 4 sides of the 2 albumen columns always about the same column of albumen has been digested, which most likely would not be the case if now and then an agar-particle prevented the entrance of the digesting fluid. And secondly we noticed that when the experiment is made with a liquid, from which the agar particles have been removed by filtration, the rate of digestion is the same as when the agar particles were still in the fluid.

If the experiment bears only upon the *pepsinogen* of the gastric mucous membrane, we place alkalic instead of neutral agar-agar on it, viz. a quantity of agar of 2% in  $\text{Na}_2\text{CO}_3$  of 3 p. mille. The investigations of LANGLEY<sup>1)</sup> have shown that in this concentration pepsin is decomposed by  $\text{Na}_2\text{CO}_3$ , pepsinogen on the other hand not.

It stands to reason that besides pepsin and pepsinogen, *chymosin* and *prochymosin* will also be absorbed by the neutral agar-agar. It was found indeed that the agar-mass had obtained the faculty of coagulating milk.

In a similar way as the gastric mucous membrane the intestinal mucous membrane may be experimented upon. We found that the neutral agar absorbs both enterokinase and erepsin. The quantity of *enterokinase* present in the agar is determined by cutting fine the agar, mixing it with water, *filtrating*, and bringing the extract thus obtained, into contact with inactive juice of a fresh pancreas gland and two albumen tubes.

The attentive reader will notice that here no agar particles are present at the digestion of the albumen as in the case of the gastric

<sup>1)</sup> LANGLEY Journal of Physiology 3 1882 p. 253.

LANGLEY and EDKINS *ibid* 7 1886 p. 371.

juice. They were removed before the action of the fluid on the albumen tubes, because it was observed that the conversion of albumen by *trypsin* was greatly retarded by the presence of the agar-agar.

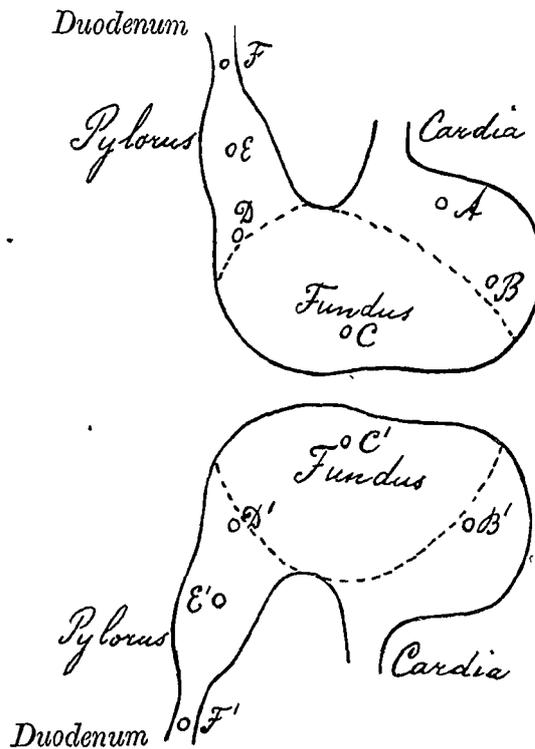
To determine the quantity of *erepsin*, drawn into the agar, we made the *clear* extract act upon the peptone.

We here append the results of some experiments carried out in accordance with the method described above. More explicit statements will be published elsewhere. Some further particulars concerning the method of investigation are mentioned below.

### III. SOME EXPERIMENTS.

#### 1. *Distribution of pepsin (incl. pepsinogen) over the gastric mucous membrane.*

A pig's stomach was cut into two symmetrical halves along the great and small curvature and washed with NaCl 0.9%. Then both halves were spread out flat and on the spots marked below *A, B, C*, etc. columns of neutral agar-agar of 2% were placed.



As will be seen *A* is situated in the cardia region.

*B* in the border region between cardia and fundus part

*C* in the fundus region

*D* in the border region between fundus and pylorus part

*E* in the pylorus region

*F* on the duodenum near to pylorus.

With respect to this figure we must point out that for *all* our experiments with gastric mucous membrane, the letters have the same meaning.

In the experiment of which table I gives the results, the agar columns of 3 cc. remained during  $14\frac{1}{2}$  hours on the mucous membrane. Then the agar was cut fine and mixed with 3 cc 0.4 % HCl and each of the mixtures thus obtained was made to exert its digestive influence on two tubes of albumen.

The four numbers which in the following table are connected by + represent the lengths of the four albumen columns, digested at the  $\perp$  sides of the two tubes.

TABLE I.

Digested after  $12\frac{1}{2}$  hrs.

<i>A</i> . . . . $\frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 2$ m.M.	<i>A'</i> . . . $\frac{1}{2} + \frac{1}{4} + \frac{1}{2} + \frac{1}{2} = 1\frac{3}{4}$ m.M.
<i>B</i> . . . . $\frac{3}{4} + \frac{3}{4} + \frac{1}{2} + \frac{3}{4} = 2\frac{1}{4}$ "	<i>B</i> . . . $\frac{3}{4} + \frac{3}{4} + \frac{3}{4} + \frac{3}{4} = 3$ "
<i>C</i> . . . . $2 + 2 + 2 + 2\frac{1}{4} = 8\frac{1}{4}$ "	<i>C'</i> . . . $2 + 2 + 2 + 2 = 8$ "
<i>D</i> . . . . $1\frac{1}{2} + 1\frac{1}{4} + 1\frac{1}{2} + 1\frac{1}{2} = 5\frac{1}{4}$ "	<i>D'</i> . . . $1\frac{1}{2} + 1\frac{1}{2} + 1\frac{1}{2} + 1\frac{1}{2} = 6$ "
<i>E</i> . . . . $1\frac{1}{4} + 1\frac{1}{4} + 1\frac{1}{2} + 1\frac{1}{4} = 5\frac{1}{4}$ "	<i>E'</i> . . . $1\frac{1}{4} + 1\frac{1}{4} + 1\frac{1}{2} + 1\frac{1}{2} = 5\frac{1}{2}$ "
<i>F</i> . . . . $\frac{1}{3} + \frac{1}{3} + \frac{1}{3} + \frac{1}{3} = 1\frac{1}{3}$ "	<i>F</i> . . . $\frac{1}{3} + \frac{1}{3} + \frac{1}{3} + \frac{1}{3} = 1\frac{1}{3}$ "

From this table is seen:

1. That in the cardia region (*A* and *A'*) the amount of pepsin is small, increases towards the fundus (*B* and *B'*), reaches its climax there (*C* and *C'*) and decreases towards the pylorus (*D* and *D'*). In the duodenum we also meet with pepsin, but its quantity is small.

2. The table shows that in both halves of the stomach the quantity of pepsin was equal in corresponding parts.

If we speak here of pepsin we mean pepsin and pepsinogen. As has been said before and will further be demonstrated pepsinogen

too enters the agar. It is by mixing with HCl converted into pepsin and so determined quantitatively with the pepsin.

## 2. *Distribution of pepsinogen.*

As has been said, the investigations of LANGLEY<sup>1)</sup> have shown that, contrary to pepsin, pepsinogen is not destroyed by a solution of Na<sub>2</sub>CO<sub>3</sub> 0.3%. We have made use of this fact to try if we could withdraw pepsinogen from the mucous membrane.

For this purpose agar columns were placed upon the mucous membrane containing 2% of agar in a Na<sub>2</sub>CO<sub>3</sub> solution of 0.3%. The column again had a diameter of 22 mm., the contents being 3 cc.

It must be casually observed that separate experiments had shown that in such an alkalic agar mass, pepsin at once loses irretrievably its digestive power.

To the method of experimenting we have not much to add. Let us only mention that the alkalic agar, after having been in contact with the mucous membrane was cut fine, neutralized with diluted hydrochloric acid, then mixed with 3 cc. HCl of 0.4%. The purpose of this was, to liberate the pepsin from the pepsinogen. The digesting-experiments with albumen-tubes gave the results tabulated below. Here the lengths of the 4 digested albumen columns have each time been added together.

TABLE III.

The agar columns were kept on the mucous membrane for 20 hours.

Digestion of albumen after 8 hours.	Digestion of albumen after 18 hours.
<i>A</i> . . . 0 m.M.; <i>A'</i> . . . 0 m.M.	<i>A</i> . . . 0 m.M.; <i>A'</i> . . . 0 m.M.
<i>B</i> . . . 0 " ; <i>B'</i> . . . 0 "	<i>B</i> . . . 1½ " ; <i>B'</i> . . . 1½ "
<i>C</i> . . . 8 " ; <i>C'</i> . . . 8 "	<i>C</i> . . . 10 " ; <i>C'</i> . . . 9½ "
<i>D</i> . . . 4.4 " ; <i>D'</i> . . . 4.2 "	<i>D</i> . . . 6.2 " ; <i>D'</i> . . . 6.9 "
<i>E</i> . . . 4 " ; <i>E'</i> . . . 4 "	<i>E</i> . . . 5 " ; <i>E'</i> . . . 5.2 "
<i>F</i> . . . 0 " ; <i>F'</i> . . . 0 "	<i>F</i> . . . 1 " ; <i>F'</i> . . . 1 "

It will be seen that from the *cardea* part (*A* and *A'*) no pepsinogen was extracted. This need not surprise us; for in several experiments with *neutral* agar, no pepsin could be extracted from it either.

In the border region between *cardea* and *fundus*, pepsinogen was found, but in a small quantity. It was considerable in the *fundus* (*C*), gradually growing less towards the *pylorus* (*D* and *E*).

<sup>1)</sup> LANGLEY, l. c

3. *To what extent does the length of time during which the agar columns are on the mucous membrane, influence the quantity of enzyme and pro-enzyme absorbed?*

For these experiments the stomach was divided into two symmetrical halves. On one half two *neutral* agar-columns were placed at *A, B, C* etc., and on the corresponding places of the other half *A', B', C'* etc. two columns of *alkalic* agar. One of the two columns near *A, near B, near C* etc. was taken away and treated, after having been on the mucous membrane for 18 hours; the same was done with those near *A', B', C'* etc. The other series *A, B, C* etc. *A', B', C'* etc. was left on the membrane for 36 hours. In both series of experiments the thus activated agar was made to act for 20 hours on the albumen columns. The tables will be plain now without further explanation.

TABLE IV.

Determination of the quantity of pepsin and pepsinogen which had passed into the neutral agar, after the latter had been on the mucous membrane for

	18 hours	36 hours
<i>A</i>	0 m.M. digested	2½ m.M. digested
<i>B</i>	1 " "	3½ " "
<i>C</i>	4.8 " "	16 " "
<i>D</i>	3.4 " "	7 " "
<i>E</i>	3 " "	5.4 " "
<i>F</i>	0 " "	2 " "

TABLE V.

Determination of the quantity of pepsinogen which had passed into the alkalic agar, the latter having been on the mucous membrane during

	18 hours	36 hours
<i>A'</i>	0 m.M. albumen digested	1½ m.M. albumen digested
<i>B'</i>	0 " " "	2½ " " "
<i>C'</i>	3.8 " " "	10 " " "
<i>D'</i>	2.4 " " "	5½ " " "
<i>E'</i>	1.2 " " "	3 " " "
<i>F'</i>	0 " " "	1 " " "

Both tables show that after 36 hours more pepsin and also more pepsinogen had passed into the agar than after 18 hours.

Further a comparison of tables IV and V makes it evident that the digestion of albumen in experiments made with neutral agar, is more considerable than where alkalic agar has been employed. This result may also tend to confirm the reliability of the method; for into the neutral agar pepsin and pepsinogen may enter, the latter of which under the influence of hydrochloric acid produces pepsin, whilst in the alkalic agar only pepsinogen is found. And as we have seen invariably in all our experiments, the quantity of enzyme and pro-enzyme at identical spots of the two symmetrical parts of the stomach turns out to be the same.

I wish to observe here that the digestion of serum-albumen takes place much more quickly than that of the egg-albumen used. GLÄSSNER was the first to point out the advantage of coagulated serum, and I may confirm it from my own experience. Serum albumen has moreover the advantage that without preparation such as cutting up and filtrating, it can be used after simply being coagulated in glass tubes.

Owing to accidental circumstances no serum-albumen has been used for the experiments described in this paper.

#### 4. *Distribution of rennet-ferment.*

To demonstrate the presence of rennet-ferment and to know its distribution in the gastric mucous membrane, about the same method was applied as that used for the investigations relating to pepsin and pepsinogen. Only the agar-columns had a greater diameter than in the pepsin experiments, viz. 35 instead of 22 mM. The contents accordingly were 5 cc. instead of 3 cc. Moreover it was self-evident that the quantitative determination of the rennet-ferment had to be effected in another way. The columns having been on the mucous membrane for some hours, the agar was cut fine and mixed in a test-tube with  $\frac{1}{2}$  cc. HCl 0.4% and afterwards with 10 cc. of milk. Then the test tube was plunged into a bath of water at 37.5°, after which it was noted down every half minute where coagulation had taken place.

The presence of some hydro-chloric acid did not impair the experiment. Previous tests had shown that in a mixture of 5 cc. neutral agar  $\frac{1}{2}$  cc. HCl of 0.4% and 10 cc. of milk coagulation did not set in till more than an hour after. As the following series of experiments demonstrates the addition of only  $\frac{1}{2}$  cc. of HCl can hardly

have had any influence of the coagulative action of the rennet-ferment.

TABLE VI.

Coagulation is visible:			
by <i>A</i> after 3 minutes;		by <i>A'</i> after 3 minutes.	
" <i>B</i> "	2 "	" <i>B'</i> "	2 "
" <i>C</i> "	1 "	" <i>C'</i> "	1 "
" <i>D</i> "	1½ "	" <i>D'</i> "	1½ "
" <i>E</i> "	2½ "	" <i>E'</i> "	2½ "

*This experiment shows that the distribution of chymosin (including pro-chymosin) runs parallel with that of pepsin (including pro-pepsin), a result agreeing with the researches of others.<sup>1)</sup>*

Secondly the experiment shows the action of the rennet in corresponding parts of the two symmetrical halves of the stomach to be equal.

#### 5. *Distribution of enterokinase in the intestinal mucous membrane.*

On the mucous membrane of the duodenum, jejunum, ileum, caecum and colon, cut open length-wise, agar-columns were placed, their contents being 3 cc. These having been left on it for 24 hours, the agar-agar was cut fine and extracted with 3 cc. of a Na Fl-solution of 2%. Then 6 cc. of diluted pancreatic juice were added to 2 cc. of the filtrate. The former had been obtained by pressing the pancreas gland of a newly killed pig, mixing the thick juice thus obtained with a Na Fl-solution of 2%, and filtrating the mixture.

In the mixture of 6 cc. diluted pancreatic juice thus obtained and 2 cc. agar-filtrate two albumen tubes were placed.

By the side of this, controlling-experiments were made with 2 cc. agar-filtrate and 6 cc. of Na Fl solution, instead of 6 cc. of the diluted pancreatic juice. The digestion of the albumen was noted down after 19 and 44 hours.

<sup>1)</sup> NENCKI u. SIEBER. Zeitschr. f. physiol. Chemie 32 1901 S. 291; PEKELHARING. Ibid. 35 1902 S.8; PAWLOW u. PARASTSCHUK. Ibid 42 1904 S. 415; SAWJALOW. Ibid 46 1905 S. 307.

The following table gives the results of one of the series of experiments made.

TABLE VII.

	2 cc duodenum-agar extract		2 cc jejunum-agar extract		2 cc ileum-agar extract	
	+ 6 cc pancreatic juice	+ 6 cc NaFl. solution	+ 6 cc pancreatic juice	+ 6 cc NaFl. solution	+ 6 cc pancreatic juice	+ 6 cc NaFl. solution
Albumen digested after 19 hours	7.2 m.M.	0 m.M.	6.4 m.M.	0 m.M.	5.6 m.M.	0 m.M.
Albumen digested after 44 hours	12.4 "	0 "	11.2 "	0 "	10 "	0 "

This series of experiments shows *the quantity of enterokinase to decrease gradually downward, a result agreeing with that obtained by CHEPOWALNIKOW, DELEZENNE, FROUIN and FALLOISE.*

I shall not discuss the experiments here, which show that in the digestion of albumen by trypsin the presence of agar has a retarding influence, nor the influence which the time during which the agar has been in contact with the intestinal mucous membrane, has on the transition of the enterokinase. These questions will be further discussed in a more explicit account.

One experiment remains to be mentioned, showing how the enterokinase diffused into the agar, distributes itself over agar and water, after the agar has been cut up and mixed with water.

5 cc of liquid agar are mixed with 2 cc. of watery extract of the intestinal mucous membrane. Of this mixture 2 × 3 cc. are taken and poured into the above mentioned cylindrical tubes. When the agar has become solid it is cut fine and mixed each time with 2 cc. of water. The mixture remains for an hour exposed to the temperature of the body in order to enable the agar to give up enterokinase.

After cooling down it is filtrated, twice 1 cc. is taken and mixed with 2 cc. of inactive pancreatic juice. In both mixtures I and II albumen tubes are placed.

Besides this experiment another one identical with it, is made; only instead of 5 cc. of agar, 5 cc. of water are taken of course. Cutting up is out of the question here. The quantities, however, remain the same.

TABLE VIII.

Liquid	Digestion after	Experiment I	Experiment II
5 cc agar + 2 cc intest. extr.; of this 2 × 3 cc cut up; each 3 cc mixed with 2 cc water; of this 2 × 1 cc mixed each with 2 cc pancreatic juice	4 hours	1 + 1 + 1 + 1 = 4 m.m.	1 + 1 + 1 + 3/4 = 3 3/4 m.m.
	16 hours	3 1/2 + 4 1/2 + 3 1/2 + 4 = 15 1/2 m.m.	3 1/2 + 3 1/2 + 3 1/2 + 4 = 14 1/2 m.m.
	25 hours	6 + 5 + 6 + 5 = 22 m.m.	5 + 5 + 6 + 5 = 21 m.m.
5 cc water + 2 cc intest. extr. of this 2 × 3 cc; each 3 cc mixed with 2 cc of water; of this 2 × 1 cc mixed each with 2 cc of pancreatic juice.	4 hours	1 1/4 + 1 1/4 + 1 + 1 = 4 1/2 m.m.	1 1/4 + 1 + 1 1/2 + 1 1/4 = 5 m.m.
	16 hours	4 + 4 1/2 + 4 + 4 = 16 1/2 m.m.	4 + 3 1/2 + 4 + 4 1/2 = 17 m.m.
	25 hours	6 + 5 + 5 + 6 = 22 m.m.	5 + 5 + 5 + 6 = 21 m.m.

This table leaves no doubt, but the method of extracting the agar with water, gives reliable results. *They turn out to be the same as if the agar itself were water. The enterokinase must distribute itself equally over agar and water.*

We observed the same with pepsin.

Finally we shall describe a series of experiments, showing that erepsin too enters the agar, and that this supplies us with a means of determining its distribution over the intestinal mucous membrane.

#### 6. *Distribution of Erepsin.*

The 2% agar used was not dissolved in water, but in NaFl of 2% because the amount of erepsin, passing from the intestine into the agar during the time taken up by the former experiments, was not great enough.

Therefore it was expedient to leave the agar for at least 24 hours on the mucous membrane, taking care to prevent putrefaction as much as possible.

The action of erepsin consists as we know in its power to change hemialbumose and peptone into products not giving the biuret-reaction.

VERNON<sup>1)</sup> has based on this a colorimetric method, to determine the degree of conversion brought about by erepsin and FALLOISE<sup>2)</sup> among others, has successfully used it. We too have applied this method, in a somewhat modified form, however. It chiefly consisted in a solution of CuSO<sub>4</sub> being mixed with a NaOH solution. The fluid thus obtained imparts a violet-red colour to peptone. The more the peptone solution from which we started is converted by erepsin, the fainter the violet-red colour will be. It was now investigated, with how much water the standard liquid had to be diluted to produce the violet-red colour observed.

One of our experiments gave the following result.

In the peptone-solution (WITTE) on which the duodenal-extract has acted, are **46.2%** of the original quantity of peptone left. In the peptone-solution acted upon during the same time by the *jejunum*-agar-extract are still **16%** of the original quality of peptone left, and lastly where the *ileum*-agar-extract acted during the same time, **14%** of the original amount.

*It follows from this that in jejunum and ileum there was more erepsin present than in duodenum*, which corroborates so far FALLOISE's results inasmuch as we too found much more erepsin in jejunum than in duodenum. In the ileum, however, the amount of erepsin is much greater than in the duodenum; FALLOISE, indeed, notes a difference in the same direction, but it is only slight. It must be kept in mind though, that our experiments relate to the pig, FALLOISE's to the dog.

I may add that in PEYER's plâques hardly any erepsin or enterokinase was found.

A number of experiments, made for the researches described above, have been carried out by Mr. R. A. B. OOSTERHUIS, Med. cand., assistant at the physiological laboratory.

#### CONCLUSION.

The above researches have shown:

1. That when agar columns are placed upon the mucous membrane of stomach and intestines, enzymes and pro-enzymes are

<sup>1)</sup> VERNON. *Journal of Physiology*. **30**, 1903, p. 330.

<sup>2)</sup> FALLOISE. *Archives internat. de Physiol.* **2**, 1903/4, p. 299.

absorbed from them and enter the agar. As such were examined pepsin, including pepsinogen, chymosin and prochymosin, enterokinase and erepsin.

2. The above-mentioned ferments can be extracted, partly at least, by water from the agar-agar. Quantitative investigations have shown even that pepsin + pepsinogen and enterokinase as well, distribute themselves equally over the agar and water.

3. The facts mentioned sub 1 and 2 suggest a simple means of extracting the above-named ferments from the mucous membrane, and of determining quantitatively the distribution of them.

We have only to leave solid agar-agar columns of equal dimensions on various parts of the mucous membrane for some time and make subsequently a comparative quantitative determination of the specific action of the watery agar extract.

4. The results obtained with this new method with respect to the distribution of the above-named ferments in the digestive tube of the pig confirm those obtained by most investigators with the usual extraction methods on the dog.

5. The advantages of the method over the usual one consist, besides in its greater simplicity, also in the fact that the enzyme under investigation is much less polluted by decomposition products of the mucous membrane.

Especially for the investigation of the distribution of enzymes in individuals who, when alive suffered from diseases of the stomach or intestinal canal (ulcers in the stomach, the intestines, etc.) the method seems to me likely to be of use.

Moreover it is to be expected that besides the ferments examined till now, others will also pass into the agar-agar, which will enable us to make quantitative determinations of them in a similar way.

Finally the method seems to me to deserve recommendation as it can be applied in experiments at a lecture; at the same time, by adding congo-red or a similar indicator to the agar, the amount of acid or alkali can be demonstrated ocularly.

*Groningen, September 1907.*

**Mathematics.** — “*The extension of the Configuration of KUMMER to spaces of  $(2^p-1)$  dimensions.*” By MR. J. A. BARRAU. (Communicated by Prof. D. J. KORTEWEG.)

(Communicated in the meeting of September 28, 1907).

§ 1. If we represent by  $S_1$  the system  $\begin{matrix} a & b \\ b & a \end{matrix}$ , built up out of two letters and by  $S_2$  the same system in new letters  $c$  and  $d$ ; if likewise we represent by  $T$  the system of signs  $\begin{matrix} + & + \\ + & - \end{matrix}$  and by  $-T$  the opposite  $\begin{matrix} - & - \\ - & + \end{matrix}$ , we obtain by connecting these

$$\begin{matrix} S_1 & S_2 & & T & T \\ & & \text{and} & & \\ S_2 & S_1 & & T & -T \end{matrix}$$

the two systems

$$\begin{matrix} a & b & c & d & & + & + & + & + \\ b & a & d & c & & + & - & + & - \\ c & d & a & b & \text{and} & + & + & - & - \\ d & c & b & a & & + & - & - & + \end{matrix}$$

By giving *each* row of four letters in turn the signs of *each* row of the system of signs sixteen quadruplets of algebraic quantities appear which, as is known<sup>1)</sup>, represent the elements of the  $Cf(16_6)$  of KUMMER whether they are considered as homogeneous coordinates of points or as coefficients of planes in  $Sp_3$ . For, to each element are incident the elements of another kind, represented by the three permuted letter quadruplets and for each of them with half of the sign combinations.

§ 2. If now we call  $S_1$  and  $T$  the letter- and the sign-system of 4 resp. and if we repeat the combination described above such-like systems of 8 are formed of which that one of the letters furnishes the permutations of a *regular*  $G_8$  of order 8<sup>2)</sup>, consisting exclusively of binary substitutions, whilst that of the signs is *anallagmatic*<sup>3)</sup>, i. e. every two rows show as many sign variations as

<sup>1)</sup> See a.o. JESSOP *Line-Complex* p. 23 or HUDSON *Kummer's Surface* p. 5.

<sup>2)</sup> Compare MILLER *Quart. Journ.* 28 p. 255, group 8 No. 4.

<sup>3)</sup> LUCAS *Récréations Mathématiques* II p. 113; *Nieuw Archief voor Wiskunde* 7 p. 256.

sign-permanencies. The systems become (that of the signs somewhat differently arranged):

I	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	1	+	+	+	+	+	+	+
II	<i>b</i>	<i>a</i>	<i>d</i>	<i>c</i>	<i>f</i>	<i>e</i>	<i>h</i>	<i>g</i>	2	+	+	+	+	-	-	-
III	<i>c</i>	<i>d</i>	<i>a</i>	<i>b</i>	<i>g</i>	<i>h</i>	<i>e</i>	<i>f</i>	3	+	+	-	-	+	+	-
IV	<i>d</i>	<i>c</i>	<i>b</i>	<i>a</i>	<i>h</i>	<i>g</i>	<i>f</i>	<i>e</i>	4	+	-	+	-	+	-	+
V	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	5	+	-	-	+	-	+	+
VI	<i>f</i>	<i>e</i>	<i>h</i>	<i>g</i>	<i>b</i>	<i>a</i>	<i>d</i>	<i>c</i>	6	+	-	-	+	+	-	-
VII	<i>g</i>	<i>h</i>	<i>e</i>	<i>f</i>	<i>c</i>	<i>d</i>	<i>a</i>	<i>b</i>	7	+	-	+	-	-	+	-
VIII	<i>h</i>	<i>g</i>	<i>f</i>	<i>e</i>	<i>d</i>	<i>c</i>	<i>b</i>	<i>a</i>	8	+	+	-	-	-	-	+

By providing each of the rows of letters with each of the sign combinations there appear sixty-four octuples of algebraic numbers to which we assign the notations I1, I2, . . . VIII 8. Whether we consider these numbers as homogeneous coordinates of points or as coefficients of equations of  $Sp_6$  in a  $Sp_7$ , each element is incident with  $7 \times 4 = 28$  of another sort, namely to half of the sign combination of each letter permutation; so a  $Cf. (6\frac{1}{2}_8)$  appears, to be designated by  $K^{VII}$ .

As with  $K^{III}$  it is possible to combine the  $Cf$ -elements to simplexes  $A, B, C, D, E, F, G, H$  in various ways. Such an arrangement is i. a.:

	1	2	3	4	5	6	7	8
<i>A</i>	I 1	II 4	III 5	IV 3	V 7	VI 8	VII 6	VIII 2
<i>B</i>	I 2	II 7	III 6	IV 8	V 4	VI 3	VII 5	VIII 1
<i>C</i>	I 3	II 6	III 7	IV 1	V 5	VI 2	VII 4	VIII 8
<i>D</i>	I 4	II 1	III 8	IV 6	V 2	VI 5	VII 3	VIII 7
<i>E</i>	I 5	II 8	III 1	IV 7	V 3	VI 4	VII 2	VIII 6
<i>F</i>	I 6	II 3	III 2	IV 4	V 8	VI 7	VII 1	VIII 5
<i>G</i>	I 7	II 2	III 3	IV 5	V 1	VI 6	VII 8	VIII 4
<i>H</i>	I 8	II 5	III 4	IV 2	V 6	VI 1	VII 7	VIII 3

The table indicates that eight vertices of e.g. the simplex  $A$  are resp. the points I1, II4 etc, according to the former notation, while at the same time the eight opposite side- $Sp_6$  of the simplex are represented by those same notations.

The connection of  $Cf$ -elements can now be represented by a diagram (pl. I) the rows of which indicate the  $Sp_6$ , the columns the points, whilst incidence of a  $Sp_6$  with a point is indicated by hatching the square common to the respective row and column.

We see that the diagram can be brought to a more condensed shape :

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>
<i>A</i>	<i>S</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>
<i>B</i>	<i>a</i>	<i>S</i>	<i>g</i>	<i>f</i>	<i>e</i>	<i>d</i>	<i>c</i>	<i>b</i>
<i>C</i>	<i>b</i>	<i>g</i>	<i>S</i>	<i>e</i>	<i>f</i>	<i>c</i>	<i>d</i>	<i>a</i>
<i>D</i>	<i>c</i>	<i>f</i>	<i>e</i>	<i>S</i>	<i>g</i>	<i>b</i>	<i>a</i>	<i>d</i>
<i>E</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>S</i>	<i>a</i>	<i>b</i>	<i>c</i>
<i>F</i>	<i>e</i>	<i>d</i>	<i>c</i>	<i>b</i>	<i>a</i>	<i>S</i>	<i>g</i>	<i>f</i>
<i>G</i>	<i>f</i>	<i>c</i>	<i>d</i>	<i>a</i>	<i>b</i>	<i>g</i>	<i>S</i>	<i>e</i>
<i>H</i>	<i>g</i>	<i>b</i>	<i>a</i>	<i>d</i>	<i>c</i>	<i>f</i>	<i>e</i>	<i>S</i>

Here  $S$  indicates a simplex-filling; each of the other letters a system ( $8_3$ ) denoting the incidence connection between the elements of two simplexes. These systems ( $8_3$ ) have all degenerated into two ( $4_3$ ), each pair of our simplexes is thus connected in an equal way and forms a  $Cf(16_{1,0})$  of the same type.

§ 3. Analogous to the well-known decomposition of  $K^{III}$  into four tetrahedra lying in pairs in a MöBIUS-position, it is obvious to call the position of two of the simplexes, e.g.  $A$  and  $B$ , by that name. Each side- $Sp_6$  of one  $S$  contains three points, so a face, of the other; each vertex of one lies in three side- $Sp_6$ , so in a side- $Sp_4$  of the other; the correspondence is such that opposite elements of  $A$ , e.g. vertex  $A_1$  and side-space  $A_1$  also furnish opposite elements of  $B$ , namely resp. the side- $Sp_4$ :  $B_1B_5B_6B_7B_8$  and the face  $B_2B_3B_4$ , just as this is the case with the tetrahedra in MöBIUS-position.

There exists already however, provided with the same property, an extension of this notion, that of BERZOLARI<sup>1)</sup> where each side- $Sp_6$  of one  $S$  contains one vertex of the other, and is generated by operation with a focal system on an arbitrary simplex; let us call this position  $MI$ , then it is evident that the discussed more specialized  $MII$  is to be regarded as a threefold  $MI$ .

<sup>1)</sup> *Rendiconti del Circolo Matem. di Palermo* 22.

The elements of two simplexes  $A$  and  $B$  in  $MII$  can be arranged only in one other way to two suchlike simplexes, namely as

$$\begin{array}{l} \text{first simplex } P: A_1, A_2, A_3, -A_4, B_5, B_6, B_7, B_8, \\ \text{second ,, } Q: B_1, B_2, B_3, B_4, A_5, A_6, A_7, A_8. \end{array}$$

If we regard such a new simplex in connection with  $C, D, \dots H$ , it then shows with each of these a new sort of position; for all however of the same type, showing analogy to the pairs of tetrahedra in STEINER-position which can be separated in the same way from  $K^{III}$ <sup>1)</sup>. We find for the  $cf(16_{10})$  of two such simplexes a diagram of the shape:

$$\begin{array}{c} S \ x \\ x \ S, \end{array}$$

where  $x$  again represents a system ( $8_3$ ) which however does not degenerate now, but is identical to the cyclic system which is obtained out of the initial row: 1 2 . . . 5 . . .

Opposite elements of one simplex furnish, as in  $Sp_3$ , no opposite ones of the other.

§ 4. The 28 operations determining in each  $cf$ -space the  $cf$ -points incident to them and reciprocally, are *focal-correlations*; thus e.g. the  $Sp_6: A_1$

$$(+a, +b, +c, +d, +e, +f, +g, +h)$$

is transformed into the point  $A_2$  situated in it

$$(+b, -a, +d, -c, +f, -e, +h, -g)$$

by operating with the skew-symmetrical determinant of transformation:

$$\begin{vmatrix} 0 & +1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & +1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & +1 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \end{vmatrix}$$

These focalsystems are mutually in involution as the group of the letter substitutions as well as that of the sign variations are ABEL groups.

The 36 remaining reciprocities are polarities with respect to some 36 quadratic  $Sp_6$ , which serve for  $K^{VII}$  as the 10 fundamental-surfaces of order two for  $K^{III}$ .

<sup>1)</sup> MARTINETTI, *Rendic. Palermo* 16 p. 196.

Their equations are of two types; namely *eight* of the form

$$\pm x_1^2 \pm x_2^2 \pm x_3^2 \pm x_4^2 \pm x_5^2 \pm x_6^2 \pm x_7^2 \pm x_8^2 = 0,$$

where the combinations of signs must be derived from the sign system; and twenty-eight of the form:

$$\pm x_1 x_2 \pm x_3 x_4 \pm x_5 x_6 \pm x_7 x_8 = 0,$$

where the connection of the indices is given by the seven binary substitutions of the regular  $G_8$ , whilst the signs must be selected:

$$\begin{array}{cccc} + & + & + & + \\ + & + & - & - \\ + & - & + & - \\ + & - & - & + \end{array}$$

The sixty-three operations which transform an element into another of the same sort are *collineations*; so we obtain, analogous to the KLEIN  $G_{32}$  in  $Sp_3$ , a geometrical ABEL group  $G_{128}$ , consisting of the identity and sixty-three collineations; twenty-eight focal systems in involution and thirty-six polarities.

§ 5. The twenty-eight points in each  $Sp_6$  of  $K^{VII}$  lie on a quadratic  $Q_8$  and reciprocally.

To prove this we regard the determinant of the terms of order two, formed of seven of the eight homogeneous coordinates; so this is of order  $7 + \binom{2}{7} = 28$ . The omission of a coordinate is geometrically the projecting out of a vertex of the fundamental simplex on the opposite  $Sp_6$ ; if the projections of 28 points lie in it quadratically, then the points themselves do so in their  $Sp_6$ .

Let us first restrict ourselves to  $Sp_6 : A_1$ .

The twenty-eight points are to be divided into seven quadruplets of the same order of letters; the purely quadratic terms within such a quadruplet are in each column alike, the mixed ones may differ in sign. Let us call the four terms in a column  $p, q, r, s$ , then the substitution

$$\begin{array}{l} P = p + q + r + s \\ Q = p + q - r - s \\ R = p - q + r - s \\ S = p - q - r + s \end{array}, \text{ the } \Delta \equiv \begin{vmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{vmatrix} \text{ of which is } \neq 0,$$

causes three of the four quadratic terms to disappear, the  $\Delta_{28}$  breaks up into the product of a  $\Delta_7$  of quadratic and a  $\Delta_{21}$  of mixed terms. Here

$$\Delta_7 = \begin{vmatrix} b^2 & a^2 & d^2 & c^2 & f^2 & e^2 & h^2 \\ c^2 & a^2 & a^2 & b^2 & g^2 & h^2 & e^2 \\ d^2 & c^2 & b^2 & a^2 & h^2 & g^2 & f^2 \\ e^2 & f^2 & g^2 & h^2 & a^2 & b^2 & c^2 \\ f^2 & e^2 & h^2 & g^2 & b^2 & a^2 & d^2 \\ g^2 & h^2 & e^2 & f^2 & c^2 & d^2 & a^2 \\ h^2 & g^2 & f^2 & e^2 & d^2 & c^2 & b^2 \end{vmatrix}$$

That in general  $\Delta_7 \neq 0$  is evident i. a. from

$$h = 1, a = b = c = d = e = f = g = 0.$$

The  $\Delta_{11}$  gets after change of signs of some rows the form:

	0	0	0	0	bh	0	0	0	0	-ah	0	df	-de	0	-cf	ce	0	0	0
	0	0	bf	-be	0	0	0	-af	ae	0	0	0	0	dh	0	0	-ch	0	0
	bd	-bc	0	0	0	-ad	ac	0	0	0	0	0	0	0	0	0	0	0	fh
	0	0	0	ch	0	0	0	dg	0	-de	0	0	-ah	0	-bg	0	be	0	0
	0	0	cg	0	-ce	0	0	0	dh	0	0	-ag	0	ae	0	-bh	0	0	0
d	0	bc	0	0	0	ad	0	0	0	0	-ab	0	0	0	0	0	0	-gh	0
	0	0	dh	0	0	0	0	0	cg	-cf	0	0	-bg	bf	-ah	0	0	0	0
	0	0	0	dg	-df	0	0	ch	0	0	0	-bh	0	0	0	-ag	af	0	0
	-bd	0	0	0	0	-ac	0	0	0	ab	0	0	0	0	0	0	gh	-fh	
	0	-eh	0	0	0	-fg	0	0	0	cf	0	0	bg	0	ah	0	0	0	0
	-eg	0	0	0	ce	0	-fh	0	0	0	0	ag	0	0	0	bh	0	0	-ac
f	0	0	0	be	0	0	0	af	0	0	-gh	0	0	0	0	0	ch	-ab	0
	-fh	0	0	0	0	0	-eg	0	0	de	0	0	ah	0	bg	0	0	0	-bd
	0	-fg	0	0	df	-eh	0	0	0	0	0	bh	0	0	0	ag	0	0	0
	0	0	-bf	0	0	0	0	0	-ae	0	gh	0	0	-dh	0	0	0	ab	0
h	0	0	0	0	0	0	0	0	0	ah	-ef	0	de	0	cf	0	0	-cd	0
	0	fg	0	-dg	0	eh	0	-ch	0	0	0	0	0	0	0	0	0	-af	0
	eg	0	-cg	0	0	0	fh	0	-dh	0	0	0	0	-ae	0	0	0	0	ac
	0	0	0	0	-bh	0	0	0	0	0	ef	-df	0	0	0	-ce	0	cd	0
	fh	0	0	-ch	0	0	eg	-dg	0	0	0	0	0	0	0	0	-be	0	bd
	0	eh	-dh	0	0	fg	0	0	-cg	0	0	0	0	-bf	0	0	0	0	0

The sum of the numbers in each column amounts to zero; so

$$\Delta_{21} = 0.$$

As each element with the 28 incident to it can be transformed into any other by means of a direct or reciprocal projectivity, the quadratic position of every 28 is now proved.

§ 6. Each couple of  $Sp_6$  of the  $cf$  has twelve points in common lying thus in a  $Sp_3$ . No other  $Sp_6$  containing these twelve, all these  $Sp_6$  differ and their number is  $\binom{2}{64} = 2016$ . The  $cf$ -points form with them a  $cf$  ( $64_{3,8}$ ,  $2016_{1,2}$ ).

There are triplets of  $Sp_6$  which have six points in common, lying thus in a  $Sp_4$ , each  $cf$ - $Sp_6$  has namely in still 32  $Sp_6$  six of its points. Such a sextuple can be deduced from three groups of twelve, their number is thus  $\frac{2016 \times 32}{3} = 21504$ ; they form with the  $cf$ - $Sp_6$  a  $cf$  ( $21504_3$ ,  $2016_{3,2}$ ).

There are quadruplets of  $Sp_6$  having four points in common which therefore determine a  $Sp_3$ ; each  $cf$ - $Sp_6$  has namely four of its six points in fifteen other  $cf$ - $Sp_6$ . Every  $Sp_6$  can be derived from four  $Sp_4$ , their number is thus  $\frac{21504 \times 15}{4} = 80640$ . They form with the  $cf$   $Sp_6$  a  $cf$  ( $80640_4$ ,  $21504_{1,6}$ ).

There are sextuplets of  $Sp_6$  having three points of the  $cf$  in common, which therefore determine a  $Sp_2$ ; each  $cf$ - $Sp_6$  has namely three of its four points in eight other  $cf$ - $Sp_6$  more, these eight  $Sp_6$  furnish two by two however the same triplet; as furthermore each  $Sp_2$  can be deduced from  $\binom{2}{6} = 15$   $Sp_6$ , their number is  $\frac{80640 \times 4}{15} = 21504$ .

This could be expected as the whole consideration starting from the  $cf$ -points might have been put reciprocally, and would then have led on account of the self-reciprocity of the system to the same elements; so still 2016  $Sp_6$  are obtained, the right lines of connection of the pairs of points.

The further amounts of incidences of the kinds of elements mutually can now be easily deduced; the notation of  $K^{VII}$  becomes finally:

	$Sp_0$	$Sp_1$	$Sp_2$	$Sp_3$	$Sp_4$	$Sp_5$	$Sp_6$
	64	2016	21504	80640	21504	2016	64
incident to:							
$Sp_0$	—	2	3	4	6	12	28
$Sp_1$	63	—	3	6	15	66	378
$Sp_2$	1008	32	—	4	21	160	2016
$Sp_3$	5040	240	15	—	15	240	5040
$Sp_4$	2016	160	21	4	—	32	1008
$Sp_5$	378	66	15	6	3	—	63
$Sp_6$	28	12	6	4	3	2	—

By the method of intersecting and projecting triplets and doublets of consecutive kinds of elements are to be transformed into elements of  $Sp_3$  or  $Sp_2$ ; thus are formed e.g. a *cf*  $(21504_{2,1})$  of points and planes, with 80640 *cf*-lines, and a plane *cf*  $(2016_{3,2}, 21504_3)$  of points and lines, or reciprocally.

§ 7. If we represent the system of letters and that of signs of 8 resp. by  $S_1$  and  $T$  and if we repeat the combination

$$\begin{array}{ccc} S_1 & S_2 & T & T \\ & \text{and} & T & -T, \\ S_2 & S_1 & & \end{array}$$

we obtain systems for 16 belonging to each other, etc., the operation allowing of indefinite continuation; one always arrives at a regular ABEL substitution group  $G_{2^p}$  and a suitable anallagmatical system for the signs.

These always furnish in  $R_{2^p-1}$  a *cf*, analogous to that of KUMMER with the notation :

$$Cf \left( 2_{(2^p-1).2^{p-1}}^{2^p} \right),$$

arising from an arbitrary starting element by an operation with a geometrical ABEL group :

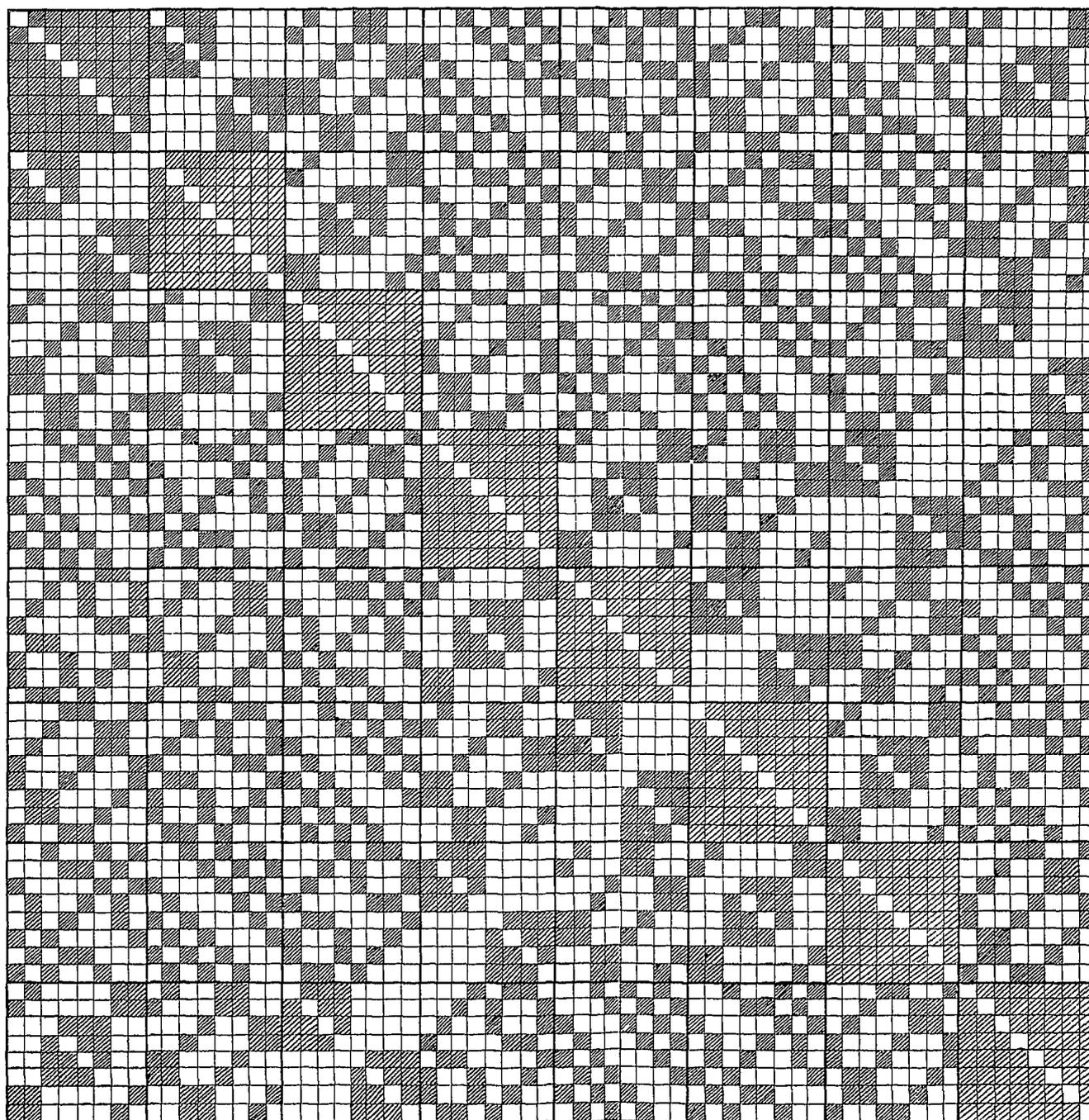
the *identity* and  $2^{2^p}-1$  *collineations* on one hand  
and  $(2^p-1) \cdot 2^{p-1}$  *focal systems* mutually in involution with  
 $(2^{p+1}-2^p+1) \cdot 2^{p-1}$  *polarities* on the other hand.

The quadratic situation of the elements incident to one element can always be proved by reduction of the determinant according to the example of § 5<sup>1)</sup>.

<sup>1)</sup> A more extensive treatment also for spaces of other numbers of dimensions will follow in the dissertation to be published: J. A. BARRAU, *Bydragen tot de theorie der cf*. (Amsterdam 1907).

A. BARRAU. "Analogon of the configuration of KUMMER in  $Sp_7$ ."

1 2 3 4 5 6 7 8 1 2 3 4 5 6 7 8 1 2 3 4 5 6 7 8 1 2 3 4 5 6 7 8 1 2 3 4 5 6 7 8 1 2 3 4 5 6 7 8 1 2 3 4 5 6 7 8



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**Mathematics.** — “The theorem of GRASSMANN in a space of  $n$  dimensions.” By LUCIEN GODEAUX, at Morlanwelz (Hainault).  
(Communicated by Prof. P. H. SCHOUTE).

We shall designate by the letter  $S$  a linear space and the number of dimensions of this space shall be the index.

The notation  $V_i^j$  represents a variety, the locus of  $\infty^i$  elements and of order  $j$ .

The order of a variety, locus of spaces  $S_k$  occurring in an  $(n-k)(k+1)-1$  times infinite number in a space  $S_n$ , is the number of  $S_k$  of an  $S_{k+1}$  through an  $S_{k-1}$  of this  $S_{k+1}$  and belonging to the variety.

1. In an  $S_2$  the theorem of GRASSMANN can be read thus:

The locus of  $S_0$  for which the  $S_1$  which unite it to three fixed  $S_0$  meet three fixed  $S_1$  in three  $S_0$  of the same  $S_1$  is a variety  $V_1^3$ .

In an  $S_3$  it has been given in the two following forms:

The locus of an  $S_0$  for which the  $S_2$  which unite it to four fixed  $S_1$  meet four fixed  $S_1$  in four  $S_0$  of a same  $S_1$  is a  $V_2^4$ . (LE PAIGE, *Sur la génération de certaines surfaces par des faisceaux quadrilatéraux*, *Bul. de Belgique*, 1884, 3<sup>e</sup> série, tome VIII).

The locus of an  $S_0$  for which the  $S_1$  which unite it to four fixed  $S_0$  meet four fixed  $S_2$  in four  $S_0$  of a same  $S_2$  is a  $V_2^4$ .

2. Let there be in an  $S_n$   $k$   $S_{r_i}$  which we shall designate by  $A_i$  and  $k$   $S_{s_i}$  which we shall designate by  $B_i$ , ( $i = 1, \dots, k$ ).

Let  $p$  be a number satisfying the  $2k$  inequalities

$$r_i + p + 1 \leq n - 1 \dots \dots \dots (1)$$

$$r_i + s_i + p + 1 > n, \quad (i = 1, \dots, k) \dots (2)$$

A space  $S_p$  determines with the  $k$  spaces  $A_i$   $k$  spaces  $S_{r_i+p+1}$ . These spaces meet the corresponding spaces  $B_i$  in  $k$  spaces  $S_{r_i+s_i+p-n+1}$ .

If these  $k$  spaces belong to an  $S_{\sum_{i=1}^k (r_i + s_i) + k(p-n+2) - 1}$ ,

the space  $S_p$  describes a variety  $V_{(n-p)(p+1)-1}$  the order of which is to be found.

Let us suppose we have

$$\sum (r_i + s_i) + k(p - n + 2) = n + 1. \dots \dots (3)$$

Let  $C$  be an  $S_{p+1}$  and  $D$  an  $S_{p-1}$  of  $C$ .

Let us designate by  $\Delta$  an  $S_p$  passing through  $D$  and situated in  $C$ .

Let us take  $k-1$  spaces  $\Delta$  and let us number them  $1, \dots, j-1, j+1, \dots, k$ .

These  $k-1$  spaces  $\Delta$  determine with  $k-1$  spaces  $A_i$  suitably chosen  $k-1$  spaces  $S_{r_i+p+1}$ . These spaces meet the corresponding spaces  $B_i$  in  $k-1$  spaces  $S_{r_i+s_i+p-n+1}$ , ( $i=1, \dots, j-1, j+1, \dots, k$ ).

These spaces determine an  $S_{\sum_{i=1}^{j-1} (r_i+s_i) + \sum_{i=j+1}^{i=k} (r_i+s_i) + (k-1)(p-n+2) - 1}$

This space has in common with  $B_j$  a space

$$S_{\sum_{i=1}^{j-1} r_i + \sum_{i=j+1}^{i=k} r_i + \sum_{i=1}^{i=k} s_i + (k-1)(p+2) - kn - 1}$$

In its turn this space determines with  $A_i$  a space

$$S_{\sum_{i=1}^{i=j+1} (r_i + s_i) + (k-1)(p+2) - kn}$$

On account of the equality (3) the latter meets  $C$  in a single point, which determines with  $D$  a space  $\Delta_j$ .

When  $j$  varies from 1 to  $k$ , one obtains  $k$  series of spaces  $\Delta$  between which exists a  $(1, 1, \dots, 1)$  correspondence. There are  $k$  coincidences.

The variety described by the space  $S_p$  is  $V_{(n-p)(p+1)-1}^k$ .

The locus of a space  $S_p$  for which the  $S_{r_i+p+1}$  which unite it to  $k$  fixed spaces  $S_{r_i}$  meet  $k$   $S_{s_i}$  in  $k$   $S_{r_i+s_i+p-n+1}$  of a same  $S_{\sum (r_i+s_i) + k(p-n+2) - 1}$ , ( $i=1, \dots, k$ ), is a variety  $V_{(n-p)(p+1)-1}^k$ .

The spaces  $A_i$  are evidently principal spaces of the locus of  $S_p$ , principal space having the same meaning as principal point or plane of a complex of rays.

In  $S_3$  we find the following theorem:

The locus of an  $S_1$  for which the  $S_2$  which join it to four  $S_0$  meet four  $S_1$  in four  $S_0$  of a same space  $S_2$  is a variety  $V_3^4$  (complex of order four).

3. If we regard the ordinary space as if generated by right lines we have a geometry of four dimensions. We shall now show two generalizations of the theory of GRASSMANN in this geometry.

Let us imagine  $k$  linear congruences  $G_1, \dots, G_k$ , and  $k$  plane pencils  $(P_1, \pi_1), \dots, (P_k, \pi_k)$ . Let us imagine moreover to be given a linear system  $C$  of linear complexes to the amount in number of  $\infty^{6-k}$ .

An arbitrary right line  $g$  determines  $k$  linear complexes with the

$k$  congruences  $G$ . These have in common with the  $k$  corresponding plane pencils  $k$  lines  $p_1, \dots, p_k$ .

Let us now find the locus of the line  $g$  when the  $k$  lines  $p$  belong to a same complex of the system  $C$ .

Let  $(A, \alpha)$  be any plane pencil. Let us take  $k-1$  lines of this pencil and let us number them  $1, \dots, i-1, i+1, \dots, k$ .

Each of these lines determines with the corresponding congruence  $G$  a linear complex, which has in common with the corresponding plane pencil  $(P, \pi)$  a line  $p$ . The  $k-1$  lines  $p$  found in this way determine a complex of the system  $C$ . This complex has a line  $p_i$  in common with the plane pencil  $(P_i, \pi_i)$ . This line determines with  $G_i$  a complex having a line  $\alpha_i$  in common with  $(A, \alpha)$ . When  $i$  varies from 1 to  $k$  we have  $k$  series of lines  $\alpha$  between which exists a  $(1, 1, \dots, 1)$  correspondence. There are  $k$  coincidences.

The locus of a right line for which the linear complexes that it determines with  $k$  fixed linear congruences meet  $k$  fixed plane pencils in  $k$  lines of a linear complex of a system of  $6-k$  terms is a complex of degree  $k$  (order and class) to which belong the given  $k$  linear congruences.

If  $k=6$ , we have a theorem of GRASSMANN.

4. Let us suppose five groups of three lines  $H_1, \dots, H_5$  and five nets of lines  $R_1, \dots, R_5$ .

An arbitrary line  $g$  determines with  $H_1, \dots, H_5$  five linear congruences which meet the five corresponding nets in five lines. If these five lines belong to a selfsame linear congruence the line  $g$  describes a congruence.

Let  $\pi$  be a plane. Let us consider in this plane five series of lines  $p_1, \dots, p_5$ .

Between the lines of these series it is easy to see that there is such a correspondence that to four right lines corresponds a fifth.

Let us suppose that three right lines are fixed, whilst the fourth describes a pencil. It is then easy to verify that the fifth also describes a pencil. According to an extension of the principle of ZEUTHEN there are fifteen coincidences.

The locus of a right line taken in such a way that the linear congruences which it determines with five systems of three lines have in common with five nets five lines of a same linear congruence is a congruence of the fifteenth class.

In the same way we can verify that this congruence is also of order fifteen and that it contains the generatrices of the same kind as the given lines of the five quadratic surfaces determined by these lines.

**Physics.** — “Contributions to the knowledge of the  $\psi$ -surface of VAN DER WAALS. XVI. On the gas phase sinking in the liquid phase for binary mixtures in the case that the molecules of one component exert only a feeble attraction.” By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEYSOM. Supplement N<sup>o</sup>. 16 to the Communications from the Physical Laboratory at Leiden.

§ 1. *Introduction.* In Comm. N<sup>o</sup>. 96<sup>b</sup>, These Proc. Dec. 1906, p. 501 a gas phase sinking in a liquid phase<sup>1)</sup>, the barotropic phenomenon, was treated for binary mixtures for a gas liquid plait, which crosses the  $\psi$ -surface as a transverse plait at lower temperature. Then the treatment for temperatures, at which the appearance of a longitudinal plait brings about a disturbance, was deferred to a later communication. Moreover, more special cases, as the appearance of minimum or maximum critical temperature or minimum or maximum pressure of coexistence, were left out of consideration, and the discussion was restricted to the case that retrograde condensation of the first kind occurs.

When for binary mixtures the conditions for the sinking of a gas phase in a liquid phase were treated in Comm. N<sup>o</sup>. 96<sup>c</sup>, These Proc. Dec. '06, p. 508 and Febr. '07 p. 660, it appeared in the first place that at least if the hypotheses mentioned there are valid, and pairs of substances are found with proper  $a_{22M}/a_{11M}$ ,  $b_{22M}/b_{11M}$  and  $M_2/M_1$ , the theory of VAN DER WAALS'  $\psi$ -surface leads us to expect that barotropic plaitpoints<sup>2)</sup> will occur.<sup>3)</sup> Further that for mixtures with

<sup>1)</sup> Considerations which are not in accord either with the limited compressibility of a gas at high pressures, first stated by NATTERER in 1844, or with our present views on the mixing of two substances, induced JAMIN, C.R. 96 (1883) p. 1448, Journ de phys. (2) 2 (1883) p. 389 to raise the question whether it should be possible that with compression of a mixture of CO<sub>2</sub> with air or with hydrogen, a liquid phase would collect above the gas phase. GAILLETET (JAMIN l.c.) did not succeed in realizing this.

<sup>2)</sup> On the peculiar phenomena which are met with in case of a barotropic plaitpoint, we hope shortly to make a communication.

<sup>3)</sup> That the barotropic plaitpoint found in Comm. N<sup>o</sup>. 96<sup>c</sup>, Dec. '06 § 5 belongs to the gas liquid plait (cf. Comm. N<sup>o</sup> 96<sup>c</sup>, Febr. '07, p. 660 footnote 1) was derived from the shape of the spinodal curve for this case, in connection with the course of the plaitpoint curve. The same thing may appear as follows: By applying the criterion (3) in Suppl. N<sup>o</sup>. 15, March '07, p. 796, we find that mixtures of a pair of substances of ratios indicated in the mentioned § belong to case (c), (cf. p. 276) while we may derive from VAN LAAR's fig. 22, Arch. Teyler (2) 10 (1907) p. 138, These Proc. Sept. '06, p. 226, fig. 1, that the plaitpoint curve crosses from the side  $x=0$  to the side  $v=b$  (VAN LAAR's type I).

certain ratio  $v_{k2}/v_{k1}$  for not too large  $T_{k2}/T_{k1}$  (from 0 up to a certain value, see Table I loc. cit. p. 662) only one barotropic plaitpoint occurs, which in connection with Comm. N<sup>o</sup>. 96<sup>b</sup> p. 503 and 504 pointed to the fact that for the knowledge of the course of the barotropic phenomena at lower temperature considerations in which only the transverse plait is taken into account, are not sufficient for these mixtures <sup>1)</sup> (see Comm. N<sup>o</sup>. 96<sup>c</sup> p. 663).

In Comm. N<sup>o</sup>. 96<sup>c</sup> p. 660 footnote 2 an estimation <sup>2)</sup> was derived about the critical temperature of helium from the observation of the barotropic phenomenon for a mixture of helium and hydrogen described in Comm. N<sup>o</sup>. 96<sup>a</sup> These Proc. Nov. '06, p. 459. In this estimation the supposition already mentioned in Comm. N<sup>o</sup>. 96<sup>a</sup>, p. 460, that the molecules of helium exert only an exceedingly slight mutual attraction, was found confirmed.

This suggested the investigation already announced in Comm. N<sup>o</sup>. 96<sup>b</sup>, p. 502 on binary mixtures one of whose components is a gas the molecules of which exert no or only feeble attraction (Suppl. N<sup>o</sup>. 15, These Proc. March '07, p. 786). Here a plait was described for the first time which at descending temperature appears on the

<sup>1)</sup> For mixtures of pairs of substances as meant in table I p. 662, for which  $0.2'9 > T_{k2}/T_{k1} > 0.196$ , three barotropic plaitpoints will occur one of which, however, does not belong to the absolutely stable region. At least for the larger ones of the mentioned ratios  $T_{k2}/T_{k1}$ , the two others belong to a plait which enters the  $\psi$ -surface from  $K_1$ , and crosses the  $\psi$  surface as a transverse plait at lower temperature For this the considerations of Comm. N<sup>o</sup>. 96<sup>b</sup> will hold at least in so far as solid phases do not cause a disturbance. For the smaller ones of these ratios one of these two barotropic plaitpoints will also fall in the not absolutely stable fluid region, and so also for these we shall have to take the occurrence of three phase equilibria into account.

<sup>2)</sup> For the calculations in note 2, p. 660 of Comm. N<sup>o</sup>. 96<sup>c</sup> we availed ourselves for  $a$  and  $b$  of hydrogen of the values calculated for this by KOHNSTAMM (LANDOLT-BÖRNSTEIN-MEYERHOFFER'S Physik. Chem. Tables 1905), which values had  $T_k = 38.6$ ,  $p_k = 20$  according to OLSZEWSKI, Wied. Ann. Bd. 56, p. 133, 1895 as starting point. If we derive the  $a$  and  $b$  for H<sub>2</sub> from  $T_k = 29$  à 32,  $p_k = 15$  according to DEWAR (B. A. Report 1902), the estimation for  $T_{kHe}$  yields about 1°, OLSZEWSKI'S newer data, Ann. d. Phys. 17 (1905) p. 986:  $T_k = 32.3$ ,  $p_k = 14.2$ , give it a value of more than 1° (the calculation according to note 2 l. c. yields  $a_{22M}/a_{11M} = 1/50$ ,  $T_{kHe} = 1.3$ ).

This would bring about these modifications in the classification of the helium mixtures mentioned in Suppl. N<sup>o</sup>. 15, Sept. '07, § 8, that mixtures of He with H<sub>2</sub>O, O<sub>2</sub>, A, Ne, NO, NH<sub>3</sub> would belong to case (b), those with H<sub>2</sub>, H<sub>2</sub>S, CO<sub>2</sub> to case (c). For the modification which another assumption about  $a_{12M}$  (cf. p. 280) would cause in the circumstances under which the plait starting from  $v = b$  occurs see Suppl. N<sup>o</sup>. 15 l. c. p. 234. A smaller  $a_{12M}$  might even again bring about a shifting in the classification in the direction from (c) towards (a).

$\psi$ -surface from the side of the small volumes, reaches the side  $x=0$  at  $T=T_h$ , and then passes into a plait crossing in a slanting direction from  $v=b$  to  $x=0$ . This description was accompanied by remarks about limited miscibility in the gas state.

In Suppl. N<sup>o</sup>. 15 § 7 These Proc. March '07, p. 795 three cases were distinguished for mixtures in which one component is a gas with a feeble attraction. They are indicated as cases (a), (b) and (c) in § 9, These Proc. Sept. '07, p. 235. Case (a) corresponds with the above mentioned one; in case (b) a plait coming from  $v=b$  and one coming from  $x=0$  join to a single plait in a double plaitpoint<sup>1)</sup>; in case (c) a plait starts from  $x=0$ , comes in contact with  $v=b$

<sup>1)</sup> On the suppositions mentioned in Comm. N<sup>o</sup>. 96c p. 509 and p. 510 the data for the two double points in the net of spinodal curves, of which this double plaitpoint is one (a node) may be found in the following way (cf. Comm. Suppl. N<sup>o</sup>. 15, p. 233, note 1):

The equation for the  $v, x$ -projection of the spinodal curve on the molecular  $\psi$ -surface:

$$RTv_M^3 = 2(1-x_M)(v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M})^2 + 2x_M(v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M})^2 \quad (1)$$

(cf. Suppl. N<sup>o</sup>. 15, March '07, p. 788) gives as conditions for the appearance of a double point after some obvious reductions:

$$(v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M})^2 = 2b_{11M}\sqrt{a_{11M}} \cdot (1-x_M)(v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M}) + \\ + 2b_{22M}\sqrt{a_{11M}} \cdot x_M(v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M}) \dots \quad (2)$$

and

$$(v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M})^2 = 2b_{11M}\sqrt{a_{22M}} \cdot (1-x_M)(v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M}) + \\ + 2b_{22M}\sqrt{a_{22M}} \cdot x_M(v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M}) \dots \quad (3)$$

From (2) and (3) follows:

$$\frac{(v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M})^2}{\sqrt{a_{11M}}} = \frac{(v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M})^2}{\sqrt{a_{22M}}} \dots \quad (4)$$

Extracting the root from this equation, we may (2) and (3) reduce to:

$$\frac{v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M}}{\sqrt{a_{11M}}} = 2b_{11M}(1-x_M) \pm 2b_{22M}x_M\sqrt{a_{22M}/a_{11M}} \quad (5)$$

and

$$\frac{v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M}}{\sqrt{a_{22M}}} = 2b_{22M}x_M \pm 2b_{11M}(1-x_M)\sqrt{a_{11M}/a_{22M}} \quad (6)$$

By eliminating  $v_M$  from (5) and (6) we obtain for  $x_M$  the equation (1) of Suppl. N<sup>o</sup>. 15, March '07, p. 796 (cf. errata Proc. Sept. '07, p. 239).

The further derivation of  $v_M$  and  $T$  (see Suppl. N<sup>o</sup>. 15, March '07, p. 798) may be left to the reader (compare with these developments VAN LAAR, These Proc. May '07, p. 38 sqq. and Arch. Teyler (2) 11 (1907) 1<sup>re</sup> partie § 5).

at lower temperature, and passes then into a plait crossing in a slanting direction<sup>1)</sup>).

For this distinction  $a_{22M}/a_{11M}$  was always supposed so small in connection with the value of  $b_{22M}/b_{11M}$ , that the plaitpoint curve crosses from  $K_1$  to the line  $v=b$  and that three phase equilibria not yet occur at the temperatures under consideration<sup>2)</sup>).

Now that the estimations concerning the  $a$  and  $b$  of helium justify the supposition that the plaitpoint curve<sup>3)</sup> crosses from  $x=0$  to the

<sup>1)</sup> KUNDT, Berl. Sitzb. Oct. 1880, S. 812—824 was of opinion that it would always be possible to convert a liquid to the gas state by pressing in a gas. This view was maintained in VAN ELDIK's thesis (Leiden 1898, p. 7, cf. Comm. Phys. Lab. Leiden, Suppl. N<sup>o</sup>. 3, p. 45), where it says that the operation mentioned, if it is realized, would be the determination of the plaitpoint pressure corresponding to the temperature of observation of the pair of substances which is subjected to the experiment. There it was tacitly assumed that with sufficiently high pressure the plaitpoint state could be reached for every temperature between the critical temperatures of the components as e.g. for mixtures of methyl chloride and carbonic acid, even though it would have to be found above 750 atmospheres for hydrogen and ether, as VAN ELDIK derived taking into account the diminution which with increasing pressure is found in the decrease of the surface tension caused by one and the same increase of pressure (KUNDT loc. cit. p. 818, VAN ELDIK Thesis, p. 5, cf. Suppl. N<sup>o</sup>. 3, p. 52). If we pay attention to the possibility now foreseen by the theory, that this diminution continues outside the region of observation, it seems probable in the light of the observations mentioned, that it would not be possible — here we treat as infinite, pressures which exert forces on the molecules greater than those joining the parts of them — to reduce the surface tension to 0 for the pair of substances mentioned (and the same remark applies to hydrogen and ethylalcohol) at the temperature of observation (KUNDT 21<sup>o</sup>, VAN ELDIK 9<sup>o</sup>.5), so that already at that temperature a plait crossing obliquely from  $x=0$  to  $v=b$  would exist on the  $\downarrow$ -surface.

In fact we should also derive from VAN LAAR's figure cited p. 274 footnote 3 that ether-hydrogen (and also alcohol-hydrogen) belong to VAN LAAR's type I, while according to the criteria laid down by us, they should belong to case (c) of this type. VAN DER WAALS' equations Contin. II p. 43, however, would point out a critical temperature of complete miscibility of about  $-200^{\circ}\text{C}$ . in the supposition of  $a_{12M} = \sqrt{a_{11M} a_{22M}}$ , so that according to these suppositions an obliquely crossing plait would only make its appearance below this temperature. If the existence of an obliquely crossing plait at the temperature of the above mentioned experiments should be confirmed, this might, among other things, point to the fact that  $a_{12M}$  would be considerably smaller than  $\sqrt{a_{11M} a_{22M}}$  for the pair of substances mentioned (cf. p. 280).

<sup>2)</sup> According to this restriction case (c) cannot occur e.g. for  $b_{22M}/b_{11M}$  larger than a certain value (cf. Suppl. N<sup>o</sup>. 15 These Proc. March '07, p. 797).

<sup>3)</sup> KUENEN, These Proc. Febr. '03, p. 473 was the first to find experimentally a plaitpoint curve starting from  $x=0$ , and directed to the side  $v=b$  for mixtures of ethane and methylalcohol.

line  $v = b$  for mixtures of helium and hydrogen<sup>1)</sup>, it is desirable to subject the barotropic phenomena for the cases mentioned to a closer examination. In this discussion for mixtures one component of which is a gas with feeble attraction, we shall again restrict ourselves and suppose that in the considered cases at the considered temperatures the second branch of the plaitpoint curve (VAN LAAR, These Proc. May '05 p. 37), starting from  $K_2$ , does not make its influence felt, so that three phase equilibria do not yet make their appearance.

§ 2. *The course of the barotropic phenomena for binary mixtures, one component of which is a gas whose molecules exert only a feeble attraction.*

In this discussion we shall have to distinguish the cases  $\alpha$ ,  $b$ , and  $c$  mentioned in § 1.

$a$ . In this case a plait starting from  $v = b$  and closed towards the side of the large  $v$ 's, appears for  $T_{km} > T > T_{k_1}$ , which plait we have called gas-gasplait in Suppl. N<sup>o</sup>. 15, March '07, p. 793. If  $b_{22} < b_{11}$ , then  $\theta_{pl}$  will be  $> \frac{\pi}{2}$  for  $T > T_{bpls}$  (see Comm. N<sup>o</sup>. 96<sup>b</sup> p. 504); at  $T = T_{bpls}$  a barotropic plaitpoint occurs (cf. Suppl. N<sup>o</sup>. 15 March '07 Pl. I, fig. 1); at  $T < T_{bpls}$  we find a barotropic nodal line on the gas-gasplait (cf. Suppl. N<sup>o</sup>. 15, Pl. I, fig. 2). At  $T = T_{k_1}$  the gas-gasplait passes into an obliquely crossing gas liquid plait. A barotropic nodal line will exist on it (see fig. 1) till it disappears under the three phase triangle, and so passes into the not absolutely stable region. As mentioned in § 1 we shall not give the description of what happens when three phase equilibria have appeared. In the same way we shall for the present disregard more complicated cases, as the appearance of two barotropic nodal lines on the gas-gasplait, three on the obliquely crossing plait etc., till further investigation may teach that these cases are possible.

If  $b_{22} > b_{11}$ , the plait coming from  $v = b$  may reach the side  $x = 0$ , and pass into an oblique plait without it being necessary that a barotropic tangent chord occurs.

$b$ . For  $b_{22} < b_{11}$  a barotropic plaitpoint will occur at  $T_{bpls} > T_{dpl}$  (cf. Suppl. N<sup>o</sup>. 15, March '07 p. 798). This barotropic plaitpoint, and also at  $T_{bpls} > T > T_{dvl}$  the barotropic tangent chord, may

<sup>1)</sup> This follows also from VAN LAAR's fig. 22, Arch. TEYLER (2) 10 (1907) p. 38 with the mentioned estimations on the critical temperature and pressure of helium (cf. p. 275 note 2) and on the suppositions made (cf. These Proc. Dec. '06 p. 509 and 510).

occur both on the plait starting from  $v = b$  and on that starting from  $x = 0$  (figs. 2 and 3). If in the homogeneous double plaitpoint the isobar should run parallel to the  $x$ -axis,  $T_{bpl}$  would coincide with  $T_{dpl}$ . For  $T < T_{dpl}$  a barotropic chord exists on the obliquely crossing plait, just as in case (a)<sup>1</sup>).

For  $b_{22} > b_{11}$ , as in this case for  $a$ , the existence of barotropic tangent chords is not required.

c. If  $b_{22} < b_{11}$ , a barotropic plaitpoint will make its appearance for  $T_{bpl} < T_{k_1}$  and  $> T_{km}$ ; at lower temperatures a barotropic tangent chord is found on the plait starting from  $x = 0$  and closed on the side of the small  $v$ 's, and at  $T < T_{km}$  on the obliquely crossing plait (fig. 4). For  $b_{22} > b_{11}$  as for  $a$  and  $b$ .

In fig. 5 the course of the spinodal curves (continuous) and of the connodal curves (lines consisting of dashes) on the  $\psi$ -surface for the unity of weight has been more fully represented for a case  $\epsilon$ . The figure has been construed with a view to mixtures of helium and hydrogen. In this we adopted the hypotheses mentioned in Comm. N<sup>o</sup>. 96<sup>c</sup>, Dec. '06, p. 509 and 510, and put for hydrogen  $T_{k_1} = 32,3$ ,  $p_{k_1} = 14,2$ , for helium  $T_{k_2} = 1,3$ ,  $b_{MH_2} = \frac{1}{2} b_{MH_4}$  (p. 275 note 2)<sup>2</sup>). The volume  $v$  is expressed in the theoretical normal volume of a molecular quantity as unity. The point  $K_m$  has been calculated according to VAN DER WAALS Cont. II, p. 43. The spinodal curves have been constructed as in Suppl. N<sup>o</sup>. 15, March '07, p. 788.  $P_b$  is the barotropic plaitpoint, calculated in the way indicated in Comm. N<sup>o</sup>. 96<sup>c</sup>, Dec. '06, p. 510. Further the plaitpoint curve  $K_1 K_m$  calculated according to the equation given by VAN LAAR,

<sup>1</sup>) In the light of our present knowledge of the behaviour of mixtures and divested of the considerations which are incompatible with it (cf. p. 274 footnote 1) the phenomenon deemed possible by JAMIN, C. R. 96 (1883) p. 1451, Journ. phys. (2) 2 (1883) p. 383, would be described as follows: On compression of a gas above a suitable quantity of liquid (see p. 281 note 2), this liquid is made to dissolve at first under plaitpoint circumstances, after which on further pressing in of the gas into the thus formed homogeneous phase a phase richer in the least volatile component (called by JAMIN liquid, by us in certain cases, cf. Suppl. No. 15, March '07, § 4, second gas phase) may separate *above* the phase which is richer in the most volatile component. If this phenomenon could be realized, we should have to deal with a case  $b$  for a temperature  $T > T_{dpl}$ , and in which the line  $RQ$  (see fig. 6) intersects the plait starting from  $v = b$  in such a way that for the intersected connodal tangent chords  $\theta > \frac{\pi}{2}$ .

<sup>2</sup>) However, on account of the uncertainty which still prevails about  $T_{kHe}$  and  $p_{kHe}$ , and in view of the probability that  $\alpha_{12M} < \sqrt{\alpha_{11M} \alpha_{22M}}$  (see p. 280) it is still to be considered as quite possible that He—H<sub>2</sub> belongs to case (b), as was supposed in Suppl. N<sup>o</sup>. 15.

These Proc. April '05 p. 652 has been included in the diagram. The second branch of the plaitpoint curve is not to be distinguished from the straight line  $HK_2$  on the scale on which the diagram has been drawn.

For the connodal curves the points of intersection with the line  $x = 0$  representing the points of saturation for pure hydrogen have been calculated. For this purpose the constants of saturation have been used, which have been calculated by DALTON<sup>1)</sup> for a substance that follows the equation of state of VAN DER WAALS with constant  $a$  and  $b$ . For the rest the course of the connodal curves for which for  $T \geq T_{lm}$  also the plaitpoints are known, has been represented schematically. This applies particularly to the points of intersection of the connodal curve for  $T = 20$  with the line  $v = b$ , so that also the course of the connodal curve, particularly of the gas branch, is uncertain in the neighbourhood of the line  $v = b$ . The line  $CD$  represents the experimentally determined barotropic tangent chord for  $T = 20$  (see Comms. N<sup>o</sup>. 96<sup>a</sup> and N<sup>o</sup>. 96<sup>c</sup> Febr. '07 p. 660 footnote 2).

The situation of the line  $CD$  with respect to the connodal curves might point to  $T_{lm}$  being higher than was calculated by us, which may be due either to the critical temperature of helium being lower than was assumed by us here, or to  $\alpha_{12M}$  being  $< \sqrt{\alpha_{11M}\alpha_{22M}}$  for mixtures of He—H<sub>2</sub><sup>2)</sup>.

The course of the barotropic plaitpoints and barotropic tangent chords in case (c), and also in case (b), if they occur on the plait starting from  $x = 0$ , corresponds for the higher temperatures with that for the case that the branch of the plaitpoint curve starting from  $K_1$  crosses the  $\psi$ -surface from  $x = 0$  to  $x = 1$ , for which case the course was described in Comm. N<sup>o</sup>. 96<sup>b</sup>. For the lower temperatures we meet with this difference that in the cases considered in this comm. the barotropic tangent chord continues to exist on the plait, till it disappears under the three phase triangle, whereas in the cases considered in Comm. N<sup>o</sup>. 96<sup>b</sup> the barotropic tangent chord may also vanish from the plait through a barotropic plaitpoint (lower barotropic plaitpoint temperature, see Comm. N<sup>o</sup>. 96<sup>b</sup> p. 504). The latter must even be the case if for  $T \geq T_{k_2}$  no three phase equilibria appear as yet (cf. p. 275 note 1).

1) J. P. DALTON, Phil. Mag. April 1907, p. 520.

2) The same remark concerning  $\alpha_{12M}$  for mixtures of H<sub>2</sub> with other substances might be derived as follows: for CO<sub>2</sub>—H<sub>2</sub> (the same holds for CO<sub>2</sub>—O<sub>2</sub>) from a comparison of the experimentally determined portion of the plaitpoint curve with that calculated in the same way as above for He—H<sub>2</sub>; for H<sub>2</sub>—ether and H<sub>2</sub>—alcohol see § 1 p. 277 note 1).

VAN DER WAALS, These Proc. Jan. '07 p. 528 calls attention to the influence of  $b_{22}$   $b_{11}$  on the occurrence of barotropic phenomena by stating this rule: "When the most volatile substance has the greatest limiting density, the gas phase can be specifically heavier than the liquid phase." In connection with what was discussed above we may now supplement this rule as follows: If of a binary mixture the more volatile component has the greater limiting density, the gas phase will be made to sink in the liquid phase by compression with suitable concentration and temperature, provided the more volatile component has so feeble an attraction that pressing in of this latter component cannot make the liquid phase of the less volatile component dissolve in the gas phase at definite <sup>1)</sup> temperatures even at the highest (comp. p. 277 note 1) pressures. <sup>2)</sup> It is implied in the terms of this rule that it has been supposed that no two liquid phases occur.

It is not excluded that also in other cases sinking of the gas phase in the liquid phase might occur. <sup>3)</sup>

If we apply this rule to pairs of substances of which data are available for  $a_{22M}$ ,  $a_{11M}$  and  $b_{2M}$ ,  $b_{1M}$ , it appears that only for He—H<sub>2</sub>, it may be expected on reasonable grounds <sup>4)</sup> that barotropic phenomena occur at not too high pressures<sup>5)</sup>. Further investigations will have to reveal whether for mixtures of pairs of substances as nitrogen

<sup>1)</sup> Also at higher temperatures than these barotropic phenomena may then occur.

<sup>2)</sup> In the case of compression of a gas above a liquid, starting from the pure substance in the way as was done in KUNDT's experiments we describe on the  $\psi$ -surface a curve the  $v, x$ -projection of which is a straight line joining a point of the line  $x = 0$  with the point  $v = 0, x = 1$ . For the liquid phase to disappear at a definite, suitable temperature just under plaitpoint circumstances, we must start from a definite quantity of liquid so that the volume is represented by  $SQ$  (see fig. 6). If the quantity of liquid from which we start, is smaller, the liquid phase will evaporate (be dissolved in the gas phase), if it is larger the gas is dissolved in the liquid phase (cf. VAN DER WAALS, Cont. II, p 136). Only if the diffusion is not rapid enough to ensure equilibrium all through the tube, solution of the liquid under plaitpoint phenomena may be observed also with other quantities of liquid as corresponding with  $v_Q$ , as has been set forth by KUENEN's experiments on the influence of phenomena of retardation.

<sup>3)</sup> See e.g. § 1, p 275, note 1.

<sup>4)</sup> Though for mixtures of e.g. helium and acetonitril the available data with application of the special hypotheses assumed in this § (concerning the equation of state etc) would point to the fact that at high pressures barotropic phenomena might still just occur, it is impossible to express a definite expectation with regard to this on account of the influence of the uncertainties, both in the data and in the validity of the mentioned suppositions.

<sup>5)</sup> This was mentioned in Comm. No. 96b Dec. '06 p. 504.

and a light oil with high critical temperature <sup>1)</sup>, nitrogen-lithium, argon-kalium, mercury-iron etc. sinking of the gas phase in the liquid phase could be realized.

§ 3. *On the conditions for the occurrence of barotropic phenomena.*

It appeared in § 2 that with a suitable ratio of the limiting densities the occurrence of the barotropic phenomena depends to a great extent on the ratio of the attractions of the molecules of the two components, hence on the ratio of the critical temperatures. The same thing may also be derived in the following way, more independent of the particular hypotheses which have led to the consideration of obliquely crossing plaits.

To bring about the phenomenon of the gas phase sinking in the liquid phase, the gas phase will have to be much more compressible than the liquid phase, and even on compression the gas phase must not dissolve in the liquid phase. For this the temperature will have to be pretty far below the critical temperature of the least volatile component ( $T_{k_1}$ ), but still far above that of the second component ( $T_{k_2}$ ). This points to a large difference between the critical temperatures of the components.

If for the pair of substances considered retrograde condensation of the first kind occurs, the coexisting phases indicated by the points  $L$  and  $G$  on the  $\psi$ -surface for the molecular quantity (see fig. 7) <sup>2)</sup>, can only have the same density if  $M_2 > M_1$ .

Only when on the plait on the molecular  $\psi$ -surface connodal tangent chords appear for which the angle with the axis  $x = 0$ :  $\theta > \frac{\pi}{2}$ , the coexisting phases can have equal density for  $M_2 < M_1$ .

As the difference between  $x_g$  and  $x_l$  is larger, and so the connodal tangent chords deflect more rapidly from the side  $x = 0$ , a smaller difference between  $M_2$  and  $M_1$  will suffice to establish equal densities in  $G$  and  $L$ .

This will be the more the case the more the plait extends towards the side  $v = b$ .

The latter is particularly furthered by a small ratio  $a_{22M}/a_{11M}$  (cf. Comm. Suppl. N<sup>o</sup>. 15 Pl. I fig. 1 and Pl. II), so by a small ratio of the critical temperatures,  $b_{22M}$  smaller than  $b_{11M}$  also tending in this direction.

<sup>1)</sup> Mr. F. M. GILLEY of Boston drew our attention to mixtures of air and oil.

<sup>2)</sup> The dotted lines indicate that the considerations of this § hold both for the case that at lower temperature the plait crosses the  $\psi$ -surface as a transverse plait, and for the case that it extends towards  $v = b$ .

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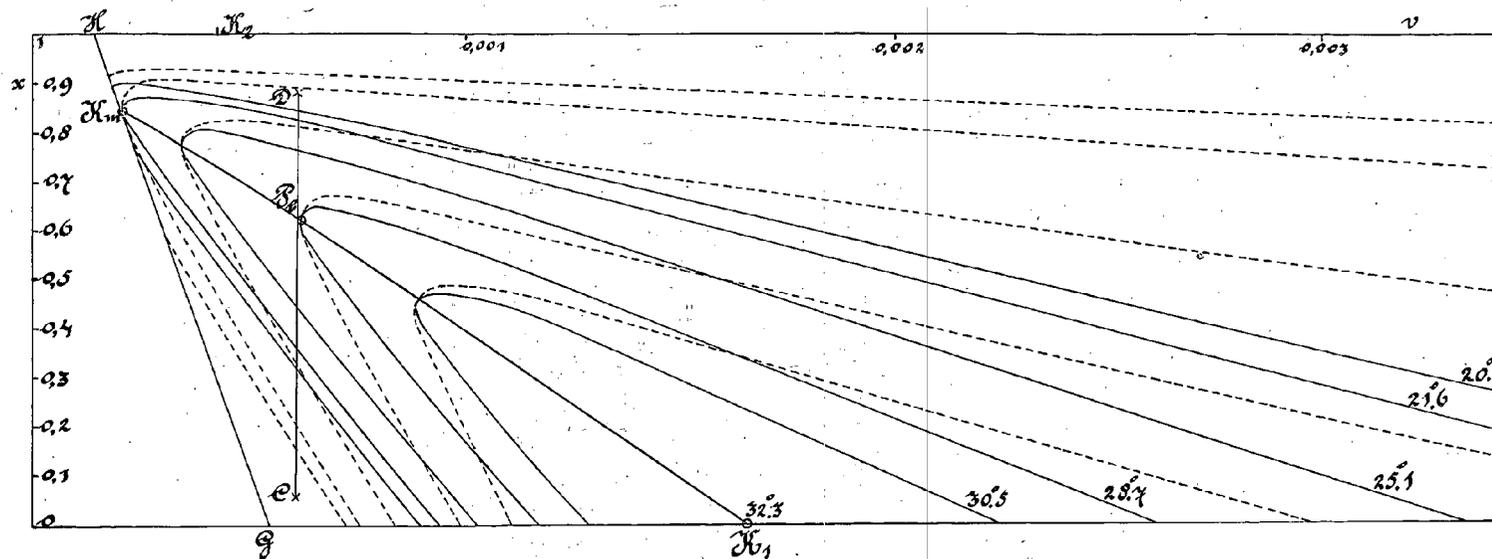


Fig. 5.

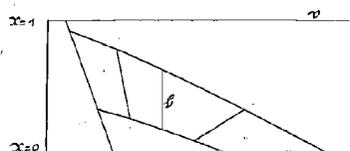


Fig. 1.

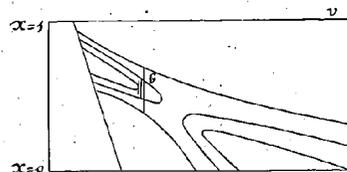


Fig. 2.

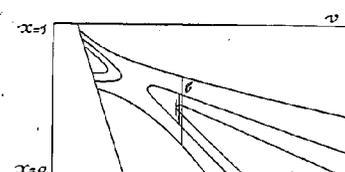


Fig. 3.

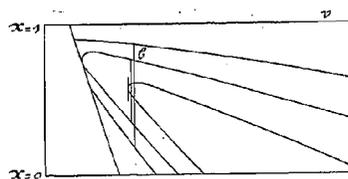


Fig. 4.

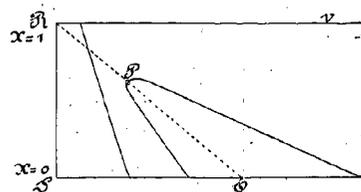


Fig. 6.

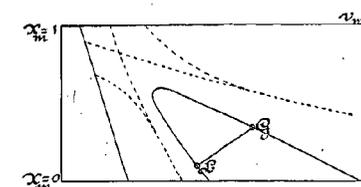


Fig. 7.

Hence we get as conditions for the possibility of the occurrence of barotropic phenomena:

The second component must have:  $T_{k_2}$  small compared with  $T_{k_1}$ , and by preference also:  $M_2 > M_1$ , and  $b_{22M} < b_{11M}$ .

This becomes still clearer by the application of equations (2) and (4) of Comm. N<sup>o</sup>. 79, April '02, p. 659:

$$x_l = x_g e^{\frac{\varphi'_g - \varphi'_l}{MRT}}$$

$$\frac{\varphi'_g - \varphi'_l}{MRT} = \left\{ \alpha \frac{T}{p_m} \frac{dp_m}{dT} - \beta \right\} \frac{p_m (v_g - v_l)}{MRT}$$

which determine the ratio of the concentrations of gas and liquid phases of a binary mixture in which the quantity of one component is small, if the law of the corresponding states may be applied. The connodal tangent chord will rapidly deflect from the side  $x = 0$ , if the exponent of  $e$  assumes a considerable negative value. The

greatest influence on this exerts  $\alpha = \frac{1}{T_{k_1}} \left( \frac{dT_{xk}}{dx} \right)_{x=0}$ , on account of

the value of the coefficient  $\frac{T}{p_m} \frac{dp_m}{dT} (> 7)$ ; so  $T_{k_2}$  will have to be small

with respect to  $T_{k_1}$ . The influence of  $\beta = \alpha - \gamma$ , if  $\gamma = \frac{1}{v_{k_1}} \frac{dv_{xk}}{dx}$

(cf. Comm. N<sup>o</sup>. 81, Oct. '02 p. 325) is only of secondary importance. To tend at least in the right direction,  $\gamma$  would have to be negative, so  $b_{22M} < b_{11M}$ <sup>1)</sup>.

**Physiology.** — “An investigation of Mr. J. W. A. GEWIN, on the relation of pepsin to chymosin.” By Prof. C. A. PEKELHARING.

That gastric juice possesses the power, on the one hand to digest proteins under acid reaction, on the other hand, to curdle milk under neutral or scarcely acid reaction, is generally attributed to the presence of two different enzymes in the gastric juice, viz. pepsin and chymosin. This opinion is chiefly based upon an observation of HAMMARSTEN, who was the first to throw light on the changes that take place in milk when it is coagulated by means of rennet. HAMMARSTEN found that an extract from the mucous membrane of the stomach, which, when prepared fresh, could digest proteins as well

1) The more elaborate mathematical treatment of the conditions for the occurrence of barotropic phenomena, as sequel to Comm. N<sup>o</sup>. 96c, will be postponed till further experiments call for a further discussion.

as curdle milk, after having been digested for a few days with hydrochloric acid at a temperature of 37° C., no longer showed the action of rennet, but had preserved its peptic action. From this it could not but follow that each of these actions depended upon a separate agent.

Meantime doubts have gradually arisen as to the correctness of this opinion. That there must at any rate be a very close connection between the proteolytic action of pepsin and the enzyme of rennet, was made probable by the experience that all enzym-solutions with a proteolytic action, no matter whether they are of animal or of vegetable origin, can also act like rennet. And, as I communicated some years ago in this Academy, and as was afterwards corroborated by NENCKI and SIEBLER, it could also be proved that all kinds of preparations of pepsin, also when a long digestion with hydrochloric acid and a purification as careful as possible had preceded, are able to act like rennet.

In 1904 there appeared an investigation by PAWLOW and PARASTSCHUK <sup>1)</sup>, in which they demonstrated that pepsin and chymosin must be considered as the same substance. These investigators found that in different liquids containing enzyme not only the proteolytic and the curdling power are always found side by side, but that also a proportionately greater curdling power corresponds to a greater proteolytic action. That this is not found in some enzym-solutions of commerce appeared to be owing to the presence of other substances; as soon as their effect was destroyed, the proportionality came to light. A solution of rennet, according to HAMMARSTEN prepared by means of carbonate of magnesia from gastric juice, which, in his opinion, no longer contained any pepsin at all, appeared to be a very good digester of albumen, if only the noxious influence of magnesia-salts was taken away. No more was it proved by HAMMARSTEN, — as PAWLOW explained — that a pepsin-solution can be freed from rennet by digestion with hydrochloric acid, as the proteolytic action had been examined, while the liquid still had an acid reaction; the curdling action, on the other hand, after neutralization, by which the enzyme might be easily destroyed.

Against PAWLOW's explanation objections have been raised. Especially two Swedish investigators, BANG <sup>2)</sup> and SCHMIDT-NIELSEN <sup>3)</sup>, have defended HAMMARSTEN's point of view. The investigation of Mr. GEWIN

<sup>1)</sup> Zeitschr. f. Physiol. Chemie, Bd. XLII, S. 415.

<sup>2)</sup> Zeitschr. f. Physiol. Chemie, Bd. XLIII, S. 358.

<sup>3)</sup> Ibid. Bd. XLVIII, S. 92.

<sup>4)</sup> PFLÜGER's Archiv. Bd. LXXIX, S. 425.

refers principally to the grounds alleged by these two authors for the duality-hypothesis.

In the first place he has occupied himself with an inquiry into the correctness of the conclusion previously drawn by BANG<sup>4)</sup> from a number of experiments, that there is not only a difference between pepsin and rennet, but also that even the enzym of rennet does not possess the same qualities in different kinds of animals. BANG continued to apply the old name, chymosin, to the enzym of rennet, as it is found in the calf. From this he distinguished by the name of parachymosin the enzym that can be got from the mucous membrane of the pig-stomach. The difference showed itself in the fact that parachymosin, when diluted, became sooner inactive than chymosin, that it showed a greater activity by the addition of chlorcalcium, was more proof against heating to 70° C. and less so against the action of alkali.

With reference to extracts from the mucous membrane of the stomach of calf or pig GEWIN could corroborate these differences; only he did not find the difference in the promotion of the activity by adding chlorcalcium as important as BANG. However, it was a different thing, if not the extracts themselves were examined but the enzym extracted therefrom by dialysis, and purified as much as possible in the way formerly communicated by me. The better the purification had taken place, the smaller the difference became. The extract from the mucous membrane of the calf-stomach loses its power to curdle milk when, neutralized, it is heated for 10 minutes to 70° C.; however, its power is but little reduced, if it is mixed with caustic soda to 0.01 % and neutralized again after half an hour. With the extract of the mucous membrane of a pig-stomach it is just the reverse. With the enzym of the calf, purified as much as possible, the resistance against heating appeared to have become great, against alkali small. From this it must therefore be deduced that the difference does not lie in the enzym itself, but that it is caused by other substances occurring in the extract. Indeed, it could be proved experimentally that the extract from the membrane of the calf-stomach contains substances which protect the enzym against the action of alkali, but make it the more sensitive to heat. Of a solution of purified pig-enzym (which possesses the qualities of BANG's parachymosin) one half was diluted with water, the other with an extract from the mucous membrane of a calf-stomach, which extract had been deprived of all enzym by heating it for one hour to 80° C. and then neutralized. Of both solutions 2 cc. mixed with 8 cc. of milk caused curdling in 30 sec. A part of each was heated for

10 minutes to 70° C., another part for half an hour left in contact with 0.01 % Na HO and then neutralized again. Now the result was :

2 cc. enzym with water	+ 8 cc. milk	After heating	After action of alkali
2 " " " extract	+ 8 " "	curdling in 2½ min.	no curdling
		no curdling	curdling in 11 min.

GEWIN also examined two rennet-preparations of commerce, one Dutch of VAN HASSELT and one Danish of HANSEN. Both showed the qualities of BANG's chymosin. But when, by dialysis and precipitation with acetic acid, the enzyme had been isolated and at least for the greater part been freed from impurities, they had become much more susceptible to alkali and much less so to heating.

That the enzyme is destroyed not only by alkaline, but gradually also by neutral reaction has been made clear by PAWLOW and corroborated by GEWIN in numerous experiments. From this GEWIN explains the difference found by BANG between chymosin and parachymosin, the solution being diluted. What BANG calls chymosin is the enzyme mixed with substances protecting it from alkali. When those substances are present, it may be assumed that the enzyme is better proof against the dilution with water, by which the number of hydroxyl- and metal-ions increases. A solution of purified enzyme (parachymosin), possessing the same curdling power as a not purified solution of calf-enzyme (chymosin), shows, when diluted, sooner a decrease in action, and consequently must, also sooner, show the promoting influence of the addition of chlorcalcium.

So there is no reason for assuming different rennet-enzymes in different kinds of animals. The difference does not lie in the enzyme but in other substances originating from the mucous membrane of the stomach. If it is necessary to give a separate name to the enzyme of the gastric juice that can curdle milk, it is sufficient to use the word chymosin for it.

But is even this necessary? Should it be assumed that chymosin is different from pepsin?

To the solution of this question GEWIN has devoted the second part of his investigation. It was tried in vain to divide the enzyme into a proteolytic and a curdling part. It is a well-known fact that proteins, undissolved and at a temperature of 15° C. put into a pepsin-solution, take up and keep back this enzyme, so that it is not to be separated from it by washing it out. Coagulated and minced hen's albumen was put in a solution of purified pepsin in 0.2 % HCl. Now, if chymosin were a different matter from pepsin, only the last mentioned would perhaps be extracted from the solution by the albumen. It appeared, however, that the liquid filtered from the

albumen after some hours, had lost not only the peptic but also the curdling power. Indeed, the same negative result had already been arrived at by JACOBY, who for these experiments did not use hen's albumen but caseine <sup>1)</sup>.

In the second place it was examined whether a separation into two enzymes could be brought about by dialysis. When pepsin, dissolved in hydrochloric acid, is dialyzed against distilled water, it is partly precipitated, most completely at a low temperature, as soon as the quantity of acid has gone down to about 0.02% HCl. Always, however, a considerable part remains dissolved, which, with the aid of ammonium-sulfate — if the solution does not contain much albumose through 50% saturation with this salt — can be precipitated. If pepsin and chymosin are different matters, it cannot be deemed improbable that they also differ in solubility, that therefore the precipitate in the dialyser should contain more of either one or the other matter than the liquid filtered from it. Also in this way, however, a separation into two enzymes, did not succeed.

SCHMIDT—NIELSEN, however, has communicated experiments from which it appears that, though not a complete, still a partial separation of pepsin and chymosin is possible. A strongly active extract from the mucous membrane of the calf-stomach, prepared with hydrochloric acid, was divided into two parts. One was preserved at a low temperature, the other at 37° C. After some days the heated part had for the greater part lost its power to curdle milk, under a neutral reaction; at acid reaction, however, protein was still strongly digested. Now both liquids were neutralized and the one not heated so much diluted that the curdling power had become as weak as that of the one heated. After that the two liquids were rendered equally acid with hydrochloric acid and digested with fibrine. The fibrine was much quicker dissolved by the heated liquid than by the diluted one, not heated. During the process of heating, therefore, the chymosin had been chiefly lost, the pepsin however not.

This experiment would certainly be convincing, if the neutralization had the same effect on the heated liquid as on the one not heated. This, however, is not the case. The extract contains substances protecting the enzym from the action of alkali; also when no more of this is added than what is necessary to attain a neutral reaction. If the extract is preserved at a low temperature, these substances remain for a long time undisturbed, but if the acid extract is heated to 37° C., they are destroyed. GÆWIN has proved this by ample experiments, of which a detailed account is given elsewhere. At the

<sup>1)</sup> Biochem. Zeitschr. Bd. I, S. 66.

outset the enzym in the extract of rennet is quite proof against neutralizing, but after having been digested for a few days at 37° C. this power of resistance becomes smaller, and then diminishes quickly. Now, if the neutralized liquid, in order to determine the curdling power, is mixed with milk, the reaction remains neutral and no curdling arises. However, if it is rendered acid again, soon after the neutralisation, a sufficient quantity of enzym is left to digest protein. Also if the not heated solution of the enzym, before being neutralized, is sufficiently diluted with 0.2% HCl, neutralisation herein causes a rapid decrease and at last an annihilating of the curdling power. Thus, the curdling time of such a solution was, 8 times diluted, 10 seconds, directly after the neutralisation 2½ to 4 minutes, whilst the milk, mixed in the same proportion with the solution half an hour after the neutralisation, was not yet curdled after 20 minutes.

In all experiments, on the other hand, at which the noxious action of alkali was avoided, the curdling and proteolytic power of the enzym solutions appeared to keep pace with each other.

Summing up the result is therefore that not a single reason is left to assume a difference between pepsin and chymosin.

No more is there any reason to stick to the opinion of NENCKI and SIEBER, which I formerly shared, according to which pepsin should be considered as a molecule, which, through different groups of atoms, on the one hand should have a proteolytic, on the other hand a curdling action. The basis for such an idea, the opinion that the activity in one direction could be preserved, whilst that in the other direction was lost, I must now consider as having lost its foundation. The opinion defended by SAWJALOFF, is far more acceptable, who considers the alteration of caseine, of which the formation of cheese is the consequence, as the beginning of digestion, of proteolysis<sup>2)</sup>. This opinion has, I believe, become more probable by the experiments made of late about the alterations caseine undergoes under the influence of rennet, particularly by the investigation made some time ago in my laboratory by Miss VAN HERWERDEN<sup>1)</sup>. From these it has appeared that caseine, at a very weak acid or neutral reaction and at a temperature not much lower than 37° C. in a solution of rennet — either a preparation of commerce or pepsin purified as well as possible — soon falls asunder into paracaseine, which when it does not directly become insoluble as a lime-compound, cheese, continues to change, and other substances, among which

<sup>1)</sup> Zeitschr. f. Physiol. Chem. Bd. XLVI, S. 307.

<sup>2)</sup> Ibid, Bd. LII, S. 184.

a protein, provisionally called substance C by Miss VAN HERWERDEN. Not until the enzym has been able for a long time to influence these substances, does it form primary albumose from them. At the same time, however, the enzym also appeared at neutral reaction to form from coagulated albumen primary albumose, though in a small quantity. So there is every reason to consider curdling of milk as a proof of the first stage of proteolysis.

Taking this into consideration, it is not so wonderful, as it has been regarded, that all kinds of proteolytic enzymes possess the power of curdling milk, though in natural circumstances they never come in contact with caseine. For then the peculiarity is not to be sought for in the enzyme, but in the caseine, the splitting of which already can be observed in a stage of the digestion, in which with other proteins alteration is still quite imperceptible.

**Physics.** — “*The intensities of the components of spectral lines divided by magnetism*”. By Prof. P. ZEEMAN.

If a spectral line is resolved into a triplet by the application of a magnetic field, the two outer components and the middle line will generally differ in intensity. According to the elementary theory of LORENTZ of the phenomenon of magnetic resolution there exists a simple relation between these intensities.

Let  $I_1$  and  $I_3$  be the intensities of the outer components and  $I_2$  that of the middle line then we may expect that

$$I_1 = I_3 = \frac{1}{2} I_2 \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It has been often asserted, that generally this relation is not fulfilled, and that triplets frequently have in contradiction with (1) a weak middle line and strong outer components.

Really some cases <sup>1)</sup> can be cited, in which the intensities differ from what may be inferred from equation (1). In numerous cases however this contradiction is only apparent, no attention having been paid to a circumstance presently to be mentioned and not yet examined in connexion with our present subject.

In the very important investigation by RUNGE and PASCHEN<sup>2)</sup> a calcspar prism was placed before the tube placed in the magnetic field. By means of a quartz lens the two images given by the calc-

<sup>1)</sup> The lines exhibiting the partial polarization observed by EGOROFF and GEORGIEVSKY (C.R. 124, 125 1897) are meant here.

<sup>2)</sup> C. RUNGE u. F. PASCHEN Abh. der Berl. Akad. Anhang. 1902.

spar are projected in the plane of the slit of the spectroscope. The two images could be examined separately.

“Bei richtiger Stellung des Kalkspaths bestand das eine Bild aus Licht, dessen elektrische Schwingungen in der Lichtquelle parallel den Kraftlinien vor sich gehen, das andere Bild aus Licht, dessen elektrische Schwingungen in der Lichtquelle auf den Kraftlinien senkrecht stehen. Dass die Ebene der Schwingungen nach dem Durchsetzen des Kalkspaths durch die Quarzlinse gedreht wird, thut nichts zur Sache”.

Bij means of this arrangement the components with vertical vibrations are undoubtedly separated from those with horizontal ones. The main object of RUNGE and PASCHEN's investigation being the connexion between series and magnetic separation there is no objection to be made. The case is changed however as soon as the relative intensities of the components in the emitted light are under investigation, for these under certain circumstances could be essentially altered. If vertical and horizontal vibrations are reflected differently by the grating, the rotation of the direction of vibration in the beams passing through the quartz lens of course will be apparent in the observed intensity.

Polarizing effects of gratings are well known and generally the direction of vibrations relatively to the grooves must be of importance.

I had not anticipated that this circumstance would give rise to such striking effects as were observed by me in some experiments with a large ROWLAND grating. I have only made some observations with the yellow mercury lines, observing in the spectrum of the first order. The incident rays made an angle of about  $19^\circ$  with the normal to the grating, and in this latter direction observations were made or photographs taken. A vacuum tube charged with some mercury <sup>1)</sup> was placed in the magnetic field and by means of a glass lens an image was projected on the slit of the spectroscope. The light emitted at right angles to the horizontal magnetic lines of force was investigated.

In figure 1. a reproduction is given of the triplet in which the line 5769.4 is resolved. The distribution of intensities is in absolute contradiction with equation (1).

Observations with a calcspar and a sodium flame, the light of which was incident on the grating at about the same angle as above specified, the direction of observation being normal to the grating, showed at once that the light reflected from the grating

<sup>1)</sup> F. PASCHEN, Physik. Zeitschr. Jahrg. 1 p. 478. 1900.

was strongly polarized. The vertical vibrations were strongly preponderating.

The influence of a rotation of the plane of polarisation of the yellow mercury light on the distribution of intensities in the triplet was then examined. The plane of polarization was rotated by means of quartz plates with faces perpendicular to the axis placed in front of the slit. I had at my disposal two small plates of 2.15 resp 4.17 mm. thick. According to GÜMLICH <sup>1)</sup> the rotation for mercury light of wavelength 5769 in a quartz plate 1 mm. thick, is at  $t = 20^\circ$   $22^\circ.718$  and hence the rotation in my plates amounted to

$$22.72 \times 2.15 = 48^\circ.90 \text{ en } 22.72 \times 4.17 = 94^\circ.7.$$

The change in the distribution of light is at once apparent. In figure 3 the outer components are hardly visible. The negative reproduced corresponds to the case in which the plate rotating the plane of polarization  $94^\circ.7$  is in front of the slit.

Figure 2 corresponds to the case in which the incident vibrations are inclined at about  $45^\circ$  to the slit. It may be remarked that in this case the real distribution of intensities between the components, as existing in the emitted light, is observed.

Vertical and horizontal vibrations now being equally present in each of the components, and hence the circumstances as to vibrations being the same for the three components, the polarization by the grating is eliminated.

The distribution of light in figure 2 is certainly not in contradiction with equation (1) and eye observation seems to confirm it numerically also. Of course a photographic reproduction is not sufficient for a comparison of intensities and a numerical test must be reserved for a future paper.

For an estimation of the real ratio of intensities of the components of a divided spectral line henceforth care must be taken that for the region of the spectrum under review the vibrations in the incident light are inclined at an angle of  $45^\circ$  C. to the slit.

If in the case of a complicated division of a spectral line some components are weak, it will sometimes be possible to strengthen these components by placing a quartz plate of suitable thickness in front of the slit. This will be feasible in all cases in which the incident vibrations are not those most favoured by the grating.

Of course also with other spectroscopes this device does apply

<sup>1)</sup> GÜMLICH. Wied. Ann. Bd. 64 p. 333. 1898.

e. g. in the case of a MICHELSON echelon spectroscope, if the incident light has been previously analyzed by means of an auxiliary spectroscope. Reflection and refraction in the glass prisms of course weakens to different amounts vertical and horizontal vibrations.

Cases in which relation (1) fails are to be observed in some spectra with many lines (e. g. iron). Among adjacent magnetic triplets some are to be detected in which the distribution of intensity in one resembles figure 1, in the other figure 2. Without further analysis one may conclude that for the one or for the other relation (1) fails.

#### EXPLANATION OF THE PLATE.

The figures are thirtyfold enlargements of negatives concerning the mercury line 5769, 4.

In all cases the image of the source was projected on the slit with a glass lens.

Fig. 1. No quartz plate in front of slit.

Fig. 2. Quartz plate, rotating plane of polarization  $45^\circ$  in front of slit. The distribution of light corresponds to that in source.

Fig. 3. Quartz plate, rotating plane of polarization  $90^\circ$  in front of slit. Though the time of exposition was thrice that used with the other figures, there appear only traces of the outer components in the original negatives.

#### Chemistry. — “*On lupeol.*” By Prof. P. VAN ROMBURGH.

In the Comptes rendus of June 24, 1907, JUNGLEISCH and LEROUX state that lupeol cinnamate occurs in the gutta percha of *Palaquium Treubii* BRCK.

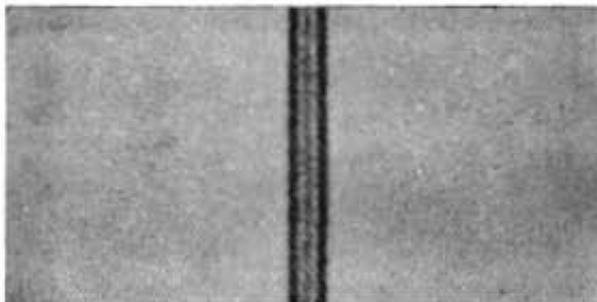
I have demonstrated previously that cinnamic acid may be obtained from this species of gutta, whereas lupeol cinnamate proved to be a constituent of different commercial varieties of gutta percha<sup>1)</sup>.

JUNGLEISCH and LEROUX have now studied the lupeol obtained by them and state that this substance on heating suddenly on the “bloc Maquenne” melts at  $190^\circ$ — $192^\circ$ , then immediately solidifies and melts again at  $212^\circ$ . They explain this phenomenon by assuming that lupeol loses water and is converted into a hydrocarbon, melting at  $212^\circ$ , to which they give the name of lupeylene. At  $130^\circ$  lupeol would lose water slowly, very rapidly so at  $150^\circ$ — $160^\circ$  and suddenly at  $190^\circ$ .

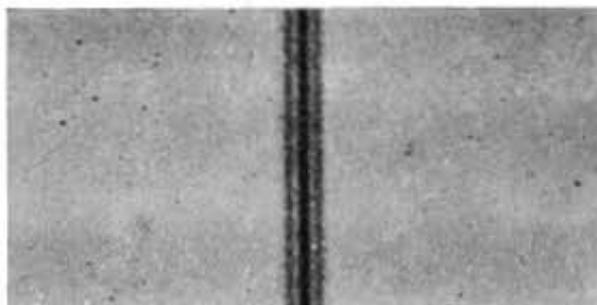
<sup>1)</sup> B.B. 37 (1904) 3442.

<sup>2)</sup> Diss. Utrecht 1906.

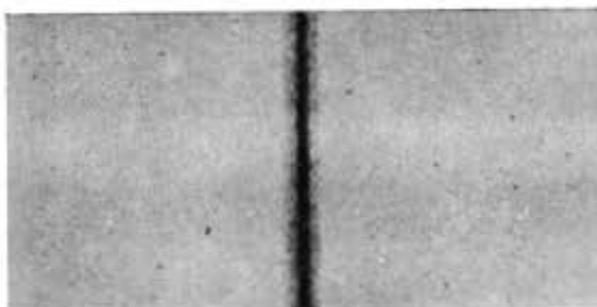
P. ZEEMAN. The intensities of the components of spectral lines  
divided by magnetism.



1. No quartz plate in front of slit.



2. Quartz plate, rotating plane of polarization  $45^\circ$  in front of slit.  
Intensities as in source.



3. Quartz plate, rotating plane of polarization  $90^\circ$  in front of slit.

Proceedings Royal Acad. Amsterdam, Vol. X.

On treating lupeol with acetic anhydride and sodium acetate at 170°, they did not obtain lupeol acetate, but lupeylene, and they argue that the acetate cannot be obtained by the ordinary methods owing to the lupeol losing water so readily.

But some time ago (*loc. cit.*) I obtained with Dr. v. D. LINDEN an acetate, by acetylating lupeol; whilst Dr. COHEN also prepared this ester and studied several of its reactions.

It, therefore, did not seem to me superfluous to repeat the experiments of these French chemists, and to again prepare and analyse the lupeol acetate, so as to make sure that this substance really exists; and that Dr. COHEN, who did not analyse it, because the properties coincided with those of my preparation, and because a mixture of his acetate with lupeol exhibited a considerable lowering of the melting point, was really in possession of the substance.

In order to observe readily an eventual separation of water, and to see and weigh the same, I, first of all, heated lupeol for many hours in one of the limbs of a reverted U vacuum tube placed in an oilbath at 190°, whilst the other limb was cooled in a Weinhold's glass containing liquefied ammonia. In the limb containing the lupeol a sublimate of beautiful crystals had deposited above the oil surface whilst a slight deposit had also formed in the cooled limb.

The weight of the lupeol was 0.5403 gram.

The deposit in the cooled limb weighed 0.0065 gram.

On heating the same at 100° there remained 0.0046 gram.

Therefore only traces of water could have been present in the cooled limb.

The sublimate in the heated limb melted at 212°—213°.

In another experiment, 1.0806 gram of lupeol was weighed in a glass boat and placed in a horizontal tube which could be heated in an airbath. The tube was connected to a reservoir with sulphuric acid and the whole apparatus was evacuated by means of a water-airpump. First I heated the apparatus for ten hours at 140°—160°; the loss of weight amounted only to 0.0066 gram, but it must be observed, however, that a sublimate had formed in the tube just above the boat. Then the substance was heated in the same manner for six hours at 190°—200°. The total loss in weight then amounted to 0.041 gram, but as the sublimate weighed 0.039 gram it was in reality only 0.002 gram. A separation of water, which would have amounted to 0.040 gram, was therefore again out of the question.

The residue of the two experiments, after being recrystallised from

acetone, was combusted with lead chromate and the result showed that the lupeol had remained unaltered.

0.1991 gram yielded 0.2147 gram H<sub>2</sub>O and 0.6172 gram CO<sub>2</sub>

	H.	C.
Found :	12.08	84.54
Calculated :	11.49	84.85 (for C <sub>31</sub> H <sub>50</sub> O) <sup>1</sup> .

On boiling with acetic anhydride (10 parts) and sodium acetate (1 part), the residue could be converted readily into an acetate melting at 213° as shown by the analysis :

0.2191 gram yielded 0.2251 gram H<sub>2</sub>O and 0.6588 gram CO<sub>2</sub>

	H.	C.
Found :	11.51	82.04
Calculated :	10.93	82.41 (for C <sub>33</sub> H <sub>52</sub> O <sub>2</sub> ).

For the purpose of comparison the acetate of non-heated lupeol was prepared and analysed in the same manner. It melted at 212°.

0.2113 gram yielded 0.2169 gram H<sub>2</sub>O and 0.6362 gram CO<sub>2</sub>

	H.	C.
Found :	11.5	82.11
Calculated :	10.93	82.41

A mixture of the two acetates analysed also melted at 212°, whilst the acetate mixed with lupeol gave a strong depression of the melting point.

In another experiment, lupeol was heated at 200° for 2½ hours in a current of dry carbon dioxide. A small calcium chloride-tube attached showed a slight increase of weight, but it appeared that a little solid matter had again volatilised with the current. The heating was then continued for six hours and the residue heated finally until the mass began to melt. On treating the same with benzoyl chloride and pyridine it was easy to obtain the lupeol benzoate, (m.p. 264°) proving that the lupeol has not passed into the hydrocarbon.

Finally I have also heated lupeol with acetic anhydride and sodium acetate in a sealed tube for three hours at 170°. The reaction product after being treated with water was recrystallised from a mixture of acetone and alcohol. The melting point of the product obtained was

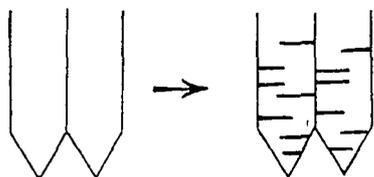
<sup>1</sup>) I will not go into the question whether it would be better to assign to lupeol the formula C<sub>30</sub>H<sub>50</sub>O.

212°. An addition of lupeol acetate from a previous preparation did not affect the melting point. If, however, it was mixed with lupeol or with lupeol which had been heated for some time at 190° a serious depression (about 20°) of the melting point could be observed.

The experiments described, therefore, prove convincingly that lupeol (obtained from bresk) is not converted into lupeylene under the circumstances mentioned by JUNGLEISCH and LEROUX.

As lupeol might perhaps exist in two modifications, Dr. F. M. JAEGER, to whom I wish to convey my best thanks, was kind enough to study the behaviour of lupeol on melting. Dr. JAEGER communicates to the following particulars me:

"If lupeol is melted to a singly-refracting liquid *L*, which takes place very sharply, the mass, on cooling, solidifies partly to an



aggregate of broad pointed needles *A*, glittering in high interference colours, partly to a horny singly-refracting mass *A'*, which frequently exhibits globular spherulites, resembling liquid droplets,

which are very feebly doubly-refracting. The needles *A* at once show a tremendous number of transversal clefts, whilst the splendour of the colours diminishes strongly; *A* passes here into a second modification *B*, the common form of lupeol. Meanwhile the horny mass has also burst and exhibits here and there a strained double refraction besides an increase in the number of droplets, that is to say, crystallisation nuclei in an embryonal condition. If heated carefully for a moment, it crystallises into the needles *A*, which pass immediately into *B* (by bursting etc.); the horny mass *A'* is identical with the needles *A*: it is *A* in a supercooled condition.

The crystallisation velocity is here nearly = 0, and by heating it is increased to such an extent (owing to the diminution of the internal friction etc.) that the mass begins to crystallise. This is a phenomenon well known to me; beautiful instances of crystallisation on heating are usnic acid and many cholesterol esters of fatty acids.

On remelting *B*, *A* is formed some times for a few short moments, afterwards *L*. The two modifications therefore appear to be related by enantiotropy."

Utrecht, Org. Chem. Lab. Univers.

**Statistics.** — “*Relations between mortality of infants and high temperatures.*” By Dr. E. VAN EVERDINGEN. (Communicated by Prof. C. H. WIND.)

In the “Statistische mededeelingen uitgegeven door het bureau van statistiek der gemeente Amsterdam” the other day a treatise appeared as N<sup>o</sup> 19: “Kindersterfte in Nederland (in de jaren 1881—1905)” by Prof. Dr. R. H. SALTET and Mr. PH. FALKENBURG.<sup>1)</sup> The authors point to the fact of the existence of a distinct maximum in the mortality of children under one year of age in the summer-months, and try to find among others a relation between the amplitude of this maximum in different places and in different periods, and the monthly means of temperature at neighbouring places in the same periods. The result is rather negative; hence they write as follows:

“Also from the chronological comparison of the mortality of infants and temperatures, as given by us here for Zealand and the town of Groningen, we are only able to draw a negative conclusion. If in a single case we may speak of parallelism, in the majority of the cases no direct relation between temperatures and mortality of infants can be traced. In so saying we do not imply that we have proved the statement, that the mortality of infants should be independent of the condition of the air. On the contrary, the diagrams we gave furnish the most evident proofs of a relation between the condition of the air in the summer and the mortality of infants. But it is not the height of the temperature which regulates this mortality. As we remarked before, in our opinion the probability remains, that the temperature-fluctuations of the summer — diurn or interdiurn — are the causes which exert an obnoxious influence. The data concerning these fluctuations fail however and cannot in our opinion be replaced by data about temperature-frequencies, which the Meteorological Institute would be able to furnish. We cannot but with a single word refer here to the theory which connects the summer mortality of babies with the presence in this season of a larger number of insects, bearers of disease-germs. Positive facts enabling to further investigate this matter are lacking at present.

Hence there is reserved here a vast field of research for the zealous investigator of the future.

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<sup>1)</sup> A German translation of this treatise appeared under the title: “Statistische Mitteilungen des Statistischen Amtes der Stadt Amsterdam N<sup>o</sup>. 19. Kindersterblichkeit besonders in den Niederlanden, bearbeitet von Prof. Dr. R. H. SALTET and Dr. PH. FALKENBURG.

2. We think we can show that the writers have expressed themselves here in too definite terms, and that a distinctly positive result is obtained if another method of research is followed.

Already in furnishing the mean monthly temperatures for periods of 5 years, which the writers used for their research, the present writer expressed his doubt as to whether these data were fitted for the purpose aimed at. If the fluctuations of the mortality of infants were merely directly proportional to the fluctuations of the mean monthly temperature, the relation sought for ought indeed to appear also in this way. As soon however as these data are otherwise connected — e.g. the increased mortality occurs only after the temperature exceeding a certain limit — it is no longer allowed to use mean values without further inquiry.

The research of Prof. SALTET and Mr. FALKENBURG did indeed not, as we saw before, reveal any relation between mean monthly temperatures and mortality of infants. We will demonstrate this here clearly once more by giving for a single town, Groningen, the deviations from the mean for 25 years of the 5-annual means of the mortality of infants in the summer months May-September, and by their side, in italics, the same deviations for the temperature. The former are given in hundredths per diem, the latter in tenths of a degree Celsius.

## GRONINGEN 1881--1905.

Period	May	June	July	Aug.	Sept.
1881—1885	10 —5	12 — 9	32 1	0 — 8	—9 —4
1886—1890	9 3	17 1	24 —11	— 1 — 6	9 — 2
1891—1895	3 5	—10 —10	—'8 — 1	—13 4	—2 4
1896—1900	—14 —5	— 5 15	—20 6	9 11	4 3
1901—1905	— 7 2	—17 4	—16 6	6 — 2	—4 —2

If high temperature-means for 5-year-periods were accompanied by high mortalities of infants, at least the signs of the two kinds of deviations ought to agree generally. We find however 12 concordances, 12 discrepancies and 1 undecided case; hence in this way no relation is apparent.

3. It might be supposed that this very unfavourable result is caused partly by adding up the numbers for five years. In this connection we might mention that Dr. OLLAND<sup>1)</sup> formerly traced a

<sup>1)</sup> A. G. OLLAND, Invloed van het weer op het sterftecijfer. Thesis, Utrecht. 1896.

difference in the general mortality by comparing very hot and very cold summer months. The principal causes however are different.

We now take as an example the mean mortality of infants at Groningen over the whole period 1891—1905, expressed for every month in percentages of one twelfth of the year-mortality; then we find in round percentages (l.c. p. 74, Table XLIII B).

April	May	June	July	Aug.	Sept.	Oct.
103	93	100	110	133	103	83

We will compare these numbers with the mean monthly temperatures, and moreover with the number of days with excessively high temperatures, which occurred during a similar period. In this respect we think in the first place of the days with maximum temperatures above  $25^{\circ}\text{C}$ ., for which the normals occur in the "Maand-overzicht der weersgesteldheid in Nederland"<sup>1)</sup>.

We thus find for the total number during the period 1894—1906.

April	May	June	July	Aug.	Sept.	Oct.
2	20	64	100	51	22	1

whereas the mean monthly temperatures in the period 1891—1905 are

8.6	13.0	16.6	18.4	17.6	14.7	9.6
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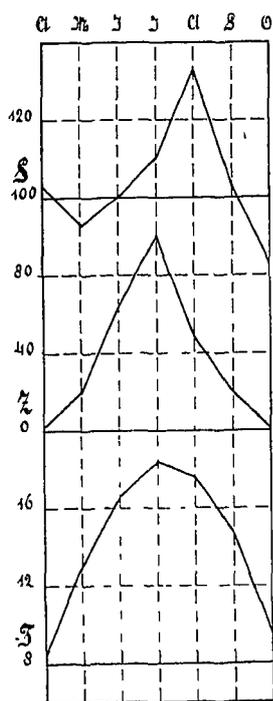


Fig. 1.

There is much more resemblance between the form of the maxima in the first two series of numbers than between those of the first and third series, as is clearly shown by fig. 1. (*S* mortality, *Z* number of days with max. temp.  $> 25^{\circ}$ , *T* mean monthly temperature); but also for the second series the epoch of the maximum does not coincide with that of the first: it seems as if there is a retardation of the mortality as compared with the high temperatures.

In itself this does not look improbable. Though the writer enters here a field where he is scarcely entitled to a judgment, he thinks he may risk the supposition, that perhaps the high temperatures favour the development of diseases which only after a certain lapse of time cause death. If this be the case, then a better agreement between the fluctuations of temperature and mor-

<sup>1)</sup> (Monthly weather review in the Netherlands) Publ. N<sup>o</sup>. 94 Kon. Ned. Meteor. Inst.

tality must be obtained if the latter are compared with mean temperatures or numbers of days with high temperatures for a period which begins and ends a little earlier.

We have tested this conclusion by calculating the mean temperatures as well as the numbers of days with temperature above  $25^{\circ}$  — which, in accordance with a terminology used in meteorology, we will call henceforth “summer days” — once for the calendar months, once for periods from the 16<sup>th</sup> of one month till the 15<sup>th</sup> of the next month.

Both the choice of the “shift” of 15 days and that of the temperature-limit  $25^{\circ}$  are somewhat arbitrary. For a preliminary research like ours there is however no objection to this. From the table below it appears that at least for some parts of our country the shift has about the size which serves the purpose; by *S* are indicated the mean values of the mortality of infants for calendar months during the period mentioned in the first column, given in percentages of one twelfth of the yearly death-rate, as we will continue doing in the following pages; by *T* the mean numbers of summerdays in 5 years, for periods of one month shifted over 15 days.

Period	Place of observation	May-June	June-July	July-Aug.	Aug.-Sept.
1891—1905	<i>S</i> Groningen	100	110	133	103
	<i>T</i> Groningen	19	21	32	16
1881—1905	<i>S</i> Utrecht	102	130	133	97
	<i>T</i> Utrecht—de Bilt	18	25	22	15
1881—1905	<i>S</i> Zeeland	72	101	159	159
	<i>T</i> Flushing	4	12	12	7

For Groningen and Utrecht the maxima now coincide wholly or almost so. For the province of Zeeland, only partially well represented as to its climate by Flushing, a difference of a month in the epoch of the maximum remains.

4. We first give here the results of the investigation for Groningen, in which we compare successively with the deviation of the mortality in 5-year periods the deviations of:

- a.* the common mean monthly temperatures,  
*b.* the means for the periods May 16<sup>th</sup>—June 15<sup>th</sup> etc.;  
*c.* the numbers of summerdays for calendarmonths;  
*d.* the number of summerdays for the periods May 16<sup>th</sup>—June 15<sup>th</sup> etc.

## GRONINGEN 1881—1905.

Period	June	July	Aug.	Sept
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*a.* Mean temperatures for calendarmonths

1891—1895	-3 -13	-5 -5	-28 0	-7 2
1896—1900	7 12	-6 2	10 7	5 1
1901—1905	-4 1	11 2	19 -6	2 -4

*b.* Mean temperatures May 16<sup>th</sup>—June 15<sup>th</sup> etc

1891—1895	-3 -7	-5 0	-28 -7	-7 4
1896—1900	7 3	-6 -2	10 8	5 5
1901—1905	-5 3	11 2	19 -2	2 -8

*c.* Summerdays calendarmonths.

1891—1895	-3 -11	-5 -12	-28 1	-7 -2
1896—1900	7 14	-6 6	10 2	5 3
1901—1905	-4 -2	11 6	19 -3	2 -1

*d.* Summerdays May 16<sup>th</sup>—June 15<sup>th</sup> etc.

1891—1895	-3 -7	-5 -1	-28 -16	-7 5
1896—1900	7 8	-6 -2	10 9	5 2
1901—1905	-4 -2	11 3	19 7	2 -8

First regarding only the signs, we find:

	concordances	discrepancies	Undecided
<i>a</i>	6	5	1
<i>b</i>	7	4	1
<i>c</i>	8	4	—
<i>d</i>	10	2	—

The differences between  $a$  and  $b$ , and between  $c$  and  $d$  give the effect of the substitution of number of summerdays for mean-temperatures, the differences between  $a$  and  $b$ , and between  $c$  and  $d$  the effect of a shift of 15 days. It appears that the improvement in the concordance of the signs is largest for the transition from  $b$  to  $d$ ; in the transition from  $c$  to  $d$  in the first place the improvement also in the quantitative agreement of the deviations of mortality and number of summerdays is remarkable. Finally the agreement in case  $d$  may be called so satisfactory, that but little doubt remains whether the high temperatures must be considered as the cause of the increased mortality of infants.

Hence the negative result arrived at by Prof. SALTET and Mr. FALKENBURG was due partly to the use of mean temperatures instead of temperature frequencies, partly to their non considering a retardation of the mortality with respect to the cause of death.

We will now test the agreement in case  $d$  also for Utrecht and Zeeland.

## UTRECHT (de Bilt).

Period	June	July	Aug.	Sept
1881—1885	16 — 7	17 10	—29 — 3	—13 — 4
1886—1890	15 — 4	—22 —11	—11 —14	— 2 1
1891—1895	—10 — 2	—10 — 7	— 6 —10	— 2 1
1896—1900	— 7 8	7 4	8 21	15 8
1901—1905	—21 5	7 6	46 8	3 — 6

## ZEALAND (Flushing)

Period	June	July	Aug	Sept.
1881—1885	— 3 1	11 9	21 3	—12 — 3
1886—1890	4 2	3 — 1	—30 — 3	7 0
1891—1895	9 0	4 — 1	—12 —10	— 8 1
1896—1900	—13 — 1	—11 — 5	21 7	38 7
1901—1905	4 0	— 7 0	1 1	—24 — 5

Hence so far as the signs are concerned we find .

	Concordance	Discrepancy	Undecided
Utrecht:	13	7	—
Zealand:	12	4	4

The number of concordances in these cases is large enough to show that the fluctuations in the number of summerdays play an important part in the matter of the mortality of infants, especially if we consider that at Utrecht as well as in Zealand most concordances occur in the months of large mortality of infants: July and August for Utrecht, August and September for Zealand. Doubtless there are besides them other important circumstances, not connected with temperature, the influence of which even in means for 5 years is not yet eliminated. This need not surprise us — it rather may be called remarkable that in the case of Groningen not *more* is shown of such circumstances. Whether a better agreement might be obtained by assuming a higher temperature limit for Utrecht, for Zealand a lower temperature limit and another value for the shift we have not tried so far.

The mean temperatures for the periods May 16<sup>th</sup>—June 15<sup>th</sup> etc. were not calculated for Utrecht—de Bilt and Flushing; a comparison of the methods *a*, *c* and *d* however favours the view, that no improvement would ensue. For, the result for Utrecht was :

	Concordance	Discrepancy	Undecided
<i>a</i>	13	7	—
<i>c</i>	13	6	1
<i>d</i>	13	7	—

for Flushing

<i>a</i>	7	7	6
<i>c</i>	12	7	1
<i>d</i>	12	4	4

It would seem as if the result for Utrecht is practically the same in the three cases. If however also the quantitative agreement is considered, this appears to be wholly lacking in the case *c*, but to be much better in case *d* than in case *a*; hence the results obtained for Groningen are also here, though not so generally, valid.

5. A drawback of the use of means or sums for periods of 5

years is this, that the total number of data for comparison is rather small, and that there remains an uncertainty as to whether really the increased mortality, appearing from these means, occurred in the *same* years in which also the number of summerdays was largest. For this reason we have compiled from the "Ned Staatscourant" the numbers expressing the death-rate of children less than one year of age for the period 1881—1905, both for Utrecht and Groningen; we have expressed the monthly values in percentages of one twelfth of the yearly death-rate, and compared these data after the method of the preceding §§, by comparing the deviations from the means for the period 1881—1905 respectively 1891—1905, with the deviations of the number of summerdays between May 16<sup>th</sup> and June 15<sup>th</sup> etc.

The results are given in the following tables.

## GRONINGEN 1891—1905.

Year	June		July		Aug.		Sept.	
1891	- 4	- 4	- 32	- 1	- 17	- 5	0	- 2
92	35	2	- 26	- 5	- 9	- 4	2	2
93	- 26	- 2	12	5	- 22	- 2	- 37	4
94	- 39	- 2	2	- 1	- 61	- 1	- 7	- 3
95	25	- 2	11	0	4	- 2	13	5
96	41	3	48	2	- 15	2	- 44	- 3
97	- 2	4	- 12	0	24	1	7	- 3
98	- 7	- 1	- 67	- 6	42	- 2	- 2	5
99	- 3	- 2	8	3	- 33	5	- 8	2
1900	12	3	- 11	- 2	36	5	61	2
01	- 5	- 3	10	3	2	13	- 30	0
02	48	2	- 21	1	- 30	- 5	- 9	- 2
03	- 11	0	- 15	- 3	1	- 4	33	- 1
04	- 21	0	13	- 4	134	5	18	- 1
05	- 38	- 2	75	5	- 21	0	6	- 3

## UTRECHT 1881- 1905.

Year	June	July	Aug.	Sept.
1881	9 - 3	-14 2	-12 1	-9 - 3
82	-17 - 3	3 - 3	-49 - 2	10 - 3
83	35 - 2	0 3	-61 - 3	-9 - 1
84	25 - 4	35 7	7 6	-40 5
85	30 3	12 1	-41 - 3	-15 - 2
86	26 - 1	-35 - 3	-15 - 2	43 10
87	23 - 4	-17 - 1	-9 0	-25 - 1
88	-9 - 1	-21 - 1	-29 - 2	-27 - 3
89	27 4	16 - 1	-8 - 4	10 - 2
90	21 - 4	-45 - 5	-3 - 2	-15 - 2
91	-21 - 4	-28 - 3	-15 - 2	-8 - 2
92	3 4	-22 - 4	-42 - 3	16 2
93	1 0	18 4	40 0	-21 2
94	-12 - 2	10 - 1	0 - 1	-17 - 3
95	-4 - 2	-6 - 2	-14 - 2	21 2
96	3 0	0 4	-13 1	8 - 3
97	17 6	19 4	0 6	-6 - 2
98	3 2	-33 - 5	15 - 1	57 8
99	-46 - 1	27 2	14 8	13 3
1900	-8 3	41 - 1	18 9	-5 2
01	-17 0	20 1	21 9	-12 0
02	-9 1	-40 1	-48 - 3	11 - 1
03	-25 3	-18 1	18 - 3	27 0
04	-45 - 1	35 - 2	174 7	6 - 2
05	-8 0	44 5	36 0	-17 - 3

For comparison we give the same table, with the mean temperatures at Groningen for the periods May 16<sup>th</sup>—June 15<sup>th</sup> etc. (case *b* § 4). The deviations for these temperatures are given in tenths of degrees.

## GRONINGEN 1891—1905 (b).

Year	June		July		Aug.		Sept.	
1891	- 4	-23	-32	2	-47	- 9	-27	3
92	35	9	-26	-16	- 9	-17	4	10
93	-26	6	12	13	-22	- 4	-35	7
94	-39	-18	2	3	-61	- 1	- 5	-19
95	25	- 6	11	- 4	4	- 3	15	20
96	41	11	48	6	-15	1	-42	- 1
97	- 2	27	-12	2	24	12	9	- 8
98	- 7	- 9	-67	-22	42	- 5	0	25
99	- 3	-13	8	9	-33	14	- 6	5
1900	12	3	-11	- 4	36	15	63	3
1	- 5	- 4	10	2	2	21	-28	- 8
2	48	- 2	-21	2	-30	-29	- 7	- 6
3	-11	0	-15	-14	1	-15	35	-13
4	-21	8	23	- 4	134	13	20	- 4
5	-38	10	75	24	-21	1	8	- 8

It was to be expected that in these tables more cases would be found where the signs do not agree, or the magnitude of the deviation in one series of numbers is not proportional to that in the other series; indeed, all disturbing causes exert their full influence here. If however we leave out of consideration those cases where one of the deviations is zero, and those where the deviation of the number of summerdays is but one, or the deviation of the mean temperature not more than  $0.2$  (Groningen *b*) then we obtain the following résumé :

Signs equal.			Signs opposite.		
Number of cases	Sums <i>T</i>	Sums <i>S</i>	Number of cases	Sums <i>T</i>	Sums <i>S</i>
31	114	927	13	42	191
Groningen			Utrecht		
50	186	1275	19	54	308
Groningen (b)			Groningen (b)		
31	38,4	836	17	14,9	366

20

Hence in the two first tables the number of concordances is much larger than that of the discrepancies, and, moreover, in the favourable cases the mean deviations of number of summerdays and mortality are greater, so that in our opinion no doubt remains concerning the relation between the two phenomena.

The résumé for the third table clearly shows that the parallelism with the deviations of the mean monthly temperatures is not so good as with the number of summerdays.

We may now try to find the factor, which can express this relation approximately. For this purpose we take the sum of all positive deviations of the number of summerdays, and compute the algebraic sum of the corresponding deviations of the mortality of infants. Likewise for the negative deviations of the summerdays. We thus find:

	Sum pos. dev. $T$	Sum $S$	Sum neg. dev. $T$	Sum $S$
Groningen	+ 81	+ 463	— 83	— 352
Utrecht (town)	+ 120	+ 502	— 120	— 465

Without giving all numbers in detail we may add here the result for the province of Utrecht, where 54 concordances occur against 17 discrepancies:

Utrecht (prov.)	+ 133	+ 543	— 118	— 433
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The difference between sum  $S$  for positive and negative deviations of  $T$ , rather large for Groningen, is probably an indication of a non linear relation. If we overlook this and combine the two kinds of deviations, we find for the factor sought for Groningen about 5.0, for Utrecht (town) about 4.0, Utrecht (prov.) about 3.9.

6. What precedes still leaves open to doubt whether the high temperatures themselves cause the increased mortality, or, as Prof SALTET and Mr. FALKENBURG supposed, temperature-fluctuations connected with them. It might indeed be imagined that, as a rule, numerous high temperatures would be accompanied by numerous large temperature fluctuations. Though, from a meteorological point of view, this supposition did not look very probable, we have tested it likewise, for which purpose the annals of the Royal Netherlands Meteor. Institute are quite sufficient. For the same periods from the middle of one month to the middle of the next for which the summerdays had been counted, we computed for Groningen the sum of the differences of the maximum temperature from one day to another, for simplicity neglecting the tenths of degrees. The results were dealt with in the same way as before: hence the deviations of the

temperature fluctuation sums are expressed in entire degrees. The result follows here:

## GROÏNINGEN 1891—1905.

Period	June	July	Aug.	Sept.
1891—1895	— 3 —19	— 5 22	—28 —16	— 7 20
1896—1900	7 31	— 6 9	10 45	5 — 1
1900—1905	— 4 —11	11 —31	19 —30	2 —18

Among 12 cases there is concordance in 5, discrepancy in 7 cases, so that in this way no relation between the temperature-fluctuations from day to day and the fluctuations of the mortality of infants is shown. Also the annual range of the mean amplitude of the temperature-fluctuations from day to day has another character than that of the frequency of high temperatures, the maximum of the temperature-fluctuations falls in June, not in August. Therefore we thought it useless to separately investigate the *large* or the diurn temperature-fluctuations.

7. In concluding our investigation we are well aware that it is far from complete and leaves room for various questions. If we succeeded in convincing the reader that one of the prominent causes of increased mortality of infants is an increase of the number of very hot days, we express a hope that others, may it be competent in medical matters, will feel inclined to trace the more direct relations, to explain the different character of the phenomenon in various parts of the country, perhaps with the aid of other temperature limits and other shifts. The data the Meteorological Institute is able to furnish for this purpose, also concerning other elements than temperature, will readily be put at the disposal of the future investigator.

The results obtained so far may be summed up as follows.

1<sup>st</sup>. The fluctuations of the mortality of infants bear hardly any relation to those of the mean monthly temperatures in the same months, neither with those of the mean amplitude of the temperature-fluctuations from day to day.

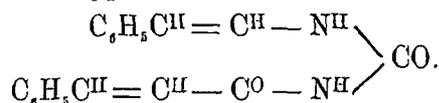
2<sup>nd</sup>. The number of days with maximum temperature above  
20\*

25° C. ("summerdays") counted for periods from May 16<sup>th</sup> to June 15<sup>th</sup>, June 16<sup>th</sup>—July 15<sup>th</sup> etc shows fluctuations, which in a large majority of cases agree in sign with those of the mortality of infants in June, July etc.

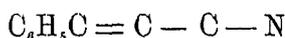
3<sup>d</sup>. If a simple proportionality is assumed between the deviation from the normal of the number of "summerdays" and that of the mortality in a period beginning and ending 15 days later, then for each summerday above or below the normal number the mortality of infants is increased or diminished at Groningen with 5, at Utrecht with 4% of the mean monthly death-rate.

**Chemistry.** — "*Action of potassium hypochlorite on cinnamide*", (2<sup>nd</sup> communication). By Dr. R. A. WEERMAN. (Communicated by Prof. S. HOOGWERFF).

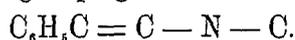
It has been stated in a previous communication <sup>1)</sup> that from cinnamide and potassium hypochlorite was obtained cinnamoylstyrylurea.



This proved that in the action of potassium hypochlorite on cinnamide an intramolecular rearrangement of atoms takes place, and that it therefore becomes possible to arrive from a compound with the atomic grouping:



at one with the atomic grouping:



A compound of this structure may be very readily obtained from cinnamide by treating this in methylalcoholic solution with an alkaline solution of potassium hypochlorite. In this way a yield of about 70 % of the urethane is obtained:



styrylaminoformic methyl ester.

B. p. 181°—182° at 14 mm. M. p. 122°—123° (corr.)

0,1674 gr. yielded 0,0914 gr. H<sub>2</sub>O and 0,4141 gr. CO<sub>2</sub>

0,1733 „ „ 12 cc. N<sub>2</sub> at 14° and 761 mm.

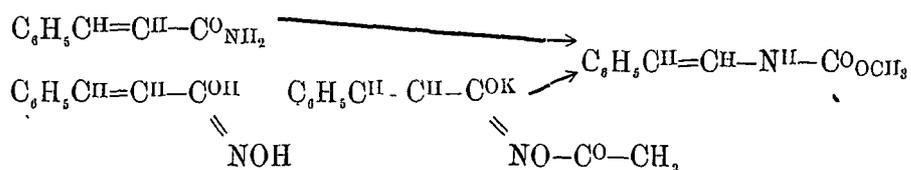
Found: 67,45 % C; 6,11 % H and 8,12 % N.

Calculated for C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>N: 67,76 % C; 6,27 % H and 7,91 % N.

<sup>1)</sup> Proc. 1906, 303.

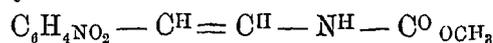
A substance of the same structure has been described by THIELE and PICKARD<sup>1)</sup>, who prepared it from the potassium salt of the acetylated cinnamo-hydroxamic acid. As they give the melting point as 115°, and as, in another respect, their observations do not quite agree with mine, the urethane was prepared by Mr. W. OCHTMAN, in the manner indicated by THIELE and PICKARD for the purpose of comparison.

The two substances appeared to be quite identical; the melting point was found to be 122°—123° and a mixture of the two melted at the same temperature.



This ready formation of urethane in an aqueous-alcoholic alkaline medium is remarkable.

I ascertained that this reaction also takes place with a derivative of cinnamic acid. From o-nitro-cinnamide is formed the o-nitrostyryl-aminofornicmethyl ester :



This crystallises in bright yellow needles mp. 149°—150°.

0,2009 gr. yielded 0,3956 gr. CO<sub>2</sub> and 0,0781 gr. H<sub>2</sub>O.

0,1457 „ „ 15,8 cc. N<sub>2</sub> at 15° and 758 mM.

Found : 53,70 % C; 4,36 % H and 12,60 % N.

Calculated for C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>N<sub>2</sub>: 54,03 % C; 4,55 % H and 12,61 % N.

A fuller communication will follow in the *Receuil*.

Delft, July 1907.

*Chemical Laboratory of the  
Technical High School.*

**Meteorology.** — “*The analysis of frequency-curves of the air-temperature.*” By Dr. J. P. VAN DER STOK.

1. The question in what way the characteristic details of frequency-curves of different kinds may be pointed out in a striking way in a pliant, analytical form has again been treated extensively in a recent work<sup>2)</sup>.

The aim of this communication is to fix the attention on the

<sup>1)</sup> Ann. 309, 197.

<sup>2)</sup> H. BRUNS, *Wahrscheinlichkeitsrechnung und Kollektivmasslehre*, Leipzig und Berlin, TEUBNER, 1906.

method of treatment suggested in it and to give some applications of it to frequency-numbers concerning air-temperature, deduced from observations made on board the lightship "Schouwenbank".

2. The method suggested by BRUNS deserves the more the consideration of all who are occupied with the treatment of frequencies as it is based on the classical works of BESSEL and FECHNER and can be regarded as a logical outcome of the principles indicated by these investigators.

As a basis is taken the well-known function

$$\Phi_0(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \dots \dots \dots (1)$$

for which in various works tables are given; the first derivative of this function:

$$\Phi_1(x) = \frac{2}{\sqrt{\pi}} e^{-x^2} \dots \dots \dots (2)$$

assumes after substitution of  $hx$  for  $x$  and multiplication by  $h$  the form of the specific probability of a deviation  $x$  according to the law of errors of GAUSS in its simplest form. The derivatives of higher order can be written thus:

$$\left. \begin{aligned} \Phi_2(x) &= \frac{2^2}{\sqrt{\pi}} e^{-x^2} \cdot 1! \left[ -\frac{x}{0!1!} \right] \\ \Phi_3(x) &= \frac{2^3}{\sqrt{\pi}} e^{-x^2} \cdot 2! \left[ \frac{x^2}{0!2!} - \frac{1}{1!0!2^2} \right] \\ \Phi_4(x) &= \frac{2^4}{\sqrt{\pi}} e^{-x^2} \cdot 3! \left[ -\frac{x^3}{0!3!} + \frac{x}{1!1!2^2} \right] \\ \Phi_5(x) &= \frac{2^5}{\sqrt{\pi}} e^{-x^2} \cdot 4! \left[ \frac{x^4}{0!4!} - \frac{x^2}{1!2!2^2} + \frac{1}{2!0!2^4} \right] \\ \Phi_6(x) &= \frac{2^6}{\sqrt{\pi}} e^{-x^2} \cdot 5! \left[ -\frac{x^5}{0!5!} + \frac{x^3}{1!3!2^2} - \frac{x}{2!1!2^4} \right] \end{aligned} \right\} \dots (3)$$

etc.

Now BRUNS' suggestion is as follows: the specific probability (sum of the numbers = 1) of a deviation from a groundvalue assumed arbitrarily be represented by the series:

$$y = h [D_0 \Phi_1(hx) + D_1 \Phi_2(hx) + D_2 \Phi_3(hx) + \dots] \dots (4)$$

from which ensues, that the integral of this equation, called the curve of the sums, is expressed by the form

$$D_0 \Phi_0 + D_1 \Phi_1 + D_2 \Phi_2 + \text{etc.} \dots \dots \dots (5)$$

where  $\Phi$  means  $\Phi(wx)$ . as is the case in what follows.

From (4) it is immediately evident when regarded in connection with (3) that the suggested analysis of the curve (called by BRUNS not frequency-curve but curve of distribution) shows a resemblance to the development of a function in terms of a FOURIER series.

In the different  $\Phi_p$  terms appear polynomial functions of order  $p-1$ ; the  $\Phi_p$  curve shows  $p$  maxima and minima and intersects the  $x$  axis in  $p-1$  points and alternately will be found for  $x=0$  either an extreme value (order uneven) or a point of intersection (order even).

The constants  $D$  are determined in the well-known way by evaluating the moments of various orders with respect to the  $y$ -axis through the origin of coordinates; if we take for this origin the value of  $x$  corresponding to the arithmetical mean and if we put:

$$\int_{-\infty}^{\infty} x^n y dx = \mu_n,$$

we find evidently  $D_0 = \frac{1}{2}$  on account of  $\mu_0$  being equal to 1; furthermore  $\mu_1$  must be  $=0$  on account of the choice of the origin, so  $D_1$  must be put equal to 0, whilst, if one defines the value of the constant  $h$  in such a way that

$$2 h^2 \mu_2 = 1,$$

it is then easy to deduce that also  $D_2$  must be 0.

The expressions (4) and (5) can thus be simplified and they become

$$y = h [\frac{1}{2} \Phi_1 + D_3 \Phi_3 + D_4 \Phi_4 \dots] \dots \dots (4^a)$$

and

$$\frac{1}{2} \Phi_0 + D_3 \Phi_3 + D_4 \Phi_4 \dots \dots \dots (5^a)$$

The constants  $D_3, D_4$ , etc. can easily be calculated by means of the formula (3) where, with a view to this, the above mentioned form is given.

To calculate  $2D_n$  we have namely, to consider the form appearing between square brackets in the expression for  $\Phi_{n+1}$  and to substitute in it  $h^n \mu_n$  for  $x^n$ .

Our finding in this way  $2D_n$  instead of  $D_n$  is due to the same reason why  $D_0$  must be put equal to  $\frac{1}{2}$ ; namely to the form of (1) in which the number 2 stands as coefficient.

TABLE I.

Air temperature. Schouwenbank. Frequencies of Daily-means

Celsius	January	February	March	April	May	June	July	August	September	October	November	December
-8.9 to -8.0	1	—	—	—	—	—	—	—	—	—	—	1
-7.9	—	—	—	—	—	—	—	—	—	—	—	—
-6.9	—	1	—	—	—	—	—	—	—	—	—	1
-5.9	2	2	—	—	—	—	—	—	—	—	1	—
-4.9	2	3	—	—	—	—	—	—	—	—	—	3
-3.9	5	5	—	—	—	—	—	—	—	—	1	7
-2.9	18	14	3	—	—	—	—	—	—	—	—	10
-1.9	32	23	6	—	—	—	—	—	—	—	3	27
-0.9	53	37	15	—	—	—	—	—	—	—	2	21
0.1	56	48	25	—	—	—	—	—	—	—	—	27
1.1	77	89	50	—	—	—	—	—	—	—	13	39
2.1	112	123	69	8	—	—	—	—	—	—	23	85
3.1	134	134	111	13	—	—	—	—	—	—	30	77
4.1	150	176	150	36	—	—	—	—	—	—	45	101
5.1	147	142	202	96	—	—	—	—	—	1	55	163
6.1	113	111	157	167	41	—	—	—	—	6	81	163
7.1	70	82	95	206	36	4	—	—	—	28	131	122
8.1	24	10	69	186	112	3	—	—	—	57	158	91
9.1	4	—	25	142	161	3	—	—	—	73	158	48
10.1	—	—	15	97	215	49	—	—	4	105	167	14
11.1	—	—	2	45	166	71	—	—	6	194	86	—
12.1	—	—	6	3	130	165	8	—	51	189	41	—
13.1	—	—	—	1	87	180	27	4	67	182	4	—
14.1	—	—	—	—	46	218	85	49	149	87	1	—
15.1	—	—	—	—	32	160	170	152	222	53	—	—
16.1	—	—	—	—	4	94	275	254	230	18	—	—
17.1	—	—	—	—	—	57	245	245	152	3	—	—
18.1	—	—	—	—	—	19	130	137	71	4	—	—
19.1	—	—	—	—	—	7	64	106	29	—	—	—
20.1	—	—	—	—	—	—	24	32	15	—	—	—
21.1	—	—	—	—	—	—	1	15	4	—	—	—
22.1	—	—	—	—	—	—	1	3	—	—	—	—
23.1	—	—	—	—	—	—	—	3	—	—	—	—

For the values of  $\Phi_1, \Phi_2 \dots \Phi_6$  BRUNS has given tables, so there are no further difficulties about the calculations which can easily be done after some practice

We must suffice with this short and for that reason incomplete survey of the method, for further details we must refer to the above-mentioned work, where all questions which may arise are discussed extensively.

3. When applying this method to observations of air-temperature it has been assumed that the series need not be continued farther than to the third term, so that only asymmetrical ( $D_3$ ) deviations and symmetrical ones ( $D_4$ ) of order one of the simple law are regarded, which, with these kinds of curves not differing much from the bell-shape, proves to be sufficient. When introducing terms of higher order the disadvantage moreover appears that with the evaluation of the higher moments the single extreme deviations, therefore inaccurately determined, play an unduly important part. As first example have been selected the daily-means of the air-temperature, because with these frequency-curves their obliquity changes sign along with the season and can therefore be regarded as a climatological factor. The daily-means are calculated from observations on temperature taken six times a day during the years 1882—1904.

In Table I the frequencies are given from degree to degree, calculated at a total of 1000, the number of data amounts of course for every month to about

$$23 \times 30 = 690 \text{ or } 23 \times 31 = 713.$$

The obliquity is immediately evident; in winter we find extreme temperatures or negative deviations which are not compensated by equally large positive deviations, in summer we find on the contrary important positive deviations not contrasted by negative ones. The constants of the curve, namely, the mean temperature  $M$  indicating the origin of coordinates, the factor of consistency  $h$  and the coefficients  $D_3$  and  $D_4$  by which the deviations of the curve from the regular bell-shape are determined are found in survey in Table II, the last two quantities having reference to  $\mu_0 = 1$ , so that they must still be multiplied by 1000 for the calculation of the numbers comparable to the frequencies of Table I.

TABLE II  
 Constants of the frequency-curves.  
 Daily-means of air-temperature.

	$M$	$h$	$D_1$	$D_2$
January	3 762 C.°	0 2587	+ 0 01657	- 0 00043
February	3 842	0 2773	+ 0 01959	+ 0 00048
March	5 321	0 2908	+ 0 00214	+ 0 00213
April	7 953	0 3738	+ 0 00313	- 0.00145
May	11 068	0 3540	- 0 00847	- 0 00166
June	14.320	0 3708	- 0 00015	+ 0 00114
July	16 871	0 4442	- 0 00216	+ 0 00007
August	17 367	0 4380	- 0 01170	- 0 00026
September	16 032	0 3893	- 0 00634	+ 0 00106
October	12.142	0 3335	+ 0 00470	- 0 00002
November	8 399	0 2662	+ 0.02657	+ 0.00659
December	5.174	0.2377	+ 0 02463	+ 0 00390

From these results of the calculation it is evident that in contrast to most frequency-curves, the  $D_2$  deviations from the simple exponential law for the frequency-curve of the daily-means of the air-temperature are slight and may be regarded as being within the limits of the errors of observation.

In order to investigate how far the calculation agrees with the observation, the numbers of Table I for the months of January and December are taken together as being the most asymmetrical. The numbers obtained in this way are indicated in Table III by  $O$  (observed).

The constants of these curve are:

$$M = 4.469 \text{ C}^\circ$$

$$h = 0.2403$$

$$D_1 = + 0.01764$$

$$D_2 = + 0.00130$$

TABLE III.

Analysis of the frequencies Jan. + Dec of Table I.

$O$	$C_0$	$O-C_0$	$C_1$	$O-C_0-C_1$	$C_2$	$O-\Sigma C$
1	0	1.0	0.1	0.9	—	1
0	0.1	— 0.1	0.2	— 0.3	0.1	0
0 <sup>s</sup>	0.2	0.3	0.3	0.0	0.2	0
1	0.4	0.6	1.3	— 0.7	0.3	— 1
2 <sup>s</sup>	1.4	1.1	2.5	— 1.4	0.4	— 2
6	3.4	2.6	4.0	— 1.4	0.4	— 2
14	8.4	5.6	5.0	0.6	0.1	1
29 <sup>s</sup>	17.5	12.0	3.7	8.3	— 0.9	9
37	32.9	4.1	— 0.3	4.4	— 2.0	6
41 <sup>s</sup>	54.9	— 13.4	— 8.7	— 4.7	— 2.5	— 2
58	81.5	— 23.5	— 16.0	— 7.5	— 1.7	— 6
98 <sup>s</sup>	108.0	— 9.5	— 25.2	15.7	0.6	15
105 <sup>s</sup>	127.9	— 22.4	— 11.9	— 10.5	3.1	— 13
125 <sup>s</sup>	134.9	— 9.4	0.4	— 9.8	4.1	— 14
155	127.0	28.0	12.6	15.4	2.9	13
138	106.6	31.4	18.2	13.2	0.5	13
96	79.7	16.3	15.7	0.6	— 1.8	2
57 <sup>s</sup>	53.3	4.2	8.2	— 4.0	— 2.6	— 1
26	31.7	— 5.7	0.6	— 6.3	— 1.9	— 4
7	16.9	— 9.9	— 3.9	— 6.0	— 0.8	— 5
—	8.4	— 8.4	— 5.0	— 3.4	0.1	— 4
—	3.0	— 3.0	— 3.9	0.9	0.4	1
—	1.2	— 1.2	— 2.4	1.2	0.5	1
—	0.3	— 0.3	— 1.2	0.9	0.3	1
—	0.3	— 0.3	— 0.5	0.2	0.1	0
—	0.1	— 0.1	— 0.2	0.1	0.1	0
$\Sigma = 1000$		$\Sigma = 214.6$		$\Sigma = 118.4$		$\Sigma = 117$

In the second column is given under  $C_0$  (calculated) the distribution derived according to the simple exponential law; in the fourth column we find the values of the second term in the series having  $D_3$  as factor; from the third and fourth columns is evident that the sum of the differences is lessened by this term from 215 to 118 a thousand. As has been noticed before, the influence of the third term with  $D_4$  is slight.

The sum of the differences remains 12%, also after introducing this term, which can be called satisfactory considering that the total number of observations is not more than:

$$2 \times 31 \times 23 = 1426$$

and that the most unfavourable months have been taken as an example. In fact, from the regular course of the differences it is evident that there might be a possibility of making the differences smaller still by addition of a fourth or a fifth term with  $D_5$  and  $D_6$ .

For  $D_6$  we find the value  $-0.00036$ , from which ensues that of by far the greater part the differences are due to incompleteness of the material of observation, so that extension of the series would avail but little.

4. As fitting material for a second application of the method to meteorological quantities all the observations of temperature have been chosen, taken six times a day in the month of July on the same lightship during the years 1882—1906. The number of observations is now six times greater than for the daily-means and amounts to 4516.

On account of this greater number the frequency-curve will have a more regular shape and the obliquity which was easily discernible for the daily-means also for the summer months, will now come more clearly to the front.

The observations are arranged according to the different quarters of the wind, so that we obtain (Table IV) frequencies of the so-called thermic windrose. On board the lightships the direction of the wind is determined in accordance with the indications of the compass; for the period 1882—1906 we can assume that these observed directions of the wind can be reduced to the proper direction by applying as correction the mean deviation,  $-15^\circ$ .

TABLE IV. Frequencies of air-temperatures for different quarters of the wind (Magnetic), Schouwenbank, July, 1882—1906.

	<i>N</i>	<i>NNE</i>	<i>NE</i>	<i>ENE</i>	<i>E</i>	<i>ESE</i>	<i>SE</i>	<i>SSE</i>	<i>S</i>	<i>SSW</i>	<i>SW</i>	<i>WSW</i>	<i>W</i>	<i>WNW</i>	<i>NW</i>	<i>NNW</i>	<i>C</i>	Total
10.6—11.5 C	1	—	—	—	—	—	—	—	1	1	—	—	—	1	—	—	—	4
11.6—12.5	4	1	1	—	—	—	—	—	0	0	—	—	1	0	3	13	—	23
12.6—13.5	29	17	5	1	2	2	—	—	1	1	2	2	0	2	13	25	—	102
13.6—14.5	44	26	12	2	11	4	5	4	3	4	15	11	9	20	43	51	3	267
14.6—15.5	71	49	35	21	18	9	13	4	13	9	30	66	69	72	77	49	18	623
15.6—16.5	67	66	80	41	27	14	18	18	19	27	70	164	152	73	50	42	24	952
16.6—17.5	56	38	79	39	35	18	28	15	37	31	94	182	147	51	44	37	37	968
17.6—18.5	34	29	56	38	32	23	25	15	22	22	62	140	119	31	41	26	27	742
18.6—19.5	26	13	48	16	27	13	16	7	14	14	35	67	52	13	21	10	27	419
19.6—20.5	9	10	29	16	16	6	13	4	5	10	19	17	24	6	9	6	18	217
20.6—21.5	4	4	18	10	10	1	6	6	5	4	2	5	6	1	6	3	7	98
21.6—22.5	2	2	7	3	2	4	4	3	3	1	4	2	5	1	2	1	15	61
22.6—23.5	2	2	3	3	1	0	2	1	1	0	1	—	1	0	2	1	4	24
23.6—24.5	—	1	1	0	2	1	—	—	—	1	3	—	—	0	—	—	1	10
24.6—25.5	—	—	1	1	1	—	—	—	—	—	—	—	—	1	—	—	1	5
25.6—26.5	—	—	—	—	1	—	—	—	—	—	—	—	—	—	—	—	—	1
Sum	349	258	375	191	185	95	130	77	124	125	337	656	585	272	311	264	182	4516

More clearly than in the numbers of Table IV does the influence of the direction of the wind on the temperature show itself in the mean temperature  $M$  and the factor of consistency  $h$ , arranged in Table V.

TABLE V.

Direction of wind Magn.	Number of observ.	Mean Temp. $M$ .	$h$
<i>N</i>	349	13.10	0.3485
<i>NNE</i>	258	16.33	0.3478
<i>NE</i>	375	17.50	0.3477
<i>ENE</i>	191	17.61	0.3561
<i>E</i>	185	17.68	0.3155
<i>ESE</i>	95	17.53	0.3491
<i>SE</i>	130	17.77	0.3527
<i>SSE</i>	77	17.67	0.3436
<i>S</i>	124	17.39	0.3713
<i>SSW</i>	125	17.38	0.3754
<i>SW</i>	337	17.23	0.4037
<i>WSW</i>	656	17.08	0.5124
<i>W</i>	585	17.10	0.4685
<i>WNW</i>	272	16.32	0.4391
<i>NW</i>	311	16.27	0.3512
<i>NNW</i>	264	15.65	0.3418
<i>Calm</i>	182	18.56	0.3295

From this table is evident that in this summermonth by far the highest temperatures are observed when there are calms; for the rest we have the lowest temperatures with the northerly seawind, the highest with a landwind; the transition from NNE (W 7°.5 E prop. dir.) to NE (N 30° E prop. dir.) is sharp, much sharper than that from SW (N 210° E prop. dir. landwind) to WNW (N 277°.5 E proper dir. seawind).

This sharp difference we do not find for the factor of consistency, which shows for WSW wind a distinct maximum and for calm a minimum.

The numbers of observations being rather slight for many directions

of the wind, the numbers of Table IV have been arranged in Table VI to five groups where as much as possible comparable series have been added together.

TABLE VI.  
Frequencies deduced from Table IV.

	$\frac{WNW}{NNE}$	$\frac{NE}{E}$	$\frac{ESE}{SW}$	$\frac{WSW}{W}$	C	Total
10.6—11.5 C°.	2	—	2	—	—	4
11.6—12.5	21	1	0	1	—	23
12.6—13.5	86	8	6	2	—	102
13.6—14.5	184	25	35	20	3	267
14.6—15.5	318	74	78	135	18	623
15.6—16.5	298	148	166	316	24	952
16.6—17.5	226	153	223	329	37	968
17.6—18.5	161	126	169	259	27	742
18.6—19.5	83	91	99	119	27	419
19.6—20.5	40	61	57	41	18	217
20.6—21.5	18	38	24	11	7	98
21.6—22.5	8	12	19	7	15	61
22.6—23.5	7	7	5	1	4	24
23.6—24.5	1	3	5	—	1	10
24.6—25.5	1	3	—	—	1	5
25.6—26.5	—	1	—	—	—	1
Sum	1454	751	888	1241	182	4516

The comparatively low temperatures for WNW—NNE winds with a small factor of consistency (great distribution) in contrast to the high temperatures and small distribution for WSW—W winds is very clear from this table.

At the same time is evident from these data how the combination of series with different mean values decreases the obliquity in the total, so that we can expect that the obliquity factor  $D_s$  will be considerably smaller for the total series than  $D_s$ , calculated for the various series, which is confirmed by the following table.

TABLE VII.

Constants of the frequency-numbers of Table VI.

	$M$	$h$	$D_3$	$D_4$
<i>WNW-NNE</i>	16.135	0.3576	- 0.01778	0.00385
<i>NE-E</i>	17.589	0.3428	- 0.01657	0.00343
<i>ESE-SW</i>	17.430	0.3710	- 0.01540	0.00477
<i>WSW W</i>	17.089	0.4869	- 0.01300	0.00297
<i>C</i>	18.555	0.3295	- 0.01153	0.00108
Total	16.971	0.3603	- 0.01116	0.00331

The (negative) obliquity  $D_3$  is therefore strongest for the northerly seawinds with low temperature and decreases further regularly with the azimuth counted from North through East. The symmetrical deviation  $D_4$  is greatest for southerly winds and smallest for calms.

TABLE VIII.

Analysis of the frequencies of Table VI.

$O$	$C_0$	$O-C_0$	$C_3$	$O-C_0-C_3$	$C_4$	$O-\Sigma C$
1	2.6	- 1.6	- 3.5	1.9	2.9	- 1
5	8.7	- 3.7	- 4.4	0.7	1.0	0
23	27.2	- 4.2	- 3.3	- 0.9	- 3.6	3
59	65.5	- 6.5	4.5	- 11.0	- 8.8	- 2
138	122.7	15.1	15.1	0	- 6.1	6
211	178.4	32.6	14.7	17.9	7.3	11
214	201.2	12.8	- 0.5	13.3	15.4	- 2
164	175.8	- 11.8	- 15.3	3.5	6.4	- 3
93	119.2	- 26.2	- 14.5	- 11.7	- 6.5	- 5
48	62.7	- 14.7	- 4.0	- 10.7	- 8.9	- 2
22	25.5	- 3.5	3.6	- 7.1	- 3.0	- 4
14	8.1	5.9	4.3	1.6	1.1	1
5	2.0	3.0	2.3	0.7	1.7	- 1
2	0.4	1.6	0.8	0.8	0.8	0
1	0.0	1.0	0.2	0.8	0.3	1
$\Sigma = 1000$		$\Sigma = 144.2$		$\Sigma = 82.6$		$\Sigma = 42$

Let us remark here that a negative  $D_2$  refers to the ascending slope of the curves on the left being steeper than the descending slope on the right and that a positive sign of  $D_4$  means that small deviations appear in greater number than would be the case in accordance with the simple exponential law.

In order to show clearly the part played by the various terms of the series in the composition of the curve of distribution a comparison has been given in table VIII, as in table VI, of the observed and calculated frequency-numbers of the last series of table IV; the number of observations 4516 has here been reduced in the first column under  $O$  to 1000.

From this table is evident that, if only a great number of observations is at hand, the frequency-curve of the air-temperature can be very satisfactorily determined by the three constants of the series of BRUNS, the total of the differences between observation and calculation amounting in round numbers to 4 %.

**Anthropology.** — “*Is red hair a nuance or a variety?*” By Prof. L. BOLK.

Concerning the anthropological importance of red hair the literature relating to it contains up till now little more than opinions based upon general impressions or suppositions, founded on statistical data, which when looked at more closely are open to more or less unfavourable criticism. There is in those opinions and suppositions a definite main current according to which it is generally assumed that a closer affinity of redhairiness exists to what, for the sake of brevity, I shall indicate as the blonde race, characterized as to the pigmentation by blonde hair and blue eyes.

The nature of the relation between blonde and red-haired people is expressed by TOPINARD<sup>1)</sup> as follows: the red-haired type has arisen from the blonde type “par une action des milieux”. Also BEDDOE and RIPLEY, to mention the principal English and the best known American anthropologist, assume a closer connection between blonde and red hair. VIRCHOW looks upon the subject from a somewhat different standpoint, when he says that redhairiness probably arises in two manners, viz. by a decrease of pigment in brown hair or an increase in blonde hair<sup>2)</sup>. This opinion of VIRCHOW is based upon

<sup>1)</sup> *Éléments d'Anthropologie générale*. Paris 1885 p. 334

<sup>2)</sup> Das jedoch scheint mir nicht unwahrscheinlich zu sein, dass es eine doppelte Art von Rothhaarigkeit giebt, von denen die eine als eine Steigerung des Pigments bei den Blondes, die andere als eine Verminderung desselben bei den Braunen anzusehen ist. *Archiv für Anthropol.* XVI Bnd. p. 338.

his statistics of the extension of redhaired people in Germany. Now it would not be difficult to prove that VIRCHOW was in no way entitled to such a conclusion on the ground of his statistics; his data were very incomplete and the relations found by him he himself calls "ganz unzutreffend". I intend to revert to this in another place, but would like to examine another side of VIRCHOW'S conclusion somewhat more closely. For where he says that redhairiness arises, either by an increase or by a decrease of the hair-pigment, this implies that in VIRCHOW'S opinion redhairiness is the consequence of quantitative difference, and that, in other words, this quality is consequently only a question of gradation. Moreover I do not wish to enter into the question whether VIRCHOW has a right to place blonde or brown over against each other as primary or pure hair-colours. Let it suffice for the present to state that VIRCHOW sees no contrast between red and blonde hair, but that the former is only a nuance, either of blonde or of brown. I know only one anthropologist who, in contradistinction to the great majority, raises his voice against the existence of a closer relationship between red and blonde hair, viz. AMMON, who in his Anthropology of the Baden population hazards the suggestion that the difference between blonde and red hair is not founded on a quantitative difference of the pigment, but on a qualitative distinction. So AMMON is more inclined to the opinion that in redhairiness not a nuance, but a variety renders itself manifest <sup>1)</sup>.

In working up my anthropological material concerning the population of Holland I have naturally come to the question about the importance of redhairiness, and the conclusion at which I have arrived deviates from the general opinion. The extension of redhairiness in our country causes me to deny every closer relationship with the blonde race.

Let me begin by pointing out that the composition of our population is very favourable for an answer to this question. A few years ago I had the pleasure in this meeting to throw light upon the main features of the composition of our population from the so-called blonde and brown-haired race. And I could then establish how the composition of our population differs, if the northern part of our country is compared with the southern. The blonde type decreases regularly in a southern direction, going hand in hand with an increase of mixed types, and though of course in a smaller proportion, an increase of the pure brown type. The differences

<sup>1)</sup> Die von manchen Anthropologen beliebte Vereinigung der roten Haare mit den blonden, halten wir für unzulässig, denn die roten stehen in vielen Fällen den braunen näher und sind jedenfalls stärker pigmentiert, haben vielleicht ein Pigment von anderer Beschaffenheit. Zur Anthropologie der Badener. blz. 129.

between the northern and southernmost parts of our country are in the end rather considerable, and it is for this very reason that our population is so extremely fit to answer a question like this. If it should after all be true that redhairiness is more closely related to blondness, then the variation in the number of blondes cannot but cause a similar change in the number of redhaired people.

The materials for the following illustration have again been borrowed from my inquiry made at the time into the distribution of the colour of hair and eyes among the population of Dutch schools. On the schedules that were distributed for that purpose I distinguished four colours of hair: blonde, brown, red and black, and four colours of eyes: blue, grey, brown and brownish-green. The total number of children examined, amounted, with the exception of the Israelites, to 478.976. The total number of redhaired individuals among them is 11772, so that there are on an average 2.45% redhaired children. The figures from which this proportion has been borrowed, are high enough to consider this as the exact average.

The first question we shall answer is: in what proportion do red-haired persons occur in the different provinces of our country. This appears from Table I. In the first column is found the total number of the children examined in each province, in the last the number of red-haired ones among them, also in the proportion expressed by the percentage. What appears from this last column? Suppose that in round numbers the general average is 25 red-haired individuals in 1000 inhabitants, then we see that in four provinces: Friesland, Gelderland, N. Holland and Utrecht the same proportional number appears, that there occurs in Z. Hollând only one in 1000, in Groningen 2 in 1000 and in Overijssel and Limburg 3 in 1000 less — in N. Brabant 1 and in Drenthe 2 more in 1000 inhabitants. These figures differ so little, also from the general average, that we are in my opinion fully entitled to conclude that in the provinces mentioned the extension of red-haired persons is much the same everywhere.

This slight difference in the percentage of redhaired persons in our country is corroborated by Table II in which the absolute numbers and the proportions are mentioned of all the places in our country in which the number of the children examined was more than 2500. It was to be expected that where the absolute numbers are sometimes relatively low here, the variation of the percentage would be greater. But yet nowhere does the proportion fall below 2% and only once a percentage of 2.9 is reached as the most favourable proportion. Where the absolute figures are high, as in Amsterdam and Rotter-

TABLE I.

Province	Total	Blondhaired- blue-eyed	Blackhaired brown-eyed	Redhaired
Friesland . . . . .	33.053	14.282=43.2%	566=1.7%	857=2.5%
Groningen . . . . .	32.223	13.401=41.3	446=1.4	755=2.3
Drenthe . . . . .	15 169	5.959=39.4	205=1.3	422=2.7
Overijssel . . . . .	41 389	14.713=35.5	689=1.6	919=2.2
Gelderland . . . . .	46 786	16 078=34.4	1340=2.8	1198=2.5
Zuid Holland . . . . .	108 073	33.043=31.4	2 712=2.5	2640=2.4
Noord Holland . . . . .	97 050	30 291=31.2	1791=1.8	2472=2.5
Utrecht . . . . .	22 017	6.626=30.1	528=2.4	545=2.5
Zeeland . . . . .	20.986	5.707=28.4	834=4.1	395=1.8
Noord Brabant . . . . .	41.155	9 173=22.3	1661=4.0	1072=2.6
Limburg . . . . .	21.902	4 790=21.8	1013=4.7	497=2.2

TABLE II.

Municipality	Total	Redhaired	Percent.
the Hague . . . . .	13.184	276	2.01
Enschede . . . . .	3 667	77	2.1
Maastricht . . . . .	3.812	86	2.2
Utrecht . . . . .	8 668	205	2.3
Haarlem . . . . .	9 908	229	2.3
Hengelo . . . . .	2.876	68	2.3
Rotterdam . . . . .	25 828	647	2.5
Amsterdam . . . . .	44.118	1164	2.6
Dordrecht . . . . .	4.586	123	2.6
Zwolle . . . . .	3.618	101	2.7
Deventer . . . . .	3.754	105	2.7
Leeuwarden . . . . .	3 562	102	2.8
Leiden . . . . .	5.648	161	2.8
Gouda . . . . .	3.640	102	2.8
Groningen . . . . .	5.039	142	2.8
Arnhem . . . . .	6.269	170	2.9

dam, the general figure of proportion, which has been found, reappears again.

Thus far I have left one province out of consideration, Zeeland. There is no denying that this province takes up a place somewhat separated from the others, since here the number of redhaired persons falls suddenly to 1.8%. This contrast with the other provinces is too great not to see here the influence of a definite cause. Yet this decrease in redhairiness in Zeeland, as will be proved higher up, cannot be attributed to a rise in the number of brunettes, which really occurs here, for N. Brabant, which is no less brunette than Zeeland, does not show this decrease. I will not enter into the cause of this decrease, I only wish to point out that already repeatedly both by Belgian and Dutch investigators attention has been drawn to the fact that from an anthropological point of view our Zeeland population takes up quite a peculiar place among the inhabitants of our country. It seems to me that this opinion is corroborated by the proportion found for the redhaired persons.

This much concerning the extension of redhaired persons in our country in general. The general conclusion to which we come, may be expressed thus, that with the exception of Zeeland this extension is a very regular one all through the country. This fact was really contrary to my expectation, as I myself, when beginning to work up my data, held the general opinion that there was a closer relationship between redhairiness and blondness. So I expected that, where in our country the blonde type varies so strongly, the influence of this would also come forth in the variation of redhairiness. Let us now, in order to prove the independence of the two phenomena, pay some more attention to Table I. For through this table we also get an insight into the decrease of the blonde and the increase of the brunette race, in a direction from North to South. As I said before, I distinguished on the schedules sent round four colours of hair and four of the eyes, making together 16 combinations. Of these combinations there are two which are really characteristic for the race, namely the combination blonde hair and blue eyes for the blonde race and the combination black hair and brown eyes for the brunette race. The other 14 combinations may be considered as mixed forms between the two races. Now, in order to keep the foundation of my reasoning as pure as possible, I have inserted in Table I only these two combinations to mutually compare them.

In the third column we find the number and percentage of blond-haired blue-eyed individuals in the different provinces. Now it appears that the number of pure blondes decreases very regularly from North

to South. The number is greatest in Friesland, viz. 43.8%, smallest in Limburg 21.8%, so reduced to half of the number for Friesland. The fourth column affords a survey of the increase of pure brunettes. Herein Drente shows the smallest number, 1.3%, Limburg the greatest 4.6%. The figures in this column point to a distinct increase in a southern direction. From this table something else appears that is important for the characterisation of redhairiness. If namely the percentages of the "pure" types are added up, so the blondes and the brunettes, this gives for Friesland a total of 44.9%, for Limburg only 26.4%, while between these two numbers those of the other provinces are regularly grouped. So the number of mixed types is in the south of our country nearly 20% higher than in the north. As a general result we may state a decrease of the pure blondes, an increase of the pure brunettes and the mixed types in a southern direction.

And notwithstanding in Friesland twice as many pure blondes are found as in Limburg, a change in the number of redhaired individuals is not perceptible. Therefore I think I am entitled to deny the existence of any relation between the two phenomena on the ground of the figures found. But my table also induces me to reject the opinion which is sometimes given, that redhairiness should be a consequence of a crossing between a blonde and a brunette individual. If this were the case, an increase might be expected of the number of redhaired persons in a southern direction in connection with the increase of mixed types.

Have I therefore to deny relationship between the blonde and the redhaired type on the ground of the data mentioned, a still stronger proof for this is afforded by another fact, which I had expected as little as the others which have been explained. It is namely the extension of redhairiness among the Jewish school-population. The total number of Jewish children examined at Amsterdam, the Hague and Rotterdam amounted to 9155. Of these 228 were redhaired, i.e. 2.47%, whilst for the not Jewish population a proportion of 2.45% had been found. The agreement between the two figures is surprising and the importance of the fact for the question put by us, shows itself clearly, when I point out the fact that pure blondes i.e. blondhaired blue-eyed Jews occur only in a proportion of 8.2% pure brunettes, i. e. black-haired brown-eyed in 18.1%. From this it proceeds that in our country among the Jewish schoolpopulation with 8.2% pure blondes, there occur as many redhaired persons as in Friesland with 43.2% pure blondes. A stronger proof that there is no direct relation between redhairiness and blondness cannot be desired.

Thus far we examined redhairiness with regard to the increase or decrease of the number of blondes among our population, and we came to the conclusion that the two phenomena are independent of each other. We can now look upon the phenomena from another point of view. If it were true that redhairiness showed a preference for the blond race, the consequence of this must needs be that among the children who, as to pigmentation, belong to the blonde race, accordingly such as have blue or grey eyes, there are more redhaired individuals than among those with brown or brownishgreen eyes.

How far this is true is shown by Table III.

TABLE III.

Colour of eyes.	Total	Blondhaired	Brown	Black	Red
Blue . . .	186 033	83 340%	11 81%	2.38%	2 470%
Grey . . .	152.072	79 67	14 66	3.06	2.63
Brownish-green	58.531	60.68	28 64	8.—	2.55
Brown . .	82 338	45 05	38 61	14 28	2.03

The first column mentions the total number of children with one of the four different iris-colours, and in the four following columns we find consecutively the percentage of the combination of the iris-colour with one of the four haircolours. Phenomena make themselves manifest therein, which were to be expected beforehand. Of the blue-eyed individuals for example, 83 % have blonde hair, of the brown-eyed only 45 %; on the other hand the number of brown-haired persons with the last is more than three times as large as with the blue-eyed, and a relatively still stronger rise is found with the blackhaired. Generally speaking, it appears that with an increase of the pigmentation of the iris also the pigmentation of the hair increases. This holds good for blonde, brown and black hair. But in contradistinction to this there appears to be no relation between the degree of pigmentation of the iris and the hair with redhaired individuals. For of the blue-eyed 2.47 % are redhaired, of the grey-eyed 2.63 %, of the brownish-green-eyed 2.55 % and of the brown-eyed 2.03 %. It is true, this last figure is the lowest, but it seems to me that the difference is not so great that therein the proof may be seen that redhairiness shows less relationship to the brunette race. Moreover, this opinion could directly be refuted by the fact that I

find a somewhat lower percentage of redhaired individuals among the blue-eyed children than with the grey or brownish-greeneyed.

Red hair is therefore a quality altogether independent of the degree of pigmentation of the iris. No matter from what side we look upon the redhairiness with regard to the other phenomena of pigmentation of hair or eyes, there is — at least on the score of my-researches -- not a single proportion to be alleged on behalf of the opinion that redhairiness should by preference occur in the blonde race. So I cannot but reject as incorrect the opinion of those who, reducing redhairiness to a quantitative difference of pigment, see in it nothing but a nuance. And these results of our investigation naturally lead to considering red hair as a variety, in which the pigment is qualitatively different from that in blonde and black hair. Between these two last there is properly speaking no real difference; gradually, through numerous shades, flax-blonde hair passes into jet-black, by an increase of the quantity of pigment; also in red hair a great number of shades can be distinguished; in proportion to the quantity of pigment the colour varies between gold-blonde and fiery red.

How is the appearance and the regular extension of redhaired individuals among our population to be accounted for? It need hardly be said that, on the ground of the proportions found, I am not entitled to give any explanation. For this purpose anthropological researches of another nature would be necessary. Only for the sake of completeness I mention the opinion of TOPINARD, who explains redhairiness from a former mixing with an originally redhaired race, which in pre-historic times is said to have inhabited the plains of Russia, Siberia and Turkistan and of which one of the groups of the Finnish population (the Letts and the Esths) are said to be the purest descendants <sup>1</sup>).

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<sup>1</sup>) L'histoire de cette race est à faire. Jusqu'à nouvel ordre j'admets qu'elle a occupé le sol de la Russie aux époques préhistoriques, antérieurement à l'invasion des Asiatiques, répondant à l'un des deux types finnois actuels, je n'ose dire de celui qui a apporté la langue du Kalevala. Elle est représentée dans la plupart des kourgans anciens de la Russie. Le type en est signalé dans les annales des Han antérieurement à l'ère chrétienne en Sibérie et dans le Turkestan Chinois — *Éléments d'Anthrop. générale.* p 334.

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(November 28, 1907).

E R R A T A.

Proceedings of the meeting of September 1907.

p. 229 l. 1 and p. 230 l. 7 from the bottom: for p. 1 read p. 215

Proceedings of the meeting of March 1907.

p. 788 l. 6 from the bottom: for  $1.299 < \tau < 1.040$   
read  $1.299 > \tau > 1.040$

„ „ l. 5 „ „ „ for  $1.040 < \tau < 1$   
read  $1.040 > \tau > 1$

„ „ l. 19 „ „ „ for “becomes” read “comes”

„ „ l. 18 „ „ „ for “united” read “unite”



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

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PROCEEDINGS OF THE MEETING

of Saturday November 30, 1907.

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(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 30 November 1907, Dl. XVI).

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**Physiology.** — “*On the segmental skin-innervation by the sympathetic nervous system in vertebrates, based on experimental researches about the innervation of the pigment-cells in flat fishes and of the pilo-motor muscles in cats.*” By Dr. G. VAN RIJNBEEK. (Communicated by Prof. C. WINKLER.)

(Communicated in the meeting of October 26, 1907.)

We possess numerous, though dispersed, data, obtained either by means of experiments on animals or founded on clinical observations, tending all to confirm the opinion, that in vertebrates and in man, the efferent nervefibres, intended for the skin, which are conducted by the grey connecting branches from the lateral column of the N. sympathicus towards the mixed spinal nerves, are distributed within the area of the skin that is supplied with afferent fibres by the spinal nerve. As moreover, in general, save slight deviations, the efferent sympathetic fibres of the grey connecting branches have their origin in the ganglia of the column in which these branches apparently originate, we may assume that the zones of the skin, innervated by the ganglia of the sympathetic column are nearly identical in their distribution with the zones of the skin, supplied by the different corresponding spinal ganglia. Less numerous are the data about the relative extent of the sympathetic and spinal zones of the skin, but indirect indications apparently support the view that the zones of the skin innervated by the spinal ganglia are more extensive than the zones of the different corresponding sympathetic ganglia. With this reservation however we apparently may hold it very probable, that the innervation of the skin both by the sympathetic and by the spinal ganglia is taking place according to the self-same morphological scheme. Hitherto nevertheless no direct proofs have been given by demonstrating on the self-same object the relative distribution and extent of these innervation-areas. It has been my purpose to do this now by means of a few simple experiments.

A. *The sympathetic innervation of the pigment-cells and the spinal innervation for sensibility of the skin in flat fishes.*

Since the elaborate researches of G. POUCHET<sup>1)</sup> we know that in several species of fishes the phenomenon of the variability of colouring

<sup>1)</sup> G. POUCHET. Des changements de coloration sous l'influence des nerfs. — Journal de l'anatomie et de la physiologie. Tome 12 p. 1—90, and p. 113—165, Paris 1876.

in the skin is directly influenced by the sympathetic nervous system. If in a turbot the connecting branches of some spinal nerves or these nerves themselves, in that upward turned half of the body containing the eyes, are cut through, there appears on the skin a more or less sharply defined dark zone. POUCHET considered this phenomenon to be caused by a paralysis of the pigment-cells in consequence of the section of the nerves, and he called the dark zones appearing after section, "paralytic" zones. He made however no further researches as to the significance of these zones, when considered as innervation-areas of sympathetic ganglia, and since, to my knowledge, nobody has taken up again these yet so extremely interesting researches. I have done so at the present time, and added unto this a comparative investigation about the sensible innervation of the skin.

For objects I got numerous specimens of *Solea* (*impar, vulgaris, monochir*) and *Rhomboidichthys* (*mancus seu podas*). This latter species in particular, and likewise *Solea impar*, have furnished me with excellent results, and the more detailed demonstration is principally based on experiments made on these animals. The operative part of these experiments was very simple. By a longitudinal incision, cleaving skin and muscles, and passing along the lateral line of the organ of sense in the ventral portion of the skin of the caudal part of the pigmented half of the body bearing the eyes, the origins of a few haemal vertebral spinous processes were laid bare and the

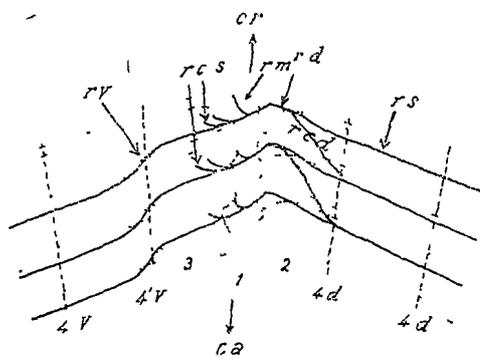


Fig. 1.

Scheme of course and distribution of the main trunks of the spinal nerves in the caudal portion of the Pleuronectidi (taken from a preparation of *Rhombus lacvis*), 1, body of vertebra, 2, neutral spinous process, 3, haemal spinous process, 4'd, 4''d, 4'v, 4''v, first and second longitudinal septum of the dorsal and ventral muscles, — *cr*, *ca*, cranial and caudal boundaries of the preparation. — *r.d.*, *r.m.*, *r.v.*, ramus dorsalis, medius and ventralis of the spinal nerves — *r.c.d.*, *r.s.*, ramus communis and ramus spinosus of the dorsal nerve-trunks. — *r.c.s.*, left sympathetic connecting branch.

ventral branches of the spinal nerves were sought. In most cases these were caught up and torn off together with the connecting branches of the N. sympathicus.

In all cases the visible consequence of these operations consisted constantly in the appearance on the skin of a more or less sharply defined dark field, i. e. darker than the surrounding skin. Distribution and extent of these dark fields were dependent on the place in the segmental arrangement of the sectioned nerves and on their number. The shape of these fields was always identical, being that of a band, beginning in the dorsal marginal fin, going somewhat obliquely cranialward to the lateral line of the organ of sense, and thence somewhat obliquely caudalward towards the ventral marginal fin, wherein it terminated. Thus much for the shape and the general distribution of these zones. As regards their extent, the following may be stated. After destroying the connecting branch of one single spinal nerve I never observed any plainly visible change in the colouring of the skin. After destroying the connecting branches of two consecutive nerves, usually a narrow, not very dark zone was observed, that might be not easily defined. Only when three consecutive branches were destroyed, there appeared a plainly visible, sharply defined dark zone.

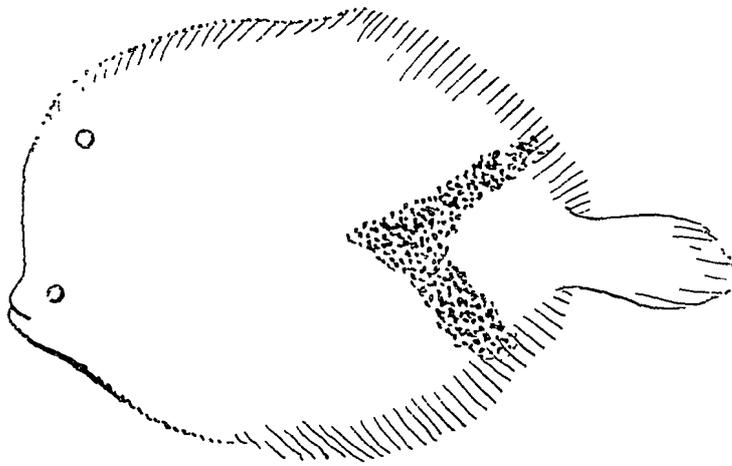


Fig. 2. 1)

*Rhomboidichthys mancus*, dark zone appearing after cutting through three spinal nerves and the sympathetic connecting branches.

If more than three branches were destroyed, there was found a dark zone, identical as to shape and position, only broader. If after a first section of viz. three branches, still another couple of branches,

1) This figure and fig. 3, 4, 6, 7, 8, 9 are reproductions of photographies counterdrawn in outline.

lying next to these first ones either cranially or caudally, were destroyed, the originally observed dark zone was afterwards constantly found uniformly broadened, either the cranial boundary being removed cranialward or the caudal boundary being removed caudalward, according to the case. By these means a series of indications was furnished, tending to prove that the skin-areas supplied with pigmento-motor fibres by each connecting branch or by the ganglia of the sympathetic column, are themselves likewise uninterrupted, zone-shaped fields. Still further data on this subject were obtained in the following manner.



Fig. 3.

*Solea impar.* Isolation of four spinal nerves between four nerves cut through cranially and four other ones cut through caudally of them.

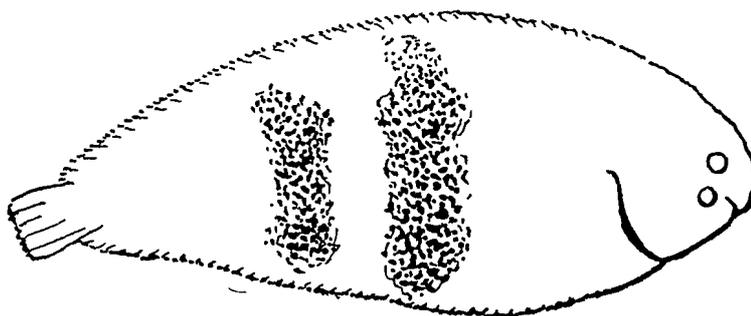


Fig. 4.

Another solea, on which a similar operation had been made.

If a few, viz. four connecting branches were destroyed, and again also four other ones cranially or caudally from these, leaving intact e. g. four branches between the two, two dark zones appeared of about equal breadth, enclosing between them a somewhat broader zone of lighter colouring, corresponding to the uninjured branches. (Fig. 3 and 4). By means of similar experiments the supposition that the ganglia of the sympathetic column innervate zone-shaped skin-areas becomes nearly a certainty. Some results too were obtained as to the extent of these areas. Comparative calculations, as shown before, starting from measurements of the darker and lighter zones, made with as much accuracy as was possible, have shown that the cranial-

caudalward breadth of a skin-area innervated by a ganglion of the sympathetic column, having an average length of 20 cm. may be approximated at 7 mm., and that the areas overlap one another somewhat more than half.

The foregoing having been duly stated, a comparison between the scheme of the spinal and that of the sympathetic innervation of the skin lay very near indeed. Once the ventral (and dorsal) branches of a couple of spinal nerves having been cut through together with the sympathetic connecting branches, it is easy enough to define the extent and the distribution of the insensible zone of the skin resulting from this operation, and to establish a comparison between these and those of the dark zone. In order to facilitate this definition, I augmented the irritability for reflex actions in the animals by intoxicating them with a small quantity of a solution of the sulphuric salt of strychnia in sea-water (1 : 10.000). After this a slight scratching of the skin by means of a pin's point was sufficient to produce a plainly visible general reaction, making it possible to define the boundaries between the sensible and insensible areas with great precision. I found the results of a series of experiments to be nearly invariable, so that I may communicate them here with sufficient certainty.

Generally then the anaesthetic areas and the dark zones, observed after the section of spinal nerves and their corresponding sympathetic connecting branches are found to accord completely as regards their extent, distribution and arrangement. Consequently the pigmento-motor sympathetic fibres, originating in a certain ganglion of the N. sympathicus and its connecting branch, are distributed precisely within that area of the skin that is supplied with sensory fibres by the corresponding spinal ganglion. Both schemes therefore cover one another completely, and the above given particulars about the innervation of the pigment-cells, holds good likewise for the sensory innervation of the skin. Thus the central innervation of the skin in Pleuronectidae is divided into a series of segmental areas, which considered in their functional significance, may be distinguished in sensory and pigmento-motor skin segments, but according completely as regards their distribution and extent.

*B. The sympathetic innervation of the pilo-motor muscles and the spinal sensory innervation of the skin in cats.*

The well-known researches of LANGLEY (1893)<sup>1)</sup> have shown that

<sup>1)</sup> J. N. LANGLEY. — Preliminary account of the arrangement of the sympathetic nervous system, based chiefly on observations upon pilomotor nerves. Proceedings

the sympathetic nerve-fibres, intended for the pilo-motor muscles of the skin of the trunk in cats, originate in the series of ganglia of the column of the N. sympathicus, that they are conducted along the grey connecting branches towards the relative corresponding spinal nerves, thence following the primary dorsal nerve-trunks and the (dorsal) skin branches of these, to terminate in the pilo-motor muscles of the dorsal portion of the skin. Besides he has demonstrated that by far the greater number of the nerve-fibres, originating in the sympathetic ganglion, the "pilo-motor" nerves as he called them were conducted along the selfsame grey connecting branch towards the one spinal nerve segmentally corresponding with it, and that along the dorsal skin-branch or branches of this nerve, they jointly reach the skin, where they are distributed within one uninterrupted area, that may be sharply defined. He found further more, that these skin-areas, supplied with pilo-motor nerve-fibres by the series of sympathetic ganglia form a regular series, arranged on both sides of the mid-dorsal line of the body. As regards the relation between the innervation of the skin by fibres for the pilo-motor muscles from the sympathetic ganglia, and the innervation by sensory fibres from the spinal ganglia, he confined himself to comparing the arrangement of the pilo-motor skin-areas innervated by the sympathetic ganglia with the results of the researches made by TÜRK and SHERRINGTON about the spinal innervation in the dog and the monkey. Direct comparisons between the sensory and the pilo-motor innervation of the skin were not made by him. These have been made recently by me.

The way in which to do this was clearly indicated. At present, especially after the anatomical studies of BOLK on man, we may take it for granted, that there does not occur an interchange of nerve-fibres destined for the skin between the spinal nerves in the trunk-area in mammalia. Consequently the serially arranged skin-branches of the dorsal portion of the body represent separately the different spinal and sympathetic nerve-fibres intended for the dorsal portion of the skin of the trunk from the spinal nerves and sympathetic connecting branches in which they originate. In order therefore to obtain a knowledge of the innervation of the dorsal skin-portion relatively by the spinal and by the sympathetic ganglia, it is sufficient to define separately and then to compare the different areas of dis-

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of the R. Society of London, vol. 52, n<sup>o</sup>. 320, p. 547—556 Februari 1893. London.  
 J. N. LANGLEY. The arrangement of the sympathetic nervous system based chiefly upon pilomotor nerves. Journal of Physiology (Foster) vol. 15 n<sup>o</sup>. 3 p. 176—244. 1893. Cambridge.

tribution of the pilo-motor and of the sensory fibres having their course in the dorsal nerve-branches of the skin. This may be done in a very simple way.

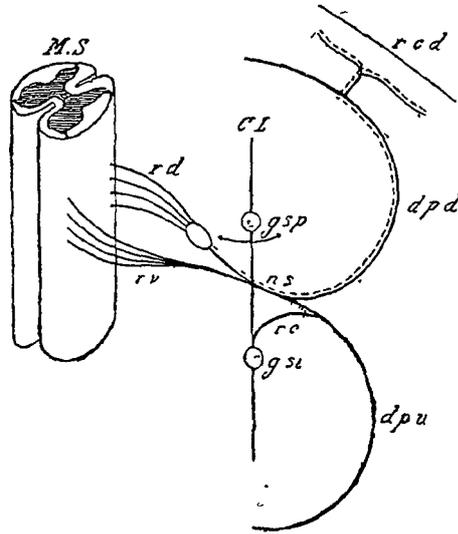


Fig. 5.

Scheme of the course of the (post ganglionic) pilomotor- and of the sensory nerve-fibres toward the skin of the trunk-area in cats.

*M.S.* = medulla spinalis. — *r.d.-r.v.* = dorsal and ventral root. — *N.S.* = mixed spinal nerve. — *d.p.d.-d.p.v.* = dorsal and ventral trunk of the spinal nerve. — *r.e.d.* = dorsal ramus cutaneus. — *C.L.* = lateral column of the N. Sympathicus. — *g.sp.-g.si.* = ganglion spinale, sympathetic ganglion. — *r.c.* = grey connecting branch — — — define the course of the spinal sensible fibres . . . . that of the pilomotor fibres.

I obtained this scheme by defining first by means of SHERRINGTON'S method of isolation the surface of the sensible area innervated by a certain skin-branch and next by the stimulus of an induced current applied to the same branch, causing the surface of the skin-area, innervated by the pilomotor fibres from this branch, to become visible. In order to do so, the hair on the trunk of the cats I made use of, were first cut uniformly by means of a so-called tondeuse to a length of about half a c.M. Afterwards, under narcotics and with aseptic precautions (as far as possible, the skin not being shorn) a longitudinal incision was made in the skin along the mid-dorsal line, and the skin was folded back to both sides. The connective tissue having been prepared the series of dorsal skin-nerves was in most cases pretty plainly distinguishable, and it was very easy to choose a definite branch for isolating and to section the three branches lying next to this one both cranialward and caudalward, either after

having loosened them from the adjacent blood-vessels that mostly follow the same course, or else together with the bloodvessels between a double ligature. The skin was then skitched and the animal was allowed a few days quiet. After this the sensible and the insensible areas to be found in the skin were defined and their boundaries carefully indicated by means of coloured demarcation-lines. Finally the animal was again brought under narcosis, the incision in the skin was reopened and the isolated nerves were laid bare and stimulated. The area-field, on which the hair was rising, was demarcated by another colour.

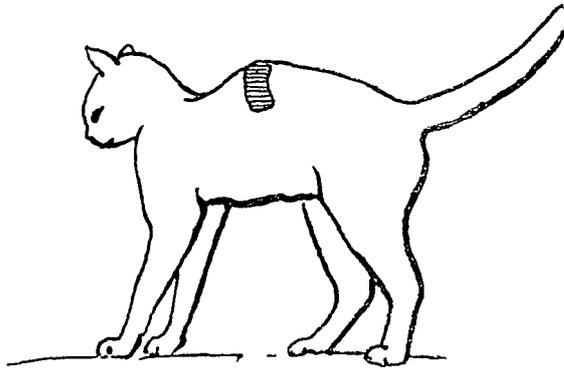


Fig. 6.  
Pilomotor area of the 7<sup>th</sup> thoracal nerve

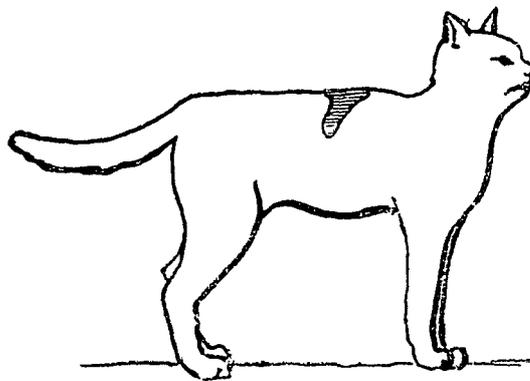


Fig. 7.  
Pilomotor area of the 8<sup>th</sup> thoracal nerve in the same cat.

As regards the pilomotor nerves I can be short, as I have hardly anything to add to the very accurate communications of LANGLEY on this subject. Like him I found in my experiments that the areas in which during the irritation of different skin-branches and on different animals the hair rose, showed rather important

differences, both as to their extent, shape and boundaries and as to the intensity of the phenomenon itself. Usually the field, in which the hair rose, was nearly rectangular, and save for a slight deviation caudal-ward, it was lying vertically on the mid-dorsal line. In the most successful experiments the pilo-motor areas extended nearly unto the dorsal axilla-inguinal line over a dorso-ventral surface of almost 60 m.M. The cranio-caudal breadth amounted on the average to 26 m.M. For an instance of the proportions of the pilomotor areas in an exceptionally favourable case I refer to the photographs represented in fig. 6 and 7.

The isolated sensible areas usually presented a shape not greatly different from that of the pilomotor areas described above. Like these they were generally nearly rectangular, lying almost vertically on the mid-dorsal line, and they showed likewise a slight deviation caudal-ward, perhaps even somewhat more marked. Cranially and caudally they were bounded by the insensible areas; ventrally they passed without any distinct boundaries into the lateral part of the body, where sensibility was retained wholly intact. The cranio-caudal breadth of the sensible areas was on the average 30 m.M., their dorso-ventral extent of course was not to be defined; that of the insensible areas was on the average 60 m.M.

We may now pass on to a comparison between the sensible and the pilomotor skin-areas. On account of what I remarked before about the variability both as to shape and extent of these latter ones, it may be inferred already that the results of this comparison presented likewise great differences. On one important point however the results of all my experiments are in accord: the pilomotor skin-area was always to be found within the sensible area of the isolated nerve-branch. In this respect the principal problem I had put before me in all my experiments, may be considered to have been solved, at least for that portion of the skin of the trunk on which I made my experiments. As regards further the relative extent of the sensible and of the pilomotor skin-areas, and the exact situation of the latter within the former, I found, as remarked before, great differences. Sometimes the pilomotor field area had an extent nearly equal to that of the sensible field, both fields being consequently almost identical. In the majority of cases however the pilomotor skin-area was less extensive in all directions than the sensible area. The place, occupied by the pilomotor field within the sensible field differed greatly in different cases. Generally it was lying almost in the midst of it, as is shown in the cats, photographs of which are represented in fig. 8 and 9.

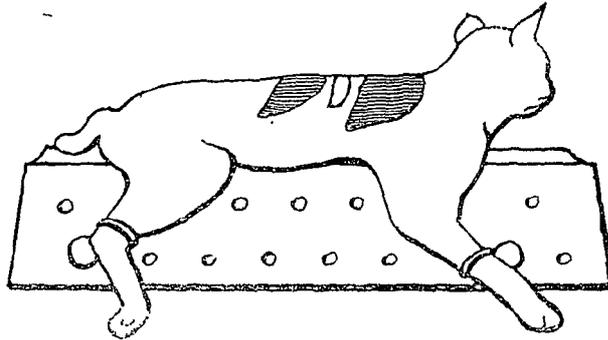


Fig. 8.

Situation of the pilomotor skin-area (white) within the sensible area nearly isolated by insensible areas (hatched transversally).

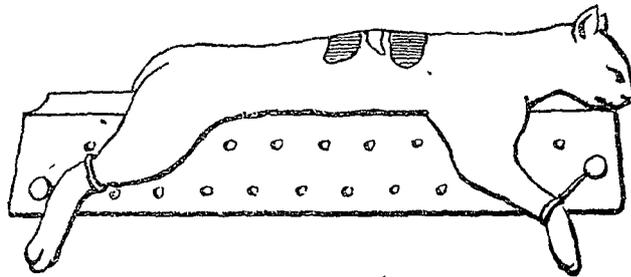


Fig. 9.

The same in another cat.

In another case however it lay nearer to the cranial or caudal boundary of the sensible area, I have not been able to state a definite rule in this respect.

Returning now to the principal problem aimed at by my researches, we find that from the above statements it has become evident that the pilomotor nerve-fibres and the sensory fibres having their course in the dorsal skin-branches of the skin of the trunk in cats, are distributed within areas of the skin that are in accordance as to situation and arrangement but not as regards their extent. Thence it follows that the sympathetic ganglia and the spinal ganglia innervate the skin after the same scheme, and although the relations in cats are less simple than those found in flat fishes, still I believe that here likewise the scheme of the pilomotor innervation of the skin by means of the marginal column of the sympathetic nervous system may be called a "segmental" scheme.

**Physics.** — “*Some remarks on the expansion of platinum at low temperatures*”. By Prof. H. KAMERLINGH ONNES and J. CLAY. Supplement N<sup>o</sup>. 17 to the Communications from the Physical Laboratory at Leiden.

(Communicated in the meeting of September 28, 1907).

The communication from the “Physikalisch-technische Reichsanstalt” by K. SCHEEL in the meeting of Jan. 11, 1907 of the “Deutsche physikalische Gesellschaft” led us to make a remark already in the Meeting of June 29, 1907 (These Proc. Sept. 1907 p. 200). In Communication N<sup>o</sup>. 95<sup>b</sup> (These Proc. Sept. '06 p. 199) we had given a quadratic formula for the expansion of platinum *below* 0°, from which followed that, as was remarked in the Introduction of that Communication, a formula of the third degree is required if we wish to represent the expansion of platinum from  $-180^{\circ}$  to  $+100^{\circ}$  by one polynomial with increasing powers of  $t$ , and if we have to deal with observations which if repeated a sufficient number of times, allow us to reach an accuracy (comp. § 1 of Comm. N<sup>o</sup>. 85, June '03, These Proc. April '05) of  $\frac{1}{300}$  in the expansion. We found this confirmed by the measurements of SCHEEL, who arrived at the same result by determining a quadratic formula for the expansion of platinum *above* 0°, and by measuring the length at  $-190^{\circ}$ .

We now consider the striking difference of the expansion at low temperatures according to the formula given by us, and that according to SCHEEL's formula, viz.:  $43 \mu$  for the expansion of a bar of 1 meter between  $-183^{\circ}$  and  $+16^{\circ}$ , (cf. SCHEEL loc. cit. p. 19, note 1), a difference much greater than could be accounted for by the inaccuracy of the observations.

For an explanation of this discrepancy we call attention to the difference of the observations of Dec. 16 1904 and Febr. 3, 1905 in Table II of Comm. N<sup>o</sup>. 95<sup>b</sup>, which give as length of the platinum bar provided with the two glass extremities, at  $16^{\circ}$ <sup>1)</sup> before it had ever been reduced to low temperature, 1027.460 m.m., and a long time after it had been reduced to low temperature for the last time, 1027.457 m.m., mean 1027.458 m.m., with that of Dec. 19, 21 and 23 in the same table which yield the mean value 1027.441 mm. (from 1027.441, 1027.442 and 1027.440) for the length at  $16^{\circ}$ , which was observed on return to the ordinary temperature a day after

<sup>1)</sup> In Table II of this communication under  $L_{16^{\circ}}$  for the ordinary temperatures the length of the bar at  $16^{\circ}$  reduced on the measuring rod *at*  $16^{\circ}$  has been given and not the length at  $\S$  as in the tables of Comm. N<sup>o</sup>. 85.

the cooling. Indeed this former mean value is  $17 \mu$  larger than the latter.

Now this difference of  $17 \mu$ , which refers to a bar of platinum of 840 mm. (for a bar of 1 M. it would be  $20 \mu$ ) exceeds the errors which may be ascribed to the inaccuracy of the observation by about half the difference which exists between SCHEEL's formula and our formula of June 1906.

As basis for the calculation of our formula the mean<sup>1</sup>, of the two lengths has been taken. We arrive at values for the expansion nearer to those of SCHEEL when for the length at the ordinary temperature we take that which was found immediately after cooling, instead of the mean of this length and the length which was found long before and after the cooling, as was done in the calculation of our formula of June 1907. If we now make use of the first-mentioned length, that which was found immediately after cooling, in order to find the coefficients now distinguished by (a) and (b) from the former a and b in the formula:

$$l_t = l_o \left( 1 + \left\{ (a) \left( \frac{t}{100} \right) + (b) \left( \frac{t}{100} \right)^2 \right\} 10^{-6} \right)$$

we find:

<b>Platinum</b> (−183° to +16°)	}	(a) 877.7	KAMERLINGH ONNES
		(b) 35.7	and CLAY (1905)
		whereas	
		(a) 861.5	SCHEEL (1906)
		(b) 37.0	

It is true that the now remaining difference of  $34 \mu$  per M. with an expansion of  $-183^\circ$  to  $+16^\circ$  remains considerably larger than the accuracy of the observations would lead us to expect, but it is considerably smaller than that found originally, and taking into consideration the different sources of uncertainty whether we observe really what we think we observe, the small number of measurements, and the difference of the methods applied at low temperatures for the first time, it is not great.

We had hoped to obtain further information on the difference in length of our bar at ordinary temperature immediately after the cooling and long after it, but have not yet been able to do so.

Differences as the one discussed now have more occurred in our measurements. We have pointed this out in Comm. N<sup>o</sup>. 95<sup>b</sup> and

<sup>1</sup>) In the calculations for the glass the values of the length immediately after the cooling, Dec. 23 in Table I, and April 15 and 16 in Table III, have been left out of account in connection with the further observations.

for glass we have expressly investigated the possibility of thermal hysteresis on cooling to the lowest temperatures. In connection with what has been said in Comm. N<sup>o</sup>. 95<sup>b</sup> we fear that for the above treated difference an irregularity in the behaviour of the place of fusion of the glass points to the platinum bar has played a part, to prevent which further experiments ought to be made with still greater care. If what we now think probable, is verified, observations in which a difference as the one considered just now, manifests itself, should be rejected.

Besides the formula of the second degree for temperatures below 0°, we have also calculated a formula of the third degree

$$l_t = l_0 \left[ 1 + \left\{ (a') \frac{t}{100} + (b') \left( \frac{t}{100} \right)^2 + (c') \left( \frac{t}{100} \right)^3 \right\} 10^{-6} \right]$$

for the expansion of platinum between  $-183^\circ$  and  $+80^\circ$  by the aid of BENOIT's observations from  $0^\circ$  to  $+80^\circ$ , in which formula (a'), (b'), (c') refer to the length at the ordinary temperature immediately after the cooling.

The agreement of

Platinum	}	$+ 80^\circ$	(a') 875.3	}	BENOIT and KAMERLINGH ONNES and CLAY (1905)
		$- 183^\circ$	(b') 31.6		
			(c') -1.49		
	}	$+ 100^\circ$	(a') 874.9	}	SCHEEL (1906)
		$- 190^\circ$	(b') 31.41		
			(c') -6.94		

is pretty satisfactory. Substitution of SCHEEL's values for those of BENOIT would bring about only a slight change in the first group of coefficients.

**Anatomy.** — “*On the Development of the Corpus callosum in the human Brain.*” By Prof. J. W. LANGEJAAN. (Communicated by Prof. T. PLACE).

The points that at this moment seem of interest in the history of the development of the corpus callosum have been clearly formulated by RETZIUS<sup>1)</sup> in the form of questions. Two of these are: 1. Where does the corpus callosum originate? 2. Of what

<sup>1)</sup> RETZIUS. Das Menschenhirn. Stockholm 1896. p. 6.

elements is it composed at its first appearance? The third question of RETZIUS has been amplified by ZUCKERKANDL.<sup>1)</sup> and may be formulated as follows: what are the changes occurring in the mesial wall of the pallium in consequence of the development of the corpus callosum?

For the answering of the first question a human embryo of the beginning of the fourth month was at my disposal. The fronto-occipital diameter of the corpus callosum amounted to but 0.5 m.m. Figure I shows a frontal section through the more posterior part of the lamina terminalis.

The plane of section deviating a little from the frontal plane, that which is shown in the right part of the drawing is more frontally placed than that which is shown in the left part.

As appears from the drawing the corpus callosum lies in the lamina terminalis; especially on the left this is clearly evident, where the underborder of the pallium goes over into a taenia (*T*) which is bent in and passes over into the lamina terminalis (*L.t.*). The fact that the ependyma of the lamina terminalis, which is continued into the ependyma of the taenia, also spreads underneath the corpus callosum, obviates all doubt as to the existence of this relation. If now the sections are examined more frontally, it will be seen, that the more frontal part of the corpus callosum no longer lies in the lamina terminalis. This part of the corpus callosum exceeds the limits of the lamina and is situated in the zone of union of the mesial walls of the pallium. This zone is built up of glia-tissue and in immediate continuity with the glia-layer covering the fore-side of the lamina terminalis.

On the ground of this observation I believe that the corpus callosum originates in the lamina terminalis, very soon, however, in consequence of the enlargement of the commissure, preponderantly in a frontal direction, it encroaches on the lamina and lies partially in the zone of union of the pallia.

Another embryo, of the middle of the fourth month, exhibits a corpus callosum with a maximum diameter of 2.5 m.m. Here the commissure is still entirely situated in front of the foramen Monroi. Figure II shows a frontal section through the more posterior part of the corpus callosum. In this section the corpus callosum (*C.c.*) lies most dorsally, laterally going over into the mesial wall of the pallium. In this wall, aside from the callosum, we find the fornix

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<sup>1)</sup> ZUCKERKANDL. Sitzb. K. Acad. der W. Math. Naturw. cl. Bd. CX. h. VIII. Wien 1901. p. 234.

(*F.*) which, in the mesial wall of the pallium, is not clearly distinguishable from the corpus callosum. Downwards, the fornix may be followed as far as the anterior commissure (*C.a.*). In the angle, where callosum and fornix meet, lies a bundle of fibres (*Ps.*) ventrally from the corpus callosum and coming from behind. This bundle crosses in the middle-line another bundle of the same kind coming from the opposite direction. This crossing-system is the fornix-commissure. More frontally this commissure is wanting and only the callosum and the fornix are present in the relation I just now described.

From the topographical relation of the corpus callosum to the fornix-commissure the deduction may be made that the more posterior part of the callosum is equivalent to the splenium. In the same way it follows from the relation of the callosum to the fornix-bundle that the more anterior part of the callosum corresponds with the genu of that structure. The origin of the corpus callosum therefore comprises the whole commissure, and consequently the growth of the corpus callosum does not take place by means of the apposition of new systems of fibres, but by an equable enlargement in correspondence with the growth of the pallium.

The most preponderant change in the structure of the mesial wall of the pallium at the place of origin of the callosum consists in the cortex-layer bending a little inward and ending with a sharp edge. The middle-layer of the wall of the pallium gets richer in nuclei; these nuclei surround the callosum and the fornix like a cap. Along the lower edge of the cortex-layer they penetrate into the marginal-zone of the wall of the pallium. By this process the marginal-zone disappears as a separate layer.

In the zone of union of the mesial walls of the pallium the changes in the structure of this wall are more considerable; the observation, that the most mesial bundles of the fornix pass through the glia-tissue of this zone of union, seems of importance here, as from this fact may be derived, that the re-constructed mesial wall of the pallium — the later septum lucidum — comprises more than the original mesial wall.

Fig. I.

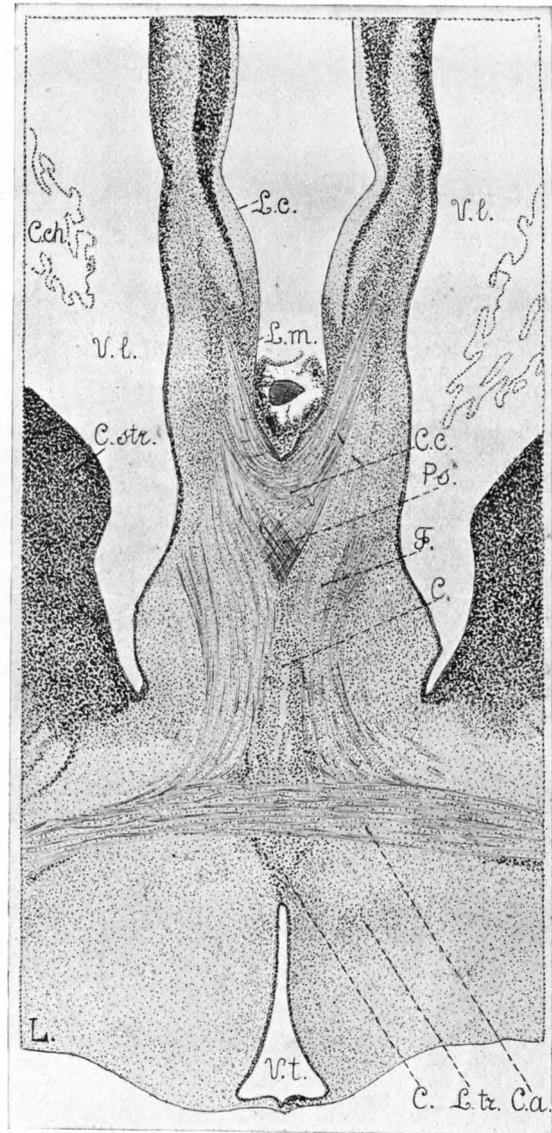
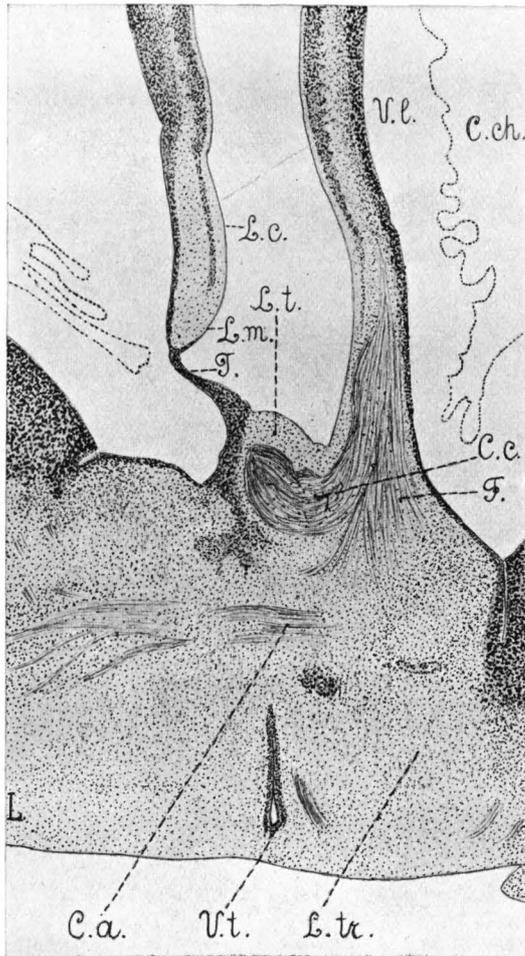
Frontal section of the more posterior part of the lamina terminalis. Section 20  $\mu$  stained with haematoxylin and eosin. Enl. 16.5 diam.

*C.a.* Anterior commissure.  
*C.c.* Corpus callosum.  
*C.ch.* Corpus chorioideum.

*L.t.* Lamina terminalis.  
*L.tr.* Lamina trapezoidea.  
*T.* Taenia.

Fig. II.

Fig. I.



<i>F.</i> Fornix.	<i>V.l.</i> Lateral ventricle.
<i>L.c.</i> Limbus corticalis.	<i>V.t.</i> Third ventricle.
<i>L.m.</i> Limbus medullaris.	

Fig. II.

Frontal section through the more posterior part of the corpus callosum. Section 15  $\mu$  stained with haematoxylin and eosin. Enl. 13 diam.

<i>C.</i> Zone of union of the pallia.	<i>L.c.</i> Limbus corticalis.
<i>C.a.</i> Anterior commissure.	<i>L.m.</i> Limbus medullaris.
<i>C.c.</i> Corpus callosum.	<i>L.tr.</i> Lamina trapezoidea.
<i>C.ch.</i> Corpus chorioideum.	<i>Ps.</i> Fornix commissure.
<i>C.str.</i> Corpus striatum.	<i>V.l.</i> Lateral ventricle.
<i>F.</i> Fornix.	<i>V.t.</i> Third ventricle.

**Mathematics.** — “On an infinite product, represented by a definite integral.” By Prof. W. KAPTEYN.

The object of this paper is to write the infinite product

$$\prod_{s=0}^{\infty} \left( 1 + \frac{v^2}{(u+s)^2} \right)$$

in the form of a definite integral.

This product is connected with *mod.*  $\Gamma(u + iv)$ , for

$$\text{mod. } \Gamma(u + iv) = \Gamma(u) \cdot e^{-P(u,v)} \quad (u > 0)$$

where

$$P(u,v) = \frac{1}{2} \sum_{s=0}^{\infty} \lg \left( 1 + \frac{v^2}{(u+s)^2} \right) \quad ^1)$$

thus

$$\text{mod.}^2 \quad \Gamma(u + iv) = \frac{\Gamma^2(u)}{\prod_{s=0}^{\infty} \left( 1 + \frac{v^2}{(u+s)^2} \right)}$$

and

$$\prod_{s=0}^{\infty} \left( 1 + \frac{v^2}{(u+s)^2} \right) = \frac{\Gamma^2(u)}{\text{mod.}^2 \Gamma(u + iv)}$$

To write the second member of this equation in the form of a definite integral, we start from WEIERSTRASS' definition

$$\frac{1}{\Gamma(z)} = \frac{1}{2\pi i} \int_W e^t t^{-z} dt$$

where the integral is taken along a curve *W* commencing at negative

<sup>1)</sup> Nielsen. Handbuch der Theorie der Gammafunctionen p. 23.

infinity, circulating around the origin in the positive direction, and returning to negative infinity again; thus

$$\frac{2\pi i}{\Gamma(z)} = e^{\pi iz} \int_0^{\infty} e^{-t} t^{-z} dt - e^{-\pi iz} \int_0^{\infty} e^{-t} t^{-z} dt$$

and if  $z = u + iv$

$$\begin{aligned} \frac{2\pi i}{\Gamma(u+iv)} &= e^{-\pi v} \left( \cos(\pi u) + i \sin(\pi u) \right) \int_0^{\infty} e^{-t} t^{-u} \left( \cos(vlg t) - i \sin(vlg t) \right) dt \\ &\quad - e^{\pi v} \left( \cos(\pi u) - i \sin(\pi u) \right) \int_0^{\infty} e^{-t} t^{-u} \left( \cos(vlg t) - i \sin(vlg t) \right) dt. \end{aligned}$$

Writing

$$\begin{aligned} \int_0^{\infty} e^{-t} t^{-u} \cos(vlg t) dt &= M \\ \int_0^{\infty} e^{-t} t^{-u} \sin(vlg t) dt &= N \\ \frac{2\pi}{\Gamma(u+iv)} &= \alpha + i\beta \end{aligned}$$

we obtain

$$\begin{aligned} \alpha &= (e^{\pi v} + e^{-\pi v}) \sin(\pi u) M + (e^{\pi v} - e^{-\pi v}) \cos(\pi u) N \\ \beta &= (e^{\pi v} - e^{-\pi v}) \cos(\pi u) M - (e^{\pi v} + e^{-\pi v}) \sin(\pi u) N \end{aligned}$$

and

$$\alpha^2 + \beta^2 = (e^{2\pi v} - 2 \cos 2\pi u + e^{-2\pi v}) (M^2 + N^2).$$

Now we have

$$\begin{aligned} M^2 &= \int_0^{\infty} e^{-x} x^{-u} \cos(vlg x) dx \cdot \int_0^{\infty} e^{-y} y^{-u} \cos(vlg y) dy \\ N^2 &= \int_0^{\infty} e^{-x} x^{-u} \sin(vlg x) dx \cdot \int_0^{\infty} e^{-y} y^{-u} \sin(vlg y) dy \end{aligned}$$

so

$$M^2 + N^2 = \int_0^{\infty} \int_0^{\infty} e^{-(x+y)} (xy)^{-u} \cos\left(vlg \frac{y}{x}\right) dx dy$$

or in polar coordinates, putting

$$x = r \cos \theta, \quad y = r \sin \theta$$

$$M^2 + N^2 = \int_0^{\frac{\pi}{2}} \int_0^{\infty} e^{-r(\cos \theta + \sin \theta)} (r^2 \sin \theta \cos \theta)^{-u} \cos(vlg \tan \theta) r dr d\theta.$$

This double integral may be reduced to a single one, for

$$\int_0^{\infty} e^{-r(\cos \theta + \sin \theta)} r^{-2u+1} dr = \frac{\Gamma(2-2u)}{(\cos \theta + \sin \theta)^{2-2u}} \quad (u < 1)$$

therefore

$$M^2 + N^2 = \Gamma(2-2u) \int_0^{\frac{\pi}{2}} \cos(v \lg \operatorname{tg} \theta) \frac{(\sin \theta \cos \theta)^{-u}}{(\cos \theta + \sin \theta)^{2-2u}} d\theta$$

or

$$M^2 + N^2 = 2\Gamma(2-2u) \int_0^{\frac{\pi}{4}} \cos(v \lg \operatorname{tg} \theta) \frac{(\sin \theta \cos \theta)^{-u}}{(\cos \theta + \sin \theta)^{2-2u}} d\theta.$$

If in this integral, we change the variable by the substitution

$$\operatorname{tg} \theta = e^{-2t}$$

it takes the form:

$$M^2 + N^2 = 4\Gamma(2-2u) \int_0^{\infty} \frac{\cos(2vt) dt}{(e^t + e^{-t})^{2-2u}}$$

With this value we find

$$\frac{4\pi}{\operatorname{mod}^2 \Gamma(u+iv)} = 4\Gamma(2-2u) (e^{2\pi v} - 2\cos 2\pi u + e^{-2\pi v}) \int_0^{\infty} \frac{\cos(2vt) dt}{(e^t + e^{-t})^{2-2u}}$$

and finally

$$\prod_{s=0}^{\infty} \left(1 + \frac{v^2}{(u+s)^2}\right) = \frac{\Gamma^2(u)\Gamma(2-2u)}{\pi^2} (e^{2\pi v} - 2\cos 2\pi u + e^{-2\pi v}) \int_0^{\infty} \frac{\cos(2vt) dt}{(e^t + e^{-t})^{2-2u}}$$

which holds for all values of  $v$ , and for values of  $u$  between 0 and 1.

If for instance we put  $v = \frac{z}{2\pi}$ ,  $u = \frac{1}{4}$  and  $\frac{3}{4}$  we obtain

$$\begin{aligned} \left(1 + \frac{4z^2}{\pi^2}\right) \left(1 + \frac{4z^2}{25\pi^2}\right) \left(1 + \frac{4z^2}{81\pi^2}\right) \dots &= \\ &= \frac{\Gamma^2\left(\frac{1}{4}\right) \Gamma\left(\frac{3}{2}\right)}{\pi^2} (e^z + e^{-z}) \int_0^{\infty} \frac{\cos\left(\frac{zt}{\pi}\right) dt}{(e^t + e^{-t})^{\frac{3}{2}}} \end{aligned}$$

and

$$\begin{aligned} \left(1 + \frac{4z^2}{9\pi^2}\right) \left(1 + \frac{4z^2}{49\pi^2}\right) \left(1 + \frac{4z^2}{121\pi^2}\right) \dots &= \\ &= \frac{\Gamma^2\left(\frac{3}{4}\right) \Gamma\left(\frac{1}{2}\right)}{\pi^2} (e^z + e^{-z}) \int_0^{\infty} \frac{\cos\left(\frac{zt}{\pi}\right) dt}{(e^t + e^{-t})^{\frac{1}{2}}} \end{aligned}$$

Writing  $u = 1 - u'$  we may also conclude from the preceding that

$$\frac{1}{\text{mod}^2 \Gamma(1 - u' + iv)} = \frac{\Gamma(2u')}{\pi^2} (e^{2\pi v} - 2 \cos 2\pi u' + e^{-2\pi v}) \int_0^\infty \frac{\cos(2vt) dt}{(e^t + e^{-t})^{-u'}}$$

or, because

$$\Gamma(u' + iv) \Gamma(1 - u' + iv) = \frac{\pi}{\sin \pi (u' + iv)}$$

$$\text{mod}^2 \Gamma(u' + iv) = 4 \Gamma(2u') \int_0^\infty \frac{\cos(2vt) dt}{(e^t + e^{-t})^{2u'}}$$

which formula holds not only for  $0 < u' < 1$ , but also for  $u' > 1$ .

Introducing in this equation, the infinite product, we have

$$\int_0^\infty \frac{\cos(2vt) dt}{(e^t + e^{-t})^{2u'}} = \frac{\Gamma^2(u')}{4 \Gamma(2u')} \frac{1}{\prod_{s=0}^\infty \left(1 + \frac{v^2}{(u' + s)^2}\right)}$$

a formula which enables us to write the integral in a finite form in two cases viz.  $u' = n$  and  $u' = n - \frac{1}{2}$ . If  $u' = n =$  positive number

$$\prod_{s=0}^\infty \left(1 + \frac{v^2}{(n + s)^2}\right) = \prod_{s=n}^\infty \left(1 + \frac{v^2}{s^2}\right);$$

with

$$\frac{e^{\pi v} - e^{-\pi v}}{2\pi v} = \prod_{s=1}^\infty \left(1 + \frac{v^2}{s^2}\right)$$

this gives

$$\int_0^\infty \frac{\cos(2vt) dt}{(e^t + e^{-t})^{2u}} = \frac{\pi v \Gamma^2(n)}{2 \Gamma(2n)} \frac{\prod_{s=1}^{n-1} \left(1 + \frac{v^2}{s^2}\right)}{e^{\pi v} - e^{-\pi v}}.$$

If  $u' = n - \frac{1}{2}$ , we have

$$\prod_{s=0}^\infty \left(1 + \frac{v^2}{(n - \frac{1}{2} + s)^2}\right) = \prod_{s=n-1}^\infty \left(1 + \frac{v^2}{(\frac{1}{2} + s)^2}\right)$$

which gives with

$$\frac{e^{\pi v} + e^{-\pi v}}{2} = \prod_{s=0}^\infty \left(1 + \frac{v^2}{(\frac{1}{2} + s)^2}\right)$$

this result

$$\int_0^\infty \frac{\cos(2vt) dt}{(e^t + e^{-t})^{2n-1}} = \frac{\Gamma^2(n - \frac{1}{2})}{2 \Gamma(2n - 1)} \frac{\prod_{s=0}^{n-2} \left(1 + \frac{v^2}{(\frac{1}{2} + s)^2}\right)}{e^{\pi v} + e^{-\pi v}}.$$

**Physics.** — “*Magnetic resolution of spectral lines and magnetic force.*” By Prof. P. ZEEMAN. (Second part).<sup>1)</sup>

*Asymmetry in strong fields.*

2. By means of the method of the non-uniform field, described in the first part of this communication, it is possible to survey at one glance a phenomenon dependent upon the intensity of the magnetic field for a series of different intensities, all other circumstances surely being the same.

I there proposed to use this method for a more minute study concerning an asymmetry of the resolution of spectral lines first predicted from theory by VOIGT<sup>2)</sup> and lately considered by LORENTZ<sup>3)</sup> from another point of view.

The theoretical result of VOIGT, applying to the case of resolution into a *triplet*, may be given in his own words: “dass das normal zu den Kraftlinien wahrnehmbare Duplet der parallel zu  $R$  [magnetic force] polarisirten Componenten bei kleineren Feldstärken in der Weise unsymmetrisch ist, dass die nach Rot liegende Componente die grössere Intensität, die nach Violett hin liegende aber den grösseren Abstand von der ursprünglichen Absorptionslinie besitzt.” VOIGT here mentions an absorption line because he considers the so called inverse effect, by reason however of the parallelism of the phenomena of emission and absorption, the emission lines show analogous phenomena.

The amount of the asymmetry of the distances, i. e. the difference of the distances of the outer components from the middle line, ought to be on VOIGT's theory independent of the strength of the magnetic field. Moreover it is to be inferred that the described asymmetry must be scarcely observable.

On a former occasion<sup>4)</sup> I have given some examples of asymmetrical resolution and measurements since published by other physicists undoubtedly go far towards confirming these results.

A more minute investigation of the course of the magnetic separation, when the scale of field intensities from large to small values is traversed, is I think still of great theoretical interest. The most interesting parts of the scale are of course the very strong and the weak fields.

<sup>1)</sup> Continued from Proceedings of April 1906.

<sup>2)</sup> VOIGT. Ann. d. Phys 1. p. 376. 1900.

<sup>3)</sup> LORENTZ. These Proceedings November, December 1905.

<sup>4)</sup> ZEEMAN. *ibid.* December 1899. Archiv. Néerl. (2) T. 5. 237—242. 1900.

The most striking example of asymmetrical resolution that I know of, occurs in the case of one of the yellow mercury lines (5791). The structure of a line like this one cannot be made out by means of MICHELSON'S interferometer. Indeed the assumption of symmetry, which is, as has been proved by Lord RAYLEIGH <sup>1)</sup>, necessary to deduce the structure from the visibility curve in this case certainly is unjustified.

3. Following the method described in the first part of this paper I have made some experiments concerning the mentioned spectral line in strong fields. For the ROWLAND grating used in my observations I am indebted to the dutch Society of Sciences at Haarlem. Presently I hope to give an account of results obtained in weak fields by means of an interference method.

The grating has 10.000 lines to the inch and a radius of curvature of 6.5 M., the divided part being of 14 cm. width. In the use of my method the grating necessarily should be mounted in such a manner that to every point of the slit corresponds only one point of the spectral image. ROWLAND'S concave grating can be mounted in a non-astigmatic manner as has been remarked by RUNGE and PASCHEN <sup>2)</sup> and this arrangement was made use of in former investigations by myself, <sup>3)</sup> HALLO and GEEST. <sup>4)</sup>

All observations recorded in the present paper were made with the spectrum of the first order.

4. Whereas the mercury line 5791 is resolved asymmetrically, the neighbouring line 5770 is resolved by the magnetic field into a perfectly symmetrical triplet, or at least very approximately so. I have used this circumstance for applying the optical method of measurement of field (see § 1), the mentioned yellow lines being easily photographed simultaneously.

Fig. 1 represents a ninefold enlargement of one of the negatives. According to measurements of FABRY and PEROT the difference of wavelength of the yellow mercury lines is  $5790.66 - 5769.60 = 21.06$  A.U., hence 1 m.m. in Fig. 1 corresponds to 0.551 A.U. Inspection of Fig. 1 clearly shows that line 5791 is asymmetrically resolved. Perhaps this is still more evident in the enlargements Figures 2 and 3 of parts of Fig. 1.

<sup>1)</sup> RAYLEIGH. Phil. Mag. November 1892.

<sup>2)</sup> RUNGE and PASCHEN. Wied. Ann. Bd. 61. p. 641. 1897.

<sup>3)</sup> ZEEMAN. Archiv. Néerl. (2) T. 5. 237. 1900, T. 7. 465. 1902. These Proc. May 1902, May 1903, Dec. 1904.

<sup>4)</sup> HALLO. Archiv. Néerl. (2) T. 10. p. 148., GEEST. (2) T. 10 p. 291. 1905.

Our object of investigation is the relation between asymmetry and strength of field.

The measurements were made in the following way. The negative was placed on the comparator, in such a manner, that the middle line of one of the triplets was contained between the two parallel wires in the reading microscope. The parallel wires had been placed previously at right angles to the direction of motion of the negative. It appeared that if with one of the triplets the desired coincidence had been obtained, this was also the case with the other. An extra system of cross wires, crossing under an angle of about  $50^\circ$ , was used in the measurements and made it possible to determine the resolution in the selected point of the lines.

The resolution of one line having been measured for a definite value of the magnetic force, the corresponding resolution in the corresponding point of the second line was determined immediately afterwards.

The line 5770 appeared to be divided almost exactly symmetrically, so that the resolution could be taken as a measure of the magnetic force.

On the obtained negatives 34 series of measurements were made. They relate to different points of 10 negatives made at different times.

The vacuum tubes used were intentionally made somewhat dissimilar.

In order to control the results the negatives were taken with different maximum intensity of field.

Finally the negatives obtained can be distributed into two groups, differing by the position of the grating. After taking 7 negatives I resolved to rotate the grating in its own plane through  $180^\circ$  in order to see whether this had some influence on the asymmetry.

This appeared to be not the case, but the apparent distribution of intensities changed in a remarkable manner. Whereas in one position of the grating figures 1—5 were obtained, the middle line being strong and the outer components rather weak, the distribution of light after rotation became reversed. In this position of the grating Fig. 1 of my last paper was taken. (See these Proceedings October 1907). The middle line is very weak and the outer components predominate.

5. The results of the measurements are dealt with in the following way. The amounts of separation of line 5791 towards the red and towards the violet are supposed to be functions of the separation of line 5770, which may be treated as proportional to the magnetic force. The separations of line 5770 may be taken as abscissae, the two other separations as ordinates.

Groups of four or five single proximate results simply were combined by assigning to each mean abscissa the mean ordinate.

The  $2 \times 7$  principal values thus obtained are given in the first three columns of the following table.

Mean separation 5770	Separation 5791		Asymmetry	Intensity of field in Gauss
	towards red	towards violet		
270	234	259	25	14800
328	283	312	29	18020
362	313	345	32	19860
399	353	388	35	21910
440	394	431	37	24140
453	404	442	38	24880
532	475	523	48	29220

All these differences of wavelength are given in thousandths of an ÅNGSTRÖM unit.

The fourth column in like manner gives the amount of the asymmetry.

6. The last column contains the field intensity in Gauss. In calculating it I have assumed proportionality between separation and magnetic force.

Increasing accuracy of the measurements has furnished continually increasing arguments for this proportionality and the investigations of FÄRBER <sup>1)</sup>, WEISS and COTTON <sup>2)</sup>, PASCHEN <sup>3)</sup> and STETTENHEIMER <sup>4)</sup> have given a high degree of certainty to this simple law.

The numbers in the fifth column are deduced from those in the first by means of the separations of line 5770  $\pm 0.414$  and  $-0.415$  given by RUNGE and PASCHEN for the field used in their investigation.

The measurements of RUNGE and PASCHEN concerning the mercury lines refer, as Prof. PASCHEN has kindly communicated to me, to a field of 22750 Gauss according to measurements made in his laboratory by Frl. STETTENHEIMER, and of 22780 Gauss according

<sup>1)</sup> FÄRBER. Diss. Tübingen, 1902; Ann. d. Phys. 9, 886, 1902.

<sup>2)</sup> WEISS and COTTON. Journal de Physique. Juin 1907.

<sup>3)</sup> PASCHEN. Physik. Zeitschr. 8 Jahrgang N<sup>o</sup>. 16. 522, 1907.

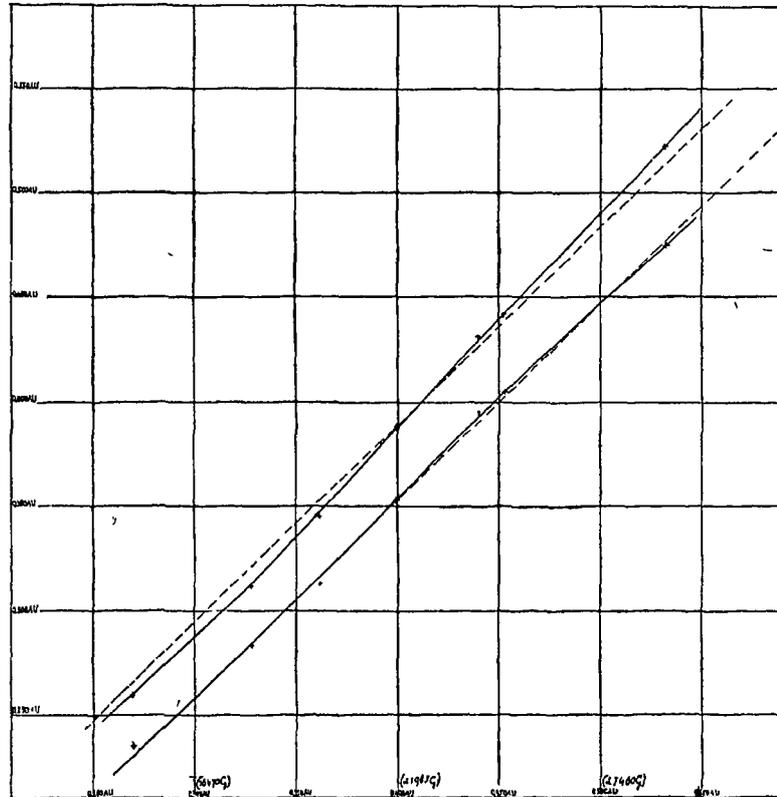
<sup>4)</sup> STETTENHEIMER. Diss. Tübingen, 1907; Ann. d. Phys. 24, 384 1907.

to measurements, not hitherto published, by GMELIN. In reducing my observations I have therefore taken 22765 as the value of the magnetic force belonging to the mean of the two numbers mentioned for the separation.

7. The results are graphically represented in the following diagram. The abscissae are the separations of line 5770 in A.U., and the corresponding field intensities in Gauss, the ordinates the corresponding separations of 5791. The small crosses represent the observations of the table in § 5.

The full freehand lines give the best mean result of the observations. (See § 9).

The signification of the upper dotted straight line is the following.



The mean of the 34 single values of the asymmetry is 0.036 A.U. The straight dotted line has been traced parallel to the lower line at a distance of 36 thousandths of an ANGSTROM unit, measured along the ordinate.

8. We may infer from our observations that with the fields used, from 15000 to 30000 Gauss, an asymmetry undoubtedly exists which

to say the least bears a very striking resemblance to the one deduced from theory by VOIGT.

In both cases, the theoretical one and that following from our experiments, there is a difference of the distances between the central line and the two outer components, in this sense that the component towards the red is nearer to the middle line than that towards the violet, just as predicted by theory.

There exists also an asymmetry of *the intensities* of the outer components in the sense indicated by theory.

An inspection e. g. of the original negative of which Fig. 1 is a nine-fold reproduction, or of the reproduction Fig. 1, or better of reprints on photographic paper of the 29-fold enlargement given in Fig. 2 or even of that figure reveals the existence of a very small asymmetry of intensity. This is perhaps most clearly seen by looking at the figure from a not too small distance, covering the central line with a small strip of paper. No trace of asymmetry can be seen in the triplet of line 5770, see also the enlargements Fig. 4 and Fig. 5 of the middle and outer parts of the right of Fig. 1.

On the other hand there seems to be a difference between theory and observation in this respect, that the amount of asymmetry appears to be not constant. The table of § 5 and the graphical representation clearly indicate that when the magnetic force decreases from 30000 to 15000 Gauss the asymmetry also is nearly halved.<sup>1)</sup>

An error of an amount sufficient to bring a single point of the upper line on the dotted one is not absolutely excluded (see § 9). [For the right part of the diagram the error ought to be three times the probable error of *one single* of the principal values (see § 5) and would happen therefore on the average in one out of every twenty three cases].

We have however reasonable security against a combination of errors which would move all the points of the full line to the dotted one.

Of course we cannot deduce from the now determined part of the upper line whether or not it will approach asymptotically to a finite distance of the lower one.

9. We may now consider the question as to the best fitting *straight* lines to our two systems of points.

Measuring the divergencies at right angles to the line the best fit will be obtained if we make the sum of the squares of the perpen-

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<sup>1)</sup> An excellent series of measurements made after the writing of this article gives a somewhat lower rate of decrease, the mean value of the asymmetry being the same.

diculars from the system of points to the line a minimum. The line thus determined will be the principal axis of inertia of the system of points<sup>2)</sup>.

Performing this calculation we find that the best fitting lower line passes through the point with the coordinates 398, 351, at a slope determined by  $\theta_1 = 43^\circ 6'$ . For the upper line these numbers become 398, 386, whereas  $\theta_2 = 45^\circ 35'$ .

In order to judge of the accuracy obtained in the representation of the observations by these straight lines the following table may serve. The third and fourth column, resp. the sixth and seventh column contain the errors of the abscissae and ordinates of the two point systems to be assumed, if the straight lines are supposed correct.

Mean separation 5770	Separation 5791 towards red	$\Delta a_1$	$\Delta o_1$	Separation 5791 towards violet	$\Delta a_2$	$\Delta o_2$
270	234	+ 1.6	- 1.8	259	+ 1.4	- 1.3
328	283	- 1.2	+ 1.4	312	- 1.6	+ 1.6
362	313	- 2.1	+ 2.2	345	- 2.0	+ 2.0
399	353	+ 0.1	- 0.1	388	0	0
440	394	+ 1.3	- 1.5	431	+ 1.0	- 0.9
453	404	+ 0.2	- 0.2	442	0	0
532	475	- 1.0	+ 1.2	523	0	0

It appears from this table that the lines completely represent the observations, if we admit mean uncertainty of 0.0013 A. U. in the observations concerning line 5770 and of 0.0014 A. U. resp. of 0.0011 A. U. in the determination of the components towards the red resp. towards the violet in the case of line 5791; we must admit these as appears from the distribution of deviations.

10. The position of one point of each line may still be checked by the observations of RUNGE and PASCHEN. They give for the separation in the case of line 5770 towards the red resp. towards the violet  $+ 414 \pm 1.7$  resp.  $- 415 \pm 1.7$ , whereas for the same magnetic

<sup>2)</sup> KARL PEARSON. On Lines and Planes of closest Fit to Systems of Points in space. Phil. Mag. p. 559. Vol. 2. 1901. Here we read: "The best fitting straight line for a system of points in a space of any order goes through the centroid of the system" cf. KEESOM. These Proceedings 31 May, 1902.

force these numbers for line 5791 become  $+ 366 \pm 6.7$  resp.  $399 \pm 6.7$ , the values preceded by  $\pm$  indicating the mean error. According to our observations to the abscissa 415 correspond the ordinates 368 and 403, hence a very good agreement.

11. From the extremely small amount of the asymmetry viz. 0.036 A. U. one might infer after comparison with the width of the spectral lines in our figures that the asymmetry is only a small part of the real width of the line. Such a conclusion would however be too rash.

It is true that from our figures and from their originals follows an apparent width of the outer components of about 0.190 A. U. The negative of Fig. 1 was not taken however with extremely narrow slit, but with a width of slit of 0.08 m.m. Other photographs taken with a width of slit of 0.02 m.m. gave a somewhat smaller apparent width of the spectral line as the first result.

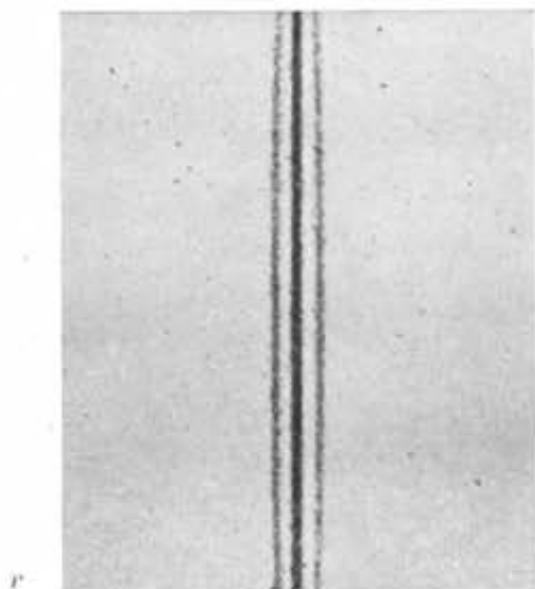
To be sure however of the real width of the line, which is of some importance here, I made an independent determination by means of an echelon spectroscope of high resolving power, the mercury tube being under the same circumstances, as in the experiments under review. The width of the spectral line appeared to be the  $\frac{1}{11}$ <sup>th</sup> part of the distance of two successive orders of the echelon. In the vicinity of the yellow mercury lines this distance is 0.694 A. U. hence the width of these lines is about  $\frac{0.694}{11} = 0.063$  A. U.

We may compare this result with a value we may deduce from results obtained by MICHELSON. MICHELSON'S analysis <sup>1)</sup> by means of the interferometer shows that in a field of 10000 Gauss the *whole* separation of the yellow mercury lines is 0.36 A. U. From his diagram on pag. 354 l. c. we infer that the width of the spectral line was under the circumstances of the case one fourth part of the separation or 0.09 A. U.

Hence taking a mean value for the width of 0.07 A. U. we conclude that the asymmetry amounts to about one half of the width of the line or at any rate that width and asymmetry are of the same order of magnitude.

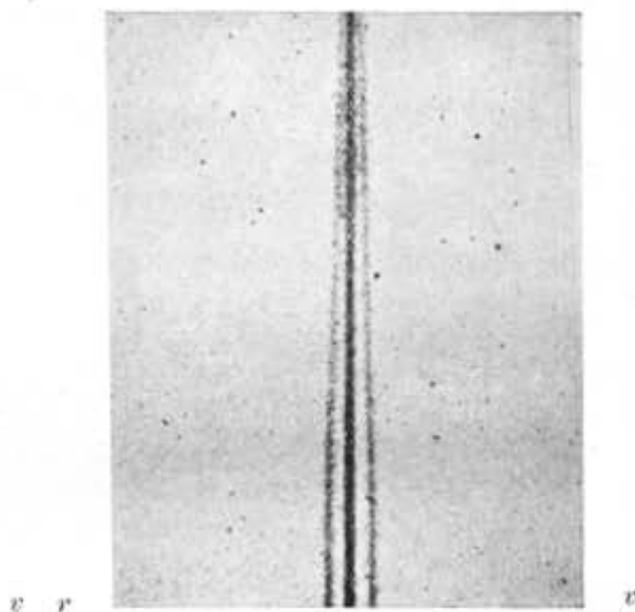
<sup>1)</sup> MICHELSON. Phil. mag. Vol. 45, p. 348. 1898.

Fig. 2.



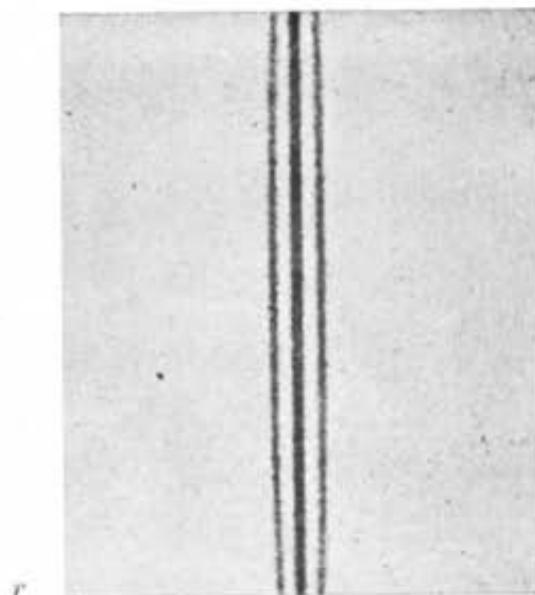
5791  
Enlargement of middle part of  
5791. Fig. 1.

Fig. 3.



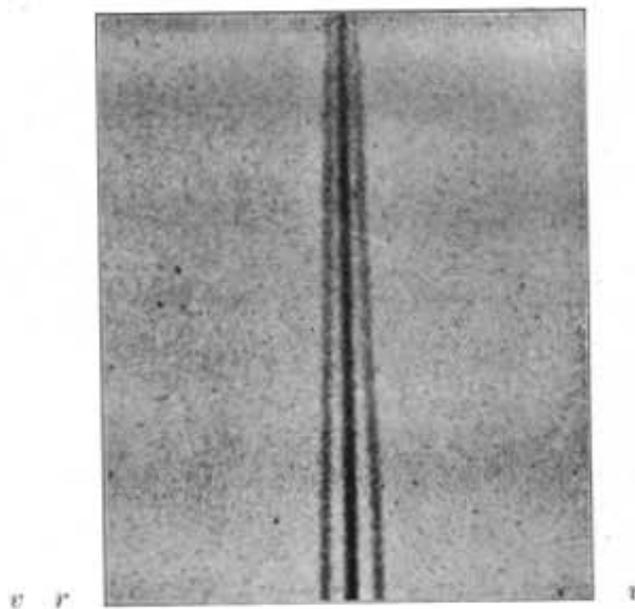
5791  
Enlargement of point of  
5791. Fig. 1.

Fig. 4.



5770  
Enlargement of middle part of  
5770. Fig. 1.

Fig. 5.



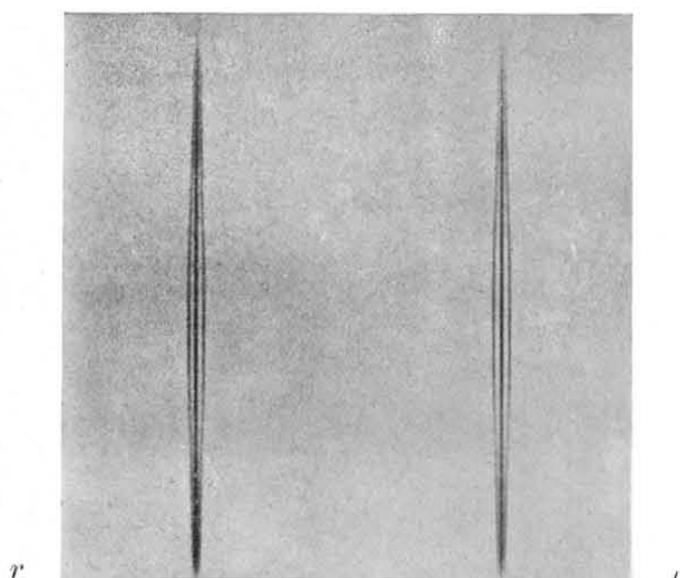
5770  
Enlargement of point of  
5770. Fig. 1.

P. ZEEMAN. "Magnetic resolution of spectral lines and magnetic force."

(Second part.)

Plate II.

Fig. 1.



5791

5770

5791 asymmetric separation.

5770 symmetric separation.

## EXPLANATION OF PLATES II AND III.

Plate II. Fig. 1. The figure is an enlargement (about nine-fold) of the original negative. The yellow mercury lines 5791 and 5770 in a non-uniform field. 1 mm. in figure is 0.551 A. U.

Plate III. Fig. 2—5 enlarged 29 times after the original.

Fig. 2. Middle part of line 5791 in Fig. 1.	} asymmetrical separation.
Fig. 3. Point of line 5791 in Fig. 1.	
Fig. 4. Middle part of line 5770 in Fig. 1.	} symmetrical separation.
Fig. 5. Point of line 5770 in Fig. 1.	

The letters *r* and *v* indicate the parts towards the red and towards the violet ends of the spectrum.

**Botany.** — “*On a double reduction of the number of chromosomes during the formation of the sexual cells and on a subsequent double fertilisation in some species of Polytrichum.*” By Dr. W. DOCTERS VAN LEEUWEN and Mrs. J. DOCTERS VAN LEEUWEN-REYNVAAN. (Communicated by Prof. F. A. F. C. WENT).

In 1904 there appeared an investigation by IKENO<sup>1)</sup> on spermatogenesis in *Marchantia polymorpha*. Since then quite a number of researches on this subject have been carried out with liverworts. Here and there an occasional reference to the true Mosses has been made, but, as far as we are aware, nothing has been published on their spermatogenesis since the appearance of IKENO's paper.

The older publications, e. g. those of GUIGNARD<sup>2)</sup> and of STRASBURGER<sup>3)</sup>, treat exclusively of the final changes of the spermatids to spermatozooids. For this reason we began the present investigation in 1904 soon after the publication of IKENO's memoir; we obtained results, differing so widely from the ordinary conceptions, that we investigated, not only the spermatogenesis, but also the development and the fertilisation of the ovum.

The material was fixed at a suitable time, mostly in the field, by a sublimate mixture, and was afterwards stained with iron-haematoxylin according to HEIDENHAIN. We used *Polytrichum piliferum*, *P. juniperinum* and *P. formosum*. It is our intention to give a more detailed account of the work and of the methods which we have employed, in the *Recueil des Travaux Botaniques Néerlandais*.

IKENO made the remarkable discovery that in the antheridial cells, immediately before division, a small round body passed out of the

<sup>1)</sup> IKENO *Beihefte zum Botan. Centralblatt*. Bd. 16, 1903.

<sup>2)</sup> GUIGNARD. *Revue gén. de botanique* I. 1889.

<sup>3)</sup> STRASBURGER. *Hist. Beitr.* Heft IV, 1892.

nucleus into the cytoplasm and divided itself into two parts, which during mitosis wandered to the poles of the spindle, like true centrosomes. Since then these centrosomes have been found again in many other liverworts, but according to some observers, they seem to be absent from the divisions in the antheridia of *Pellia*.

At the diaster stage the centrosome disappeared, only to emerge again from the nucleus at a subsequent division. At the last division only of the antheridial cells it remained in the cytoplasm and was transformed into the blepharoplast. For this reason IKENO considers the blepharoplast of the liverworts to be homologous with the centrosome.

Many arguments, both for and against this view, have afterwards been advanced, which we will not discuss further. Without a detailed review of the literature such a discussion would scarcely be possible.

Our results with *Polytrichum* agree in part with those published by IKENO and others, but also at the same time differ from them in certain respects.

I. *On the growth of the antheridial cells and on spermatogenesis.*

In the antheridia the cells are closely packed. The nuclei are spherical and contain at their centre a substance, which is deeply stained by iron-haematoxylin. We do not propose to discuss whether this is, or is not, a nucleolus. There is no agreement in the literature on this point and different investigators designate by nucleolus the most widely different structures. It is, however, usual in botanical literature to call such a body a nucleolus, though it also takes up the other chromatin stains very readily. However this may be, the dark mass lies in the middle of the nucleus, and slightly more towards the periphery there is, in addition, another fairly large, black corpuscle.

If nuclei are examined in various stages of rest and mitosis, those, which are furthest removed from their next division only show the central black mass. A little later the corpuscle also appears, at first connected to the central mass by a thin black thread. Soon this connexion disappears and the corpuscle approaches more and more the nuclear membrane. After some time it emerges from the nucleus and remains imbedded in the cytoplasm, in contact with the nuclear membrane. The corpuscle which was at first round, now becomes rod-shaped and afterwards undergoes constriction in the middle, thus assuming a dumb-bell shape. It subsequently divides into small spheres, which move along the nuclear membrane and which become more

and more widely separated. At this stage each little corpuscle is surrounded by a light border, which becomes especially noticeable, when the corpuscles separate from the nucleus.

During mitosis the two corpuscles are found at the tops of the spindle and hence may well be called centrosomes. There are, especially during division, many black granules in the cytoplasm. This always renders the investigation more difficult, but in the first place the two centrosomes are larger than the other granules and secondly they are surrounded by a lightborder. In the case of animal cells their centrosome nature would not be doubted, but with vegetable cells a certain amount of reserve is still very desirable. We do not hesitate, however, to call these bodies centrosomes. Of course they do not stain well in all mitoses. Any one who has searched for centrosomes in animal tissues, knows, that the staining of these corpuscles is difficult, even in objects which are famous for them. The centrosomes of *Polytrichum* accordingly have a chromatic origin. They originate in the nucleus and divide into two in the cytoplasm.

IKENO describes these corpuscles as disappearing in the diaster stage. This is not the case in *Polytrichum*. They do not remain in their places, but may be found in various cells moving more and more to the other side of the chromosomes, so that at last they lie opposite each other among the spindle threads, which unite the two chromosome masses. When the daughter nuclei have only just been formed and the chromosomes are therefore still more or less clearly visible, the corpuscle lies between them; afterwards everything becomes a black mass. At the last division of the antheridial cells the centrosome is also taken up in the nucleus and there is here no deviation from what is found in liverworts.

After this, such changes begin, as finally lead to the formation of the spermatozoids.

We did not succeed in finding young sporogonia with many young spore mother-cells undergoing division.

We found, however, numerous dividing nuclei in the vegetative cells of young sporogonia and hence it was not difficult to make out the actual number of the chromosomes. The chromosomes are small, but they are sharply differentiated and may be especially well recognised in the equatorial plane. We found that the cells of the sporogonium have 12 chromosomes.

Judging from analogy with what is known of liverworts and vascular cryptogams, it was safe to assume that in the formation of the spores a reduction of the chromosomes would take place, and

that their number in the gametophyte would hence be six. We did in fact, always find six chromosomes in the cells of the antheridium and in those of the female plants.

When the antheridia have arrived at the end of their development, the chromosomes assume a different appearance. At first they are, relatively to their length, fairly thick rodlets. At the last but one division, however, they have the same length, but become much thinner and are no longer so smooth. At this stage six chromosomes can always still be clearly observed. At the last division, and therefore immediately before the actual formation of the spermatozoids, three of the six chromosomes go to one pole and three to the other pole.

The nuclei of the spermatozoids therefore do not contain six, but three chromosomes, i. e. a quarter of the number contained in the nuclei of the vegetative generation.

The cells, in which the reducing division has taken place, and which therefore are about to develop into spermatozoids, may be recognized by their almost invisible cell wall and by their beginning to round themselves off. The nucleus has again a central mass of chromatin, which is, however, appreciably smaller than that in the younger cells.

This mass again extrudes a chromatin granule in the usual manner which travels to the periphery and then emerges from the nucleus. The corpuscle arises therefore in the same way as the centrosome in the cells undergoing division. It does not, however, divide but goes at once to the periphery of the cell. Meanwhile a piece is again separated from the mass of chromatin in the nucleus, and this time the part separated off is so large, that it is often almost equal to the remainder. At first the two portions remain connected, but afterwards they become completely separated and finally the part of the chromatin which has been split off, wanders out of the nucleus.

IKENO also describes in the changed spermatids of *Marchantia* the occurrence of a chromatin body by the side of the nucleus, when the centrosome has already quite reached the periphery.

Where it comes from, he does not know, nor what subsequently happens to it; he only says that the organ disappears again later and calls it "chromatoïde Nebenkörper", which name we may retain.

Having arrived outside the nucleus, it changes its shape in *Polypodium* and extends itself to a bent rodlet. This rodlet grows further, till at last it becomes a closed circular body. Afterwards it again becomes indistinct and in subsequent stages it can only be seen as a dotted ring, which finally disappears completely. We have not been able to discover anything about the significance of this body.

Meanwhile the centrosome has also changed its form. It has become somewhat longer and more or less cudgel-shaped. At the obtuse end a thin band then becomes visible, which goes along the periphery of the cell. The progressive differentiation of this band starts from the centrosome and proceeds in the direction of the nucleus. The latter has also travelled to the periphery, at that side, which is opposite the centrosome.

A similar band, which extends from the blepharoplast to the nucleus, has also been described by IKENO. According to him it originates in the cytoplasm and is stained in the same way as the latter, but more intensely.

In our preparations which were stained with iron-haematoxylin it is very clearly visible and sharply marked out in black, but a difference from the staining of the chromatin may nevertheless be observed.

While this band slowly grows out and the "chromatoïde Nebenkorper" disappears, a quantity of chromatin is separated off for the third time from the chromatin mass of the nucleus. This time however only a very small body is formed, which also emerges from the nucleus, but mostly remains very close to the nuclear membrane. The latter can only be seen very indistinctly.

In a somewhat later stage the band extends along half the circumference of the cell and has therefore nearly reached the nucleus. The third chromatin body is found at the end of the band and in contact with the nucleus, so that in the spermatozoid it lies between the band and the modified nucleus.

The changes which the nucleus itself undergoes in the formation of the spermatozoid have already been described in detail by STRASBURGER and others; it seems to us therefore unnecessary to investigate this matter further.

## II. *Development of the Ovum and Fertilisation.*

In the young archegonia the mother cell of the ovum is especially large. During the further development of the archegonium this cell divides into two and thus gives rise to an ovum and a ventral canal-cell. A point of difference from many other mosses is, that in the species of *Polytrichum*, which we have examined, the two cells are of exactly the same size. These cells now round themselves off and then lie loose in the venter of the archegonium. The venter increases in size and the cells which have been rounded off, separate from each other, till one lies at the base of the venter, and the

other close to the first of the neck canal-cells. Meanwhile these latter degenerate, i.e. their walls disappear and they become somewhat rounded, so that they lie detached in the neck.

The top of the neck opens and through the opening the neck canal-cells pass out. This could be seen in living specimens with mature archegonia; when they were placed in water, the neck soon opened and the cells appeared one by one.

At the stage when the neck-cells have become separated and the neck itself is about to open, a large number of the neck-cells may be found, in fixed preparations, in the venter of the archegonium. They lie loose round the ovum and the ventral canal-cell.

The ventral canal-cell now approaches the ovum and applies itself to the latter. No demarcation between the cytoplasm of the two cells can then be observed. The two nuclei lie side by side and gradually fuse. This was observed by us several times and in all the successive stages. The rest of the ventral canal-cell shrivels up and is extruded like the neck canal-cells.

Finally the ovum lies by itself in the venter with a large, normal, round nucleus.

A transformation of the neck canal-cells into mucilage, as described by GAYET<sup>1)</sup> and others, does not occur. Mucilage may indeed be found later in the neck, and may serve to attract spermatozoids, but it is probably secreted by the neck-cells themselves.

It now became of great importance to know the number of chromosomes in the nucleus of the ovum. Unfortunately, as has already been remarked, only a very limited number of nuclear divisions can be found in the tissues of Mosses, (except in the antheridia) and hence most of the ova were either in a stage before, or in a stage after that of nuclear division. In the other dividing cells of the archegonium there were always six chromosomes. At the stage immediately preceding mitosis, the nucleus of a young cell, which after division would form an ovum, showed six pieces of chromatin. Happily we found one very good mitotic stage. Here there was a large spindle, parallel to the axis of the archegonium, which proved that we had lighted on the division of the egg mother-cell. There were six chromosomes, and though they were still in contact with each other in pairs by one end, the other end was already directed to the top of the spindle. It was highly probable, that of the six chromosomes three were going to one and three to the other pole. The discovery of a nuclear fusion also leads to the supposition, that

<sup>1)</sup> L. GAYET. Ann. des Sc. nat. Bot. Série 8, T. III, 1897.

the number of chromosomes was again doubled in the ovum, which now awaited fertilisation in the venter; the latter already communicated with the exterior.

These two discoveries seem to us to justify the conclusion that before fertilisation the ovum contains six chromosomes.

We next had to attempt to find how there could be again twelve chromosomes after fertilisation. There were six chromosomes in the ovum and three in the spermatozoid. If fecundation were to take place in the ordinary manner, there would still only be nine chromosomes, whereas the sporogonia have twelve.

For this purpose we fixed and cut several hundred female plants of *Polytrichum*. There was of course only a small chance, that a given plant would contain a fertilized archeonium, fixed at the right moment. In a number of cases we found, however, the desired stages and so now possess a fine series of preparations, illustrating in regular succession, the fertilisation process from the penetration and modification of the spermatozoid onwards.

The number of spermatozoids which enter the venter of the archeonium is sometimes very great, but after some have penetrated into the ovum, the others no longer closely surround the ovum, but lie more in the direction of the neck. Hence it would appear that here also the fertilized egg exerts a repulsive action.

The youngest stage, which we now possess, and which has been observed several times, shows near the periphery, but without a doubt imbedded in the cytoplasm of the ovum, two spermatozoids; their length, their shape, everything agrees with that view.

In a later stage both are in contact with the nucleus; they have become thicker and shorter. This thickening and shortening proceeds until there are two oblong corpuscles, containing a few dark granules in their interior, and lying against the nucleus.

We also found a few examples of the next stage, namely an ovum which clearly showed three nuclei, each with a thick mass of chromatin, and another ovum, in which the demarcation between the three nuclei was no longer so obvious; the circumference of the nucleus in the latter case was, however, still indented and inside the nucleus there were three dark masses of chromatin. We find therefore, that the cells of the sporophyte contain twelve chromosomes, that those of the gametophyte have six, and that the spermatozoids have three. The ovum has again six chromosomes after fusion with the ventral canal-cell, and after fecundation by two spermatozoids there are once more twelve chromosomes.

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E R R A T U M.

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p. 201 l. 8 from the bottom: for 300.000 read 30.000.

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(December 24, 1907).