Koninklijke Akademie van Wetenschappen
te Amsterdam.

PROCEEDINGS

OF THE

SECTION OF SCIENCES.

VOLUME VII.

AMSTERDAM,
JOHANNES MULLER.
July 1905.

(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling van 28 Mei 1904 tot 22 April 1905. Dl. XIII.)

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(1st PART)

AMSTERDAM,
JOHANNES MÜLLER.
December 1904.

(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling van 28 Mei 1904 tot 26 November 1904. Dl. XIII.)

CONTENTS.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday May 26, 1904.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 26 Mei 1904, Dl. XII).

CONTENTS.

The following papers were read:

Chemistry. — "*Enzyme Action.*" By Dr. H. P. Barendrecht. (Communicated by Prof. J. M. van Bemmelen).

(Communicated in the meeting of April 23, 1904.)

The following is a preliminary communication of the writer's researches on enzyme actions during the last two years.

From the commencement it has been the writer's object to ascertain in how far a continued research of simple enzyme actions might confirm the hypothesis that the enzymes exert their catalytic action by radiation. This hypothesis originated in the peculiarity of the action of the enzymes which distinguishes this action so sharply from that of the acids. A graphic representation of the action of the same quantity of acid or enzyme in the same time on sugar solutions of different concentrations renders this difference very perceptible.

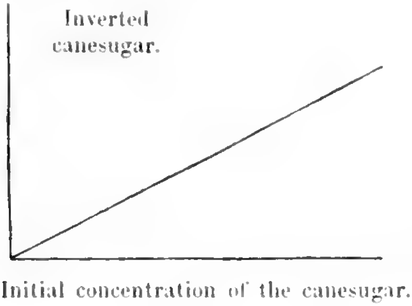

Fig. 1.

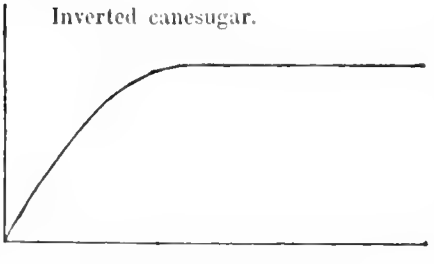

Fig. 2.

Fig. 1 gives a scheme of the inversion by acids. The line which remains straight indicates that the quantity of inverted canesugar remains proportionate to the initial concentration.

In the case of enzymes the general course is represented by fig. 2. In the inversion of canesugar for instance, the line remains straight up to an initial concentration of 0.1 %; it then inflects towards the x axis and runs henceforth parallel to this.

This characteristic behaviour of the enzymes is now at once explained by the radiation theory which will be further developed.

Let us, for the sake of convenience, confine ourselves to the action of invertin and let us suppose we have two solutions containing, respectively, 20 % and 10 % of canesugar. In the 20 % solution the radiation from each enzyme particle will be comparatively soon absorbed by the surrounding molecules of canesugar; in the 10 % solution the sphere to which the enzyme action can extend will be larger. So long as the solution is sufficiently concentrated to finally absorb by a sugar molecule all radiation emanating from an enzyme particle, before the distance has become so great that the radiation fails to cause inversion, each enzyme particle is bound to exert the same action. One might compare an enzyme particle in concentrated sugar solutions with a source of light in a fog of varying density; the denser the fog the smaller the region around the source of light which absorbs all the light.

If, however, canesugar absorbs the radiation from invertin, we must expect the same to a greater or smaller extent from the products of inversion. On account of this power of absorbing the active rays these products must retard the inversion.

The result of my often-repeated experiments showed that the inversion of canesugar by invertin prepared from carefully dried yeast (we shall see, presently, that the method of preparing the invertin is of the greatest importance) is retarded equally by glucose, laevulose and invert sugar.

For instance, the same amount of yeast-extract inverted under the same conditions [1] from

10% canesugar	49.3%
10% canesugar + 5% glucose	38.5%
10% canesugar + 5% laevulose	38.3%
10% canesugar + 5% invert sugar	38.3%

From the similarity of the last three figures it is already evident that we are not dealing here with a retardation due to a reversed reaction.

It was further ascertained that the other hexoses cause exactly twice as much retardation as glucose or laevulose:

8% canesugar	43.6%	inverted
8% canesugar + 2% galactose	35.5%	,,
8% canesugar + 2% mannose	36.1%	,,
8% canesugar + 4% glucose	36.1%	,,

From these results it is evident that the inversion phenomena behave as if there are emitted by an invertin particle two radiations in equal quantity which we may call, provisionally, glucose and laevulose radiations. Each radiation by itself is capable of inverting a canesugar molecule; the glucose radiation is not absorbed by the glucose but by the laevulose; the laevulose behaves, conversely, in the same way. In accordance with this both radiations are absorbed by any other hexose. We may, therefore, regard invertin

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[1] All sugar determinations have been made by KJELDAHL's accurate gravimetric process.

as being, probably, a proteid containing glucose and laevulose groups in a peculiar radiating condition.

At all events, the radiation hypothesis will be found to lead to further quantitative research, to explain results already obtained and to predict future results.

Let us take a sufficiently concentrated solution of a grams of canesugar in 100 c.c. of water. A given amount of invertin then yields in the first minute a quantity of invert sugar m, independent of a. As soon, however, as a little invert sugar has been formed, the condition changes. The enzyme rays are now not only absorbed by the canesugar but also by the invert sugar. If we call n the absorption power of the invert sugar in regard to that of canesugar, then after the lapse of a time t when x is the remaining canesugar, the inversion velocity $-dx$ will be no longer m, but

$$-dx = m \frac{x}{x + n(a - x)} dt.$$

If we substitute $\frac{a-x}{a} = y$ and integrate, we obtain the equation

$$l\left(\frac{1}{1-y}\right) + \frac{1-n}{n} y = \frac{m}{na} t$$

or, using ordinary logarithms

$$log \frac{1}{1-y} + \frac{1-n}{n} 0{,}434\, y = \frac{m}{na} 0{,}434\, t.$$

In this equation two constants occur. The first m may be at once determined experimentally from the initial velocity. If we take, for instance the experiments of A. J. Brown[1]), then $\frac{m}{a}$ or the fraction inverted per minute at the commencement is $\frac{0{,}130}{30}$. If in our equation we substitute this value of m, we find during the whole series of Brown's figures a value for x of about 0.5.

It is, therefore, evident that the absorption powers of the canesugar and glucose, or laevulose molecules are in the proportion of about 2 to 1, that is to say in the proportion of their masses or, perhaps, surfaces.

Then we found the retarding influence of glucose and laevulose to be equal to that of invert sugar. Per unit of weight the number of molecules in glucose for instance and in canesugar are in the

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[1]) Journ. Chem. Soc. 1902 pag. 377.

proportion of $\frac{342}{180}$. If now the absorption power of a molecule of glucose stands to that of a molecule of canesugar in the proportion of 180 : 342 and if we consider that glucose transmits without hindrance 50°/₀ of the total invertin radiation, the proportion between the absorption power of one part of glucose and that of one part of canesugar becomes:

$$\frac{342}{180} \cdot \frac{180}{342} \cdot \frac{1}{2} = \frac{1}{2}.$$

After inversion, one part of canesugar yields $\frac{360}{342}$ parts of invert sugar. Therefore n, the relative absorption power of the products of inversion of one part of canesugar, becomes $\frac{360}{342} \cdot \frac{1}{2} = 0{,}525$.

The formula for the inversion velocity thus becomes

$$log \frac{1}{1-y} + 0{,}393\, y = 0{,}827 \frac{m}{a} t.$$

Brown's experiments conform still better to this formula than to Henri's empirical formula $2k_1 = \frac{1}{t} \, log \frac{1+x}{1-x}$.

The correctness of our deduction may further be proved experimentally in the following way.

If in addition to the a grams of canesugar b grams of glucose, or laevulose are dissolved per 100 cc., the inversion velocity will be represented by:

$$-\,dx = \frac{x}{x + n(a-x) + \frac{1}{2} b} dt.$$

By again substituting $\frac{a-x}{a} = y$ we obtain, when using ordinary logarithms and calling $\frac{m}{na} 0{,}434 = k$:

$$log \frac{1}{1-y} + 0{,}393 \frac{1}{1+\frac{b}{2na}} y = \frac{1}{1+\frac{b}{2na}} kt$$

A same enzyme quantity acting under the same conditions in a solution containing canesugar only and in one containing canesugar plus glucose or laevulose gave the following figures:

10% canesugar.

t	y	$k=\dfrac{\log\frac{1}{1-y}+0{,}393y}{t}$
91	0.412	0.00432
191	0.72	0.00437

10% canesugar + 5% laevulose.

t	y	$k'=\dfrac{\log\frac{1}{1-y}+0{,}393\frac{1}{1+\frac{b}{2na}}y}{t}$
85	0.297	0.00273
181	0.555	0.00276
251½	0.72	0.00296
306	0.763	0.0027
360	0.824	0.00271

According to our formula we have:

$$k'=\frac{1}{1+\frac{b}{2na}}\,k=0.68\,k=0.00295$$

10% canesugar.

t	y	k
57	0.191	0.00293
118	0.364	0.00287
242	0.642	0.00288

10% canesugar + 10% glucose.

t	y	k'
57	0.124	0.00145
116	0.237	0.00142
237	0.435	0.00142
295	0.522	0.00144
358	0.604	0.00146

$$\text{calculated } k'=\frac{1}{1+\frac{b}{2na}}\,k=0.00149.$$

A further control is given by the determination of the initial velocity after previous addition of glucose or laevulose.

From

$$a\,dy=m\,\frac{a\,(1-y)}{a\,(1-y)+n\,a\,y+\frac{1}{2}\,b}\,dt$$

follows that the initial velocity in a solution of a canesugar + b glucose, or laevulose is:

$$\left(\frac{dy}{dt}\right)_{y=0}=\frac{m}{a}\,\frac{1}{1+\frac{1}{2}\frac{b}{a}}$$

whereas without such addition $\left(\dfrac{dy}{dt}\right)_{y=0}=\dfrac{m}{a}$.

These are the experimental results:

10% canesugar	10% canesugar + 2.5% laevulose	
inverted 14%	12.5%	$\frac{1}{1+\frac{1}{2}\frac{b}{a}}\,14 = 12.4$
10% canesugar	10% canesugar + 5% glucose	
inverted 12.4%	9.7%	$\frac{1}{1+\frac{1}{2}\frac{b}{a}}\,12.4 = 9.9$
10% canesugar	10% canesugar + 10% glucose	
inverted 19.1%	12.4%	$\frac{1}{1+\frac{1}{2}\frac{b}{a}}\,19.1 = 12.7$
8% canesugar	8% canesugar + 16% glucose	
inverted 16.6%	8.2%	$\frac{1}{1+\frac{1}{2}\frac{b}{a}}\,16.6 = 8.3$

It was now to be expected that many other neutral substances would also retard the inversion according to their capacity of absorbing the enzyme radiation.

These are some of the figures obtained:

Under the same conditions the same enzyme-quantities inverted of

10% canesugar	38.5%
10% canesugar + 5% urea	28.5%
10% canesugar + 5% mannitol	33.—%
10% canesugar + 5% erythrite	28.—%
10% canesugar + 5% glucose	29.8%

In another series:

10% canesugar	58.1%
10% canesugar + 5% dulcitol	50.4%
10% canesugar + 5% glucose	47.8%

There seems to be some kind of relation between the asymmetric carbon atoms and the absorption.

In the case of inversion of more diluted solutions of canesugar the above-mentioned simple relations will no longer exist. If we diminish the initial concentration, a dilution will soon be reached where a part of the radiation does not reach a sugar molecule in time, but is either finally absorbed by the water or when arriving has, in any case, become too weakened to cause inversion. The quantity of canesugar inverted by a given amount of invertin will, therefore, go on decreasing. In the end, however, we shall arrive at an initial concentration where, within the sphere of action of an enzyme particle, two canesugar or invert sugar molecules can no longer shade each other. From this point, the inversion caused by the given enzyme-quantity will be just proportionate to the canesugar concentration. Then, during the whole of the process, the reaction velocity merely depends on the average number of canesugar molecules present within the active radiation sphere of an enzyme particle.

The following are some of the figures obtained which always exhibited the same regularity.

Concentration canesugar in grms. per 100 cc.	Inverted in grms. per 100 cc.	Inversion in °/₀.
0.05	0.022	44.—°/₀
0.1	0.0448	44.8°/₀
0.125	0.0545	43.8°/₀
0.25	0.097	39.—°/₀
0.5	0.174	34.7°/₀
1.—	0.240	24.— °/₀
2.—	0.317	15.9°/₀

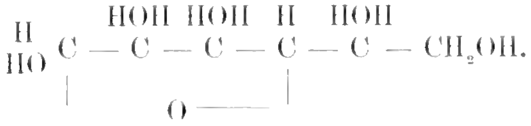
Another series gave

Concentration of canesugar in gr. per 100 cc.	Inverted in grms. per 100 cc.
3	0.86
4	0.95
5	0.96
7	0.93

The fact that, in very dilute solutions, the enzyme action really proceeds as a unimolecular reaction according to the formula $k = \frac{1}{t} \log \frac{1}{1-y}$ was further again confirmed by experimenting with a solution containing 0,096 °/₀ of canesugar.

Up to the present we have for the sake of convenience disregarded the synthetical action of the enzyme rays. Light, being a catalyzer, can act either as a synthetical or decomposing agent, so we must expect the same from the enzyme rays. That we often do not notice such action is due in the first place to the secondary change of the decomposition products, at least in the case of invertin. It has already been stated by O'Sullivan and Thompson [1]) that invertin separates glucose from canesugar in a birotatory condition. Tanret [2]) and Simon [3]) have afterwards elucidated this birotation question.

The birotatory α-glucose is the sugar of the α-glucosides and the semi-rotatory γ-glucose that of the β-glucosides; according to the said authors they are the stereoisomeric lactones:



$$\underbrace{{}^{\text{H}}_{\text{HO}}\mathrm{C} - \overset{\text{HOH}}{\mathrm{C}} - \overset{\text{HOH}}{\mathrm{C}} - \overset{\text{H}}{\mathrm{C}}}_{\mathrm{O}} - \overset{\text{HOH}}{\mathrm{C}} - \mathrm{CH_2OH}.$$

The form which in solution is stable, the β-glucose conforms to the aldehyde-formula $\mathrm{CH_2OH\,(CHOH)_4COH}$.

This conclusion is opposed by other investigators such as Armstrong [4]) and Lowry [5]), who look upon the stable form not as an aldehyde but as a condition of equilibrium between α- and γ-glucose. My investigation goes in favour of the first opinion.

Invertin is, generally speaking, the enzyme of the α-glucosides. Canesugar may also be considered as an α-glucoside in accordance with the fact that on inversion, the glucose is always separated in the α-modification. This α-glucose is now, however, gradually converted into β-glucose and, therefore, prevents the reconversion into canesugar. Owing to this, all the canesugar is always finally inverted by invertin.

A continued research, however, showed that there may be still another reason for the non-appearance of reversal phenomena. The method of preparing the invertin, that is of the yeast extract was found to greatly affect the properties of the enzyme.

At first, I used for the preparation of a powerful invertin a yeast cultivated in a solution of canesugar. This yeast after being mixed with "kieselguhr", was first dried in vacuum at a low temperature and then for half an hour at 100° in an ordinary oven.

The addition of "kieselguhr" facilitates very much the subsequent extraction and filtration. The above experiments have been made each time with a freshly prepared filtrate.

Afterwards it was found that ordinary yeast also gives an enzyme with the same properties, provided it has not been dried at too high

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[1]) Journ. Chem. Soc. 1890 pag. 861.

[2]) Zie Dictionnaire de Chimie de Würtz. 2e suppl. p. 764.

[3]) C. R. 1901 pag. 487.

[4]) Journ. Chem. Soc. 1903 pag. 1305.

[5]) Journ. Chem. Soc. 1903 pag. 1314.

a temperature. Ordinary laevulose in solution is as a rule less stable than glucose. In invertin a difference in the same direction is also usually revealed. Drying at too high a temperature, heating the "kieselguhr" mixture above 100°, or precipitation with alcohol and redrying the precipitated enzyme, repeatedly gave invertin, the action of which is retarded considerably more by laevulose than by glucose. Active laevulose therefore generally becomes inert sooner than active glucose.

This explains the difference between my results and those of VICTOR HENRI [1]) who states:

"Pour l'addition d'une même quantité de sucre interverti, le ralentissement est d'autant plus faible que la concentration en saccharose est plus grande. Ce ralentissement est produit presque uniquement par le lévulose contenu dans le sucre interverti."

Probably, HENRI has obtained his invertin from yeast dried at more elevated temperatures or has used commercial invertin, prepared by precipitation with alcohol. That the retardation of a same quantity of invert sugar becomes smaller when the canesugar concentration becomes greater is quite in harmony with the radiation theory. The fact that the laevulose contributed most to that retardation was only a pathological phenomenon of the invertin.

We must further bear in mind the possibility that, owing to those harmful actions, the radiation gets so weakened that the reversion can no longer take place, or that the radiating α-glucose has been converted into radiating β-glucose and also that only the latter is capable of inverting. It is certainly to be expected that, if only active glucose or active laevulose is left behind, the power of causing reversion has either decreased or been destroyed.

In order to counteract the first cause of the non-appearance of the reversal, namely, the secondary conversion of α-glucose into β-glucose, we may apply much enzyme and so accelerate the conversion. A larger quantity of extract of the above yeast, which had been finally dried for half an hour at 100°, caused indeed a slower inversion of the last remaining percentages of canesugar.

The reversed action was afterwards noticed more distinctly with ordinary yeast, merely dried in vacuum at about 30°. We will first give a mathematical formulation of the phenomena to be expected.

Let us imagine an aqueous solution of invert sugar, liable to reversal and consequently containing the glucose in the α-form, in

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[1]) C. R. 1902 Nov. 24. 917.

the presence of invertin particles, which render this invert sugar active. The velocity of synthesis will then be proportionate first to the product of the concentration of glucose and laevulose and further to the extent of the active radiation sphere surrounding each enzyme particle. The latter is inversely proportionate to the joint concentration of the invert sugar and the other dissolved matters eventually present, each with their own absorption coefficient.

The synthetical action of invertin in a solution containing $(a-x)$ grams of invert sugar and x grams of canesugar in 100 cc. is therefore:

$$dx = mp \frac{\left(\frac{a-x}{2}\right)^2}{x+n(a-x)} dt.$$

The complete formula for the inversion velocity of canesugar, in case the original products of inversion suffered no change, would then be [1]:

$$-dx = m \left\{ \frac{x}{x+n(a-x)} - \frac{1}{4} p \frac{(a-x)^2}{x+n(a-x)} \right\} dt.$$

The point of equilibrium would then be determined by the equation:

$$x - \frac{1}{4} p (a-x)^2 = 0.$$

Or returning to relative fractions by substituting $\frac{a-x}{a} = y$:

$$1 - y - \frac{1}{4} pa\, y^2 = 0$$

If now we have introduced into the solution such a quantity of enzyme that this equilibrium point is attained before the birotatory glucose has been converted to any great extent into ordinary glucose, the inversion will not actually come to a standstill, but the line, indicating its progressive course, will exhibit a characteristic peculiarity in that place. Then, starting from that point, the formation of fresh α-glucose by inversion will be dominated by the velocity of the inversion of the total α-glucose present into β-glucose. This velocity is proportionate to the concentration of the α-glucose. If this is continually replenished by fresh formation of α-glucose from canesugar, both the said velocity and the inversion velocity will be

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[1] The small increase in weight when $C_{12}H_{22}O_{11}$ changes into $2\, C_6H_{12}O_6$ is here neglected; we might also suppose that it is taken into account in the coefficient p. By substituting the variable y this factor in p would in any case disappear again.

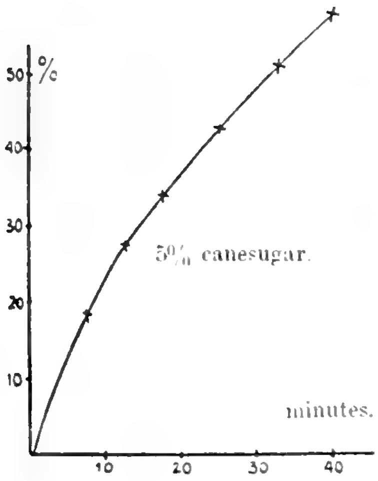

Fig. 3.

constant. From this point the line, representing the inversion as a function of the time, will of course be a straight one until the concentration of the canesugar has become too small to make the inversion keep pace with the glucose transformation.

With 5% canesugar (see fig. 3) the line commences its straight course at about $y = 0,35$. This substituted into the equation

$$1 - y - \frac{1}{4} p a y^2 = 0$$

gives $p = \frac{0,65}{0,153}$ or, practically $= 4$.

In the 10% solution (fig. 4) the equilibrium must then become perceptible at the value of y to be calculated from

$$1 - y - 10 y^2 = 0$$

therefore, at $y = 0,27$.

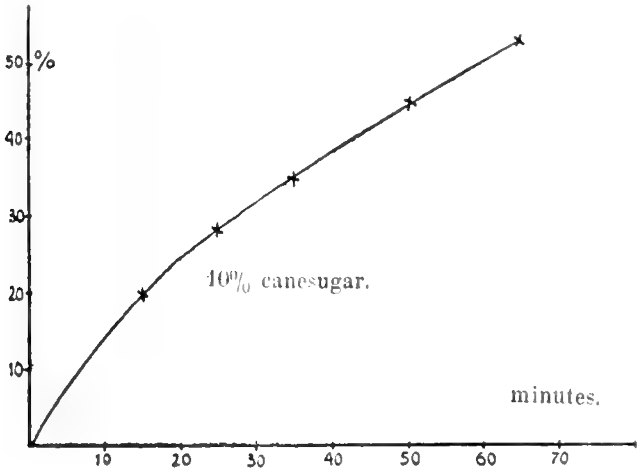

Fig. 4.

Those equilibria phenomena are observed more readily in the *inversion of maltose by yeast-extract.*

The enzyme which converts maltose into glucose is generally called maltase so as to distinguish it from invertin. It seems to me that there is no valid reason for making such a distinction. A yeast-extract, which inverts maltose, has always been found to also behave actively towards canesugar [1]), but not the reverse. This is in harmony with the radiation theory. Maltose, like canesugar, is an α-glucoside. The connecting point of the laevulose in the canesugar molecule with the α-glucose is the C of the carbonyl group of the laevulose. In maltose the α-glucose is attached to the CH_2 of the otherwise uncombined molecule of glucose. Canesugar is also much more readily inverted by acids than maltose. Both radiating α-glucose and laevulose (probably also radiating β-glucose [2])) are liable to invert canesugar. Maltose is only converted by active α-glucose, but as may be expected from its behaviour towards acids and its constitutional formula it requires a more powerful radiation than canesugar. If, therefore, yeast-extract has been weakened by elevation of temperature or by precipitation, its power of inverting maltose may have been lost or much diminished, although canesugar is still fairly rapidly inverted.

The preparation of a yeast-extract with a powerful inverting action on maltose proved to me no more difficult than when inversion of canesugar was intended. The above-described yeast, derived from a canesugar solution, and which had been actually heated at 100° for half an hour, yielded after a year and a half an extract which readily inverted maltose. In this case, I used, of course, by preference a yeast which had been mixed with "kieselguhr" and dried at a low temperature. On extracting the dried mixture, the solution never contains zymase as experiment repeatedly showed.

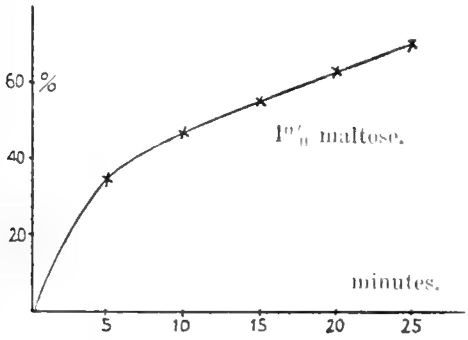

Fig. 5

Figures 5, 6, 7, 8 and 9 now clearly show the phenomena of equilibrium. If α-glucose in solution were stable, only 15 % of the total might be inverted by yeast-extract in a 10 % maltose solution.

The fact that maltose is decomposed by yeast-extract so much slower than canesugar is partly due to the circumstance that the point of equilibrium is reached so much earlier. The further decomposition then again merely keeps pace with the transformation of α-glucose into β-glucose.

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[1] Pottevin, Annales Inst. Pasteur 1903. p. 31.

[2] Separate experiments showed that glucose, previously heated and therefore in the β-form, and glucose, dissolved immediately before adding the enzyme and therefore in the α-form, both retard the canesugar inversion to the same extent. β-Glucose therefore transmits the glucose rays (then perhaps converted into β-glucose rays) quite as well as the α-glucose.

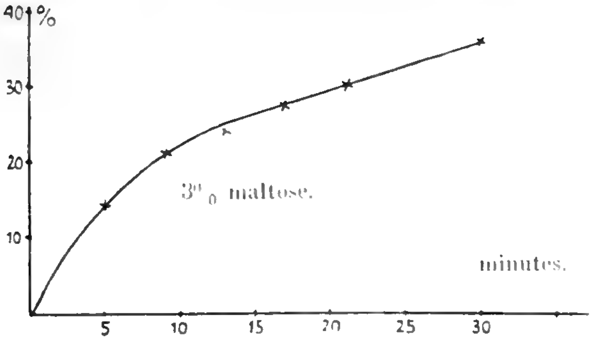

Fig. 6.

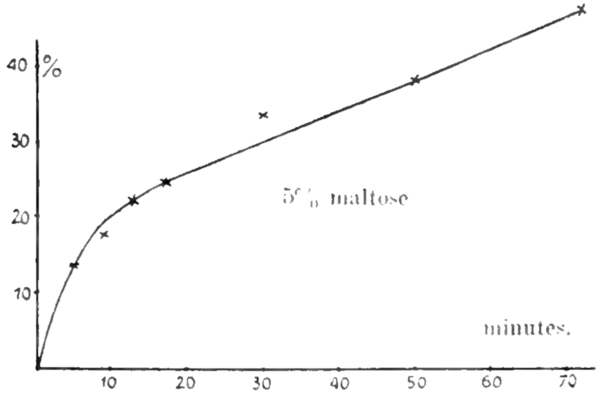

Fig. 7.

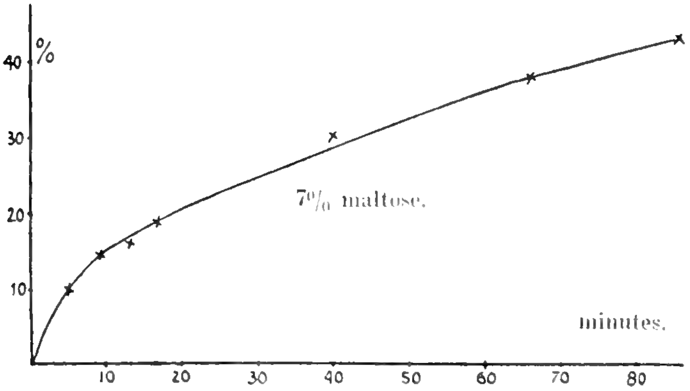

Fig. 8.

Fig. 9.

The points where the transformation lines commence to run straight, so the points of equilibrium, also conform in this case to an equation similar to that used for canesugar. Glucose is here the only product of inversion; we might, therefore, expect that the undisturbed transformation velocity would be here:

$$-dx = m\left\{\frac{x}{x+n(a-x)} - q\frac{(a-x)^2}{x+n(a-x)}\right\}dt$$

and the equilibrium equation, therefore:

$$1 - y - q\,a\,y^2 = 0.$$

For 10 grams of maltose in 100 cc. we experimentally found $y = 0.15$.

This gives $q = \frac{0.85}{0.225}$ or, practically, 4, therefore the same coefficient as for canesugar [1]).

If in the above equation we substitute $q = 4$; or

$$1 - y - 4\,a\,y^2 = 0,$$

the calculated points of equilibrium become for

a	y
10	0.146
7	0.172
5	0.20
3	0.25
1	0.39

This is therefore in accordance with the experiment.

The well-known researches of CROFT HILL [2]) on the reversal of maltose gave points of equilibrium which were situated at a more advanced transformation: for instance in a 10% solution $y = 0.945$. These equilibria were attained only after days and weeks; the above cited after a few minutes.

Afterwards [3]) HILL himself demonstrated that the resulting biose was not maltose but an isomer, which he called revertose. In HILL's numerous experiments, all the glucose was no doubt in the β-form. The synthesis found by HILL was therefore a combination of two molecules of β-glucose to a new biose, isomeric with maltose [4]).

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[1]) The diffusion velocities on which depends the velocity of meeting of two molecules, cannot differ much for glucose and laevulose.

[2]) Journ. Chem. Soc. 1898 p. 634.

[3]) Journ. Chem. Soc. 1903 p. 578. EMMERLING (Ber. 34, p. 600) had found isomaltose as reversal product.

[4]) Most of the natural glucosides appear to be compounds of bi- or semi-rotatory hexoses. When endeavouring to prepare lactose from galactose and glucose by

The retarding action of another added hexose is not studied so readily in the case of maltose inversion as in the transformation of canesugar, on account of the immediately occurring reversion. Still it was found that both laevulose and galactose cause the same retarding action, as might be expected from our theory now we are dealing with glucose-radiation only.

For instance, a same amount of yeast-extract gave under the same conditions and in the same time:

in :	inversion
6°/₀ maltose	18.9°/₀
6°/₀ maltose + 1.5°/₀ galactose	15.5°/₀
6°/₀ maltose + 1.5°/₀ laevulose	15.5°/₀

Another series gave

in :	inversion
6°/₀ maltose	26.8°/₀
6°/₀ maltose + 1.5°/₀ laevulose	24.8°/₀
6°/₀ maltose + 1.5°/₀ galactose	25.–°/₀
6°/₀ maltose + 1.5°/₀ glucose	13.5°/₀

This last figure, verified by other experiments, requires a further explanation. This 1.5°/₀ glucose was undoubtedly β-glucose. Before mixing it with the maltose, the glucose was dissolved separately and completely converted into the stable form 2) by placing the flask for some time in boiling water. The observed order of retardation shows that the β-glucose also takes part in the process of reversion. Now it is possible that in the maltose molecule the glucose with the still free carbonyl group is present in the β-modification and it is even probable that this free glucose group, when in solution, will be converted into the same stable form as glucose itself. In Hill's investigations, yeast-extract appeared capable of uniting two molecules of β-glucose; so, probably, also two molecules of α-glucose. The glucose formed in the enzyme-inversion of maltose may, therefore be called homogeneous. Each molecule of that glucose can unite itself under the influence of the enzyme radiation with any other molecule of that glucose to a biose. Therefore, the equation of equilibrium was here

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means of lactase, Emil Fischer and Frankland Armstrong only obtained an isolactose.

The synthesis of canesugar has not yet succeeded because we can only add β-glucose and not α-glucose to laevulose.

2) Separate experiments showed that unheated glucose causes the same retardation as heated, α-glucose therefore the same as β-glucose.

$$1 - y - 4\,a\,y^2 = 0.$$

It should also be mentioned that the inverting enzyme of yeast appears to be always the same whether canesugar or maltose has been present as a carbohydrate food. In an ordinary cereal extract a little canesugar occurs along with the maltose. A pure yeast-culture, cultivated by myself in a solution of pure maltose (plus the necessary salts and nitrogenous food) gave an enzyme extract which was retarded in its action equally much by glucose and laevulose, and twice as much by galactose. In the enzyme formation, therefore a partial conversion of glucose into laevulose seems to take place. LOBRY DE BRUYN and ALBERDA VAN EKENSTEIN[1]) have shown that these two hexoses may be converted into each other in an alkaline solution.

The investigations of O'SULLIVAN and THOMPSON[2]) have rendered it probable that the invertin-molecule (if we may use this expression) contains a carbohydrate group. These investigators have attempted to purify invertin and found that a constant component of the resulting proteid-complex, their so-called η-invertan, contained 18 parts of carbohydrate to one part of albuminoid.

A further development of the electron theory will probably elucidate the nature of those enzyme radiations. As LODGE[3]) observed, it is not the occurrence of radiations in matter which need cause astonishment but rather the fact that not a great many more radiation phenomena have already been discovered.

Many other catalytic phenomena such as the action of hydrogen-ions and those of BREDIG's anorganic ferments may, after all, be due to radiations. For hydrogen-ions, carriers of loose electrons and dispersed platinum cathodes probably also emit radiations owing to the motion of the electrons in or around the material particle. During the course of a same reaction, BREDIG often noticed an increase of the constant $k = \frac{1}{t}\,log\,\frac{1}{1-y}$ just as that shown by the invertin action. A retardation of the catalysis by indifferent matters has also been frequently noticed, for instance, by KNOEVENAGEL and TOMACSZEWSKI[4]) in the action of finely divided palladium or platinum on benzoin.

If the statements of the French investigators on the physiological

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[1]) Rec. Trav. Chim. 1895 p. 201.

[2]) Journ. Chem. Soc. 1890 p. 834.

[3]) "On Electrons" Journ. Electr. Engineers 1903 Vol. 32 p. 45.

[4]) Ber. 1903. 2829.

n-rays should be promoted to objective truth, our hypothesis would receive a direct experimental support.

At all events, the above has demonstrated that the principal measurable phenomena, noticed in the enzyme action are in harmony with our hypothesis.

Meteorology. — *"On a twenty-six-day period in daily means of the barometric height."* By Dr. J. P. van der Stok.

1. A few years ago [1]) Prof. A. Schuster investigated the problem, how to detect the presence of a periodical oscillation, the amplitude of which is small in comparison with large superposed fluctuations which may be considered as fortuitous with respect to the purely periodical motion.

Starting from an analogy which may be seen between this question and the problem of disturbances by vibrations in the aether — a problem treated by Lord Rayleigh [2]) in 1880 — Prof. Schuster has endeavoured to apply the theory of probability to the determination of the first couple of coefficients of a Fourier series, and the method he arrives at, and strongly advocates, is applied to records of magnetic declination observed at Greenwich during a period of 25 years.

The choice of this material, in Prof. Schuster's opinion not favourable for the discovery of small effects, is justified by the remark that "the only real pieces of evidence so far (1899) produced in favour of a period approximately coincident with that of solar rotation were derived from magnetic declination and the occurrence of thunderstorms."

In this and in an earlier paper [3]) the author emphasizes that, in inquiries of this kind, it is not at all sufficient to come to some result, but that it is necessary to apply a reliable criterion by which a judgment may be formed about the value to be attached to the result arrived at.

His mathematical investigation, however, does not lead to an outcome which in every respect can be regarded as satisfactory, in so far that a method of determining the mean and probable error of the result from the series of observations themselves is not given and,

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[1]) Trans. Cambr. Phil. Soc. Vol. XVIII. 1899.

[2]) Phil. Mag. Vol. X. II, 1880.

[3]) Terrestrial Magnetism Vol. III, 1898.

as a surrogate, the author suggests the repeated rearrangement of the records according to different periods, not much differing from the period in question. Thus, in a purely empirical way ("by trial"), a standard may be obtained by which a correct estimate can be formed in how far the outcome arrived at must be considered as a merely accidental one.

Now the same problem was treated some 15 years ago [1]) by the author of this paper after a different method, applied not only to magnetical but as well to meteorological data of different description, and Prof. SCHUSTER's important investigation gives a ready occasion for taking this problem in hand again.

It is only natural to choose in the first place for this inquiry the series of barometric observations made at Batavia which now extends over a period of 36 years (1866—1901).

An investigation into a possible synchronism between the frequency of sunspots and atmospheric temperature, commenced in 1873 [2]) and recently conducted up to date [3]), gives some ground to the expectation that, for inquiries of this kind, observations made at tropical stations are of more value than those made in regions where the atmospheric disturbances are such as experienced in higher latitudes.

In the second place it seems desirable to look for a shorter way for coming to a reliable criterion than the tedious process of the calculation of SCHUSTER's periodograph.

2. An arrangement of quantities according to a given period T may be executed by measuring out the successive data from a point O taken as origin and along straight lines drawn through this point at equal angular distances $\frac{2\pi}{T}$.

If we assume the unity of mass attached to the ends of those radii, it is evident that a judgment may be formed about the degree of symmetry in the distribution of the masses with respect to point O, by simply calculating the average value of all these vectors, or in other words to determine the situation of the centre of parallel forces supposed acting on the masses.

If the quantities T show a well marked periodicity as e.g. tidal

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[1]) Observ. Magn. Meteor. Observ. Batavia. X, 1888, Append. II also Natuurk. Tijdschr. XLVIII. 1889.

Verh. Kon. Akad. v. Wet. Amsterdam. XXVIII, 1890.

[2]) KÖPPEN. Zeitschr. Oesterr. Gesellsch. f. Meteor. VIII, 1873.

[3]) C. NORDMANN. Essai sur le rôle des ondes Hertziennes and: Astron. Phys. et sur diverses questions qui s'y rattachent, Thèse, Paris, 1903.

observations do, it will be possible to draw a line through O in such a manner, that on the one side all the vectors are greater than the corresponding opposite vectors on the other side of the line.

If, therefore, we arrange in this way a great number of quantities which show a slight tendency to asymmetry, the radial momentum will steadily increase, as the mass concentrated in the centre of parallel forces is equal to the total number of observations, whilst the distribution of accidental quantities will tend to a symmetrical distribution.

Assuming two rectangular axes going through O, we find for the coordinates, by which the centre of gravity is determined, N being the number of observations:

$$x_1 = \frac{1}{N} \Sigma \varrho \cos \theta \qquad y_1 = \frac{1}{N} \Sigma \varrho \sin \theta \quad . \quad . \quad . \quad . \quad (1)$$

The calculation, therefore, comes to the same as the determination of the first couple of Fourier coefficients:

$$a_1 = \frac{2}{N} \Sigma \varrho \cos \theta \qquad b_1 = \frac{2}{N} \Sigma \varrho \sin \theta \quad . \quad . \quad . \quad . \quad (2)$$

and, if the periodical movement is represented by the expression:

$$A \cos (nt - C).$$

$$A^2 = a_1^2 + b_1^2 \qquad \operatorname{tang} C = \frac{b_1}{a_1} \qquad n = \frac{2\pi}{T} \quad . \quad . \quad . \quad (3)$$

This way of representing the arrangement seems preferable to the development in a Fourier series: firstly because the development of a function in a series, as a representation of the function, derives its value from the composition of a great number of terms, so that, in calculating one term only, we are hardly justified in speaking of a Fourierisation of the function.

In the second place, because by this way it becomes at once evident that the problem is fully equivalent to that of the determination of a point in a plane by means of a great many inaccurate observations.

This problem has been treated by several mathematicians, but certainly in the most complete manner by the late Prof. Schols [1]), whose original conception of the question leads to the detection of some laws, which are independent of the assumption of any law

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[1]) Over de theorie der fouten in de ruimte en in het platte vlak, Amsterdam, Verh. K. Akad. v. Wet 1e Sect. XV, 1875, and: Théorie des erreurs dans le plan et dans l'espace, Delft, Ann. II, 1886.

of errors and to a remarkable analogy between this problem and that of the moments of inertia in dynamics.

If we take N, the number of observations, equal to unity, the relative frequency of the ends or representative points of the vectors may be represented by the density of these points per unity of surface. This function of probability is called by SCHOLS "the module", the "specific probability" or the "facilité de l'erreur".

We thus obtain a mechanical image of a surface of probability, the density of which will, in general, be a function of the length and direction of the vectors.

The determination of what SCHOLS calls the constant part of the error — the probability of which is $N = 1$ — is identical with the determination of the situation of the centre of gravity, and the calculation of the mean (not average) error:

$$M = \sqrt{\frac{\Sigma \varrho^2}{N}}$$

with that of the moment of inertia, which leads to the determination of two (in the plane) principal axes of inertia, which, in our case, may be called axes of probability.

Assuming that these errors in the plane are due to the cooperation of a great number of elementary errors, SCHOLS has proved that the projections of the errors on an arbitrary axis follow the exponential law of errors in a line and that the law of the resulting error can be found by supposing the error to originate in the coincidence of projections of the error upon the axes of probability, these projections being regarded as independent of each other.

The application of this theory to our case can be reduced to very simple calculations.

Errors arising from individual or instrumental causes are always distributed in a more or less systematical way, but there is no reason to suppose that the fluctuations e.g. of barometric heights within an arbitrary length of time, and cleared from their constant part, will show any tendency to systematic distribution when arranged around a point in the way described above.

SCHOLS' specific probability of an error in the plane is given by the expression:

$$F = \frac{e^{-\frac{1}{2}\left(\frac{x^2}{M_x{}^2}+\frac{y^2}{M_y{}^2}\right)}}{2\pi M_x M_y} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

in which x and y are the coordinates of the error (polar coord. ϱ and θ)

and M_x and M_y denote the principal axes of probability, so that:

$$M^2 = M_x^2 + M_y^2 = M_a^2 + M_b^2.$$

The mean error, therefore, can be calculated without any knowledge of the situation of the principal axes, when the mean error of the components relative to arbitrary rectangular axes is known.

If F is independent of θ:

$$M_x = M_y = \frac{M}{\sqrt{2}}$$

or, putting:

$$\frac{1}{M^2} = h^2$$

$$F = \frac{h^2}{\pi} e^{-h^2\varrho^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The specific probability of an error, independent of the direction, is:

$$\frac{h^2}{\pi}\int_0^{2\pi} \varrho\, e^{-h^2\varrho^2}\, d\varphi = 2\, h^2\, \varrho\, e^{-h^2\varrho^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

From this it appears that the probability of an error zero is not, as in the case of linear errors, a maximum, but a minimum, that the curve of the spec. prob. (6) (given in SCHOLS' paper) shews a maximum for the value of ϱ:

$$\varrho_m = \frac{1}{h\sqrt{2}} = \frac{1}{2} M \sqrt{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and, also, that the computation of the probable error will lead to a coefficient of M considerably different from that found for linear errors.

We have then to ask for what value r of ϱ:

$$2\, h^2 \int_0^r \varrho\, e^{-h^2\varrho^2}\, d\varrho = \frac{1}{2}$$

$$r = 0.83256\, M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This value of the coefficient of the probable error, considerably greater than is found for linear errors, 0.6745, clearly shows that and to what degree results, obtained in investigations of this kind, have to be put to an unusual severe test, and also that there is some reason to adhere to the use of the probable error, which of late years has been somewhat neglected.

A reduction of the mean error has no sense if this reduction is always in the same proportion, but it becomes important if this proportion depends on the nature of the problem.

If the distribution of errors is not independent of the direction, the coefficient of M is determined by the quantity:

$$N = \frac{M_x^2 - M_y^2}{M_x^2 + M_y^2}.$$

The coefficient of the probable error, for which SCHOLS gives the approximate value:

$$r = 0.8326 - 0.1581\, N^2 \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

is a maximum for errors independent of the direction and a minimum for linear errors, when $N = 1$.

By the assumption, therefore, that all directions are equally probable the most unfavourable case is chosen, which, in doubtful cases, is, of course, the safest way of forming a judgment.

Whether the operations, which are to be applied to the data, are considered as a determination of the first couple of constants of a FOURIER series (the very first, $\frac{1}{2}\, b_0$, is left out of consideration), or as a calculation of the average or most probable position of the end-points of the vectors, or as a determination of the situation of the centre of gravity — in all cases the result is a quantity determined by two coordinates and the operations we have to perform are:

1stly. to separate the constant part:

2ndly. if necessary to determine the situation of the axes of probability;

3rdly. to calculate the mean and probable error, in this case better called incertitude.

The same method can, of course, be applied to groups of periods, which gives a considerable saving of labour, but also leaves some want of clearness in the result.

3. The investigation of the series of daily means of barometric observations made at Batavia has been conducted in the same manner as it was commenced in 1888. The arrangement has been performed according to a period of 25.8 days, and groups of 30 rows have been taken together so that, out of the 510 periods, 17 groups have been formed.

The result of this operation is given in Table I.

If, therefore, an oscillation, periodic in 25.8 days, really exists, its amplitude is not more than:

$$\frac{1.66}{30} = 0.055 \text{ mm.}$$

TABLE I.

	Amplitude.	Argument.	Components.		Differences.	
	A	C	a_1	b_1	Δa	Δb
	mm.		*mm.*	*mm.*	*mm.*	*mm.*
1	0.69	242°	—0.32	—0.61	—0.86	0.96
2	7.63	287°	2.17	—7.32	1.63	—5.75
3	3.45	285°	0.87	—3.34	0.33	—1.77
4	3.14	68°	1.16	2.91	0.62	4.48
5	1.52	215°	—1.24	—0.88	—1.78	0.69
6	2.08	204°	—1.90	—0.84	—2.44	0.73
7	4.52	345°	4.38	—1.14	3.84	0.43
8	1.21	104°	—0.30	1.47	—0.84	2.74
9	1.78	270°	0.01	—1.78	—0.53	—0.21
10	6.31	318°	4.71	—4.20	4.17	—2.63
11	5.00	194°	—4.86	—1.17	—5.40	0.40
12	3.25	266°	—0.20	—3.24	—0.74	—1.67
13	6.00	255°	—1.54	—5.80	—2.08	—4.23
14	2.18	317°	1.59	—1.49	1.05	0.08
15	3.34	195°	—3.23	—0.84	—3.77	0.73
16	2.60	83°	0.34	2.57	—0.20	4.14
17	7.62	354°	7.58	—0.76	7.04	0.81
Mean	1.66	289°	0.54	—1.57		

By subtracting this restant, which has to be regarded as a constant part, from the corresponding values, the differences exhibited in the last columns have been found, which are to be regarded as fortuitous disturbances.

4. The value to be attached to the result may be estimated in different ways.

The first and most simple manner is to split up the series into two or more groups. From the data given in Table I we easily find:

	A	C	Number of periods.
Group 1— 6	1.68 mm.	274°	180
,, 7—11	1.62	299°	150
,, 12—17	1.76	296°	180
,, 1— 9	1.42	292°	270
,, 10 17	1.95	286°	240
,, 1—17	1.66	289°	510

From this it appears that there is certainly some indication for the existence of a periodical oscillation, and also that the arrangement has been made according to a period which practically leads to a maximum value of the amplitude.

The probability that three points, taken successively at random, are situated within an angular space of 30° is $\left(\frac{1}{12}\right)^2$ and the probability of mere chance would have been even less if we had taken into account that the amplitudes too are in good accordance.

5. A second, equally simple method is afforded by a direct view of the outcome of the arrangement itself, split up into two or more groups.

Fig. 1 gives a graphical representation of the differences given in the three last columns of Table II.

Fig. 1 shows that the curves of the two series agree satisfactorily and also that a tendency to a double period, with a maximum on the 8—9th day, which in the first group is still well marked, vanishes when the arrangement is continued.

If these results are considered as fairly conclusive, so as to justify a more exact determination of the length of the period, this may be easily done by varying the arguments C of Table I successively by $\frac{1}{2}x$, $\frac{3}{2}x$, $\frac{5}{2}x$ etc., x denoting the variation of each group-argument which leads to the most constant value of C.

In this way 17 equations are obtained from which the most probable values of C and the period T can be calculated. If to each equation the weight is given of the corresponding amplitude, the equations will assume the form:

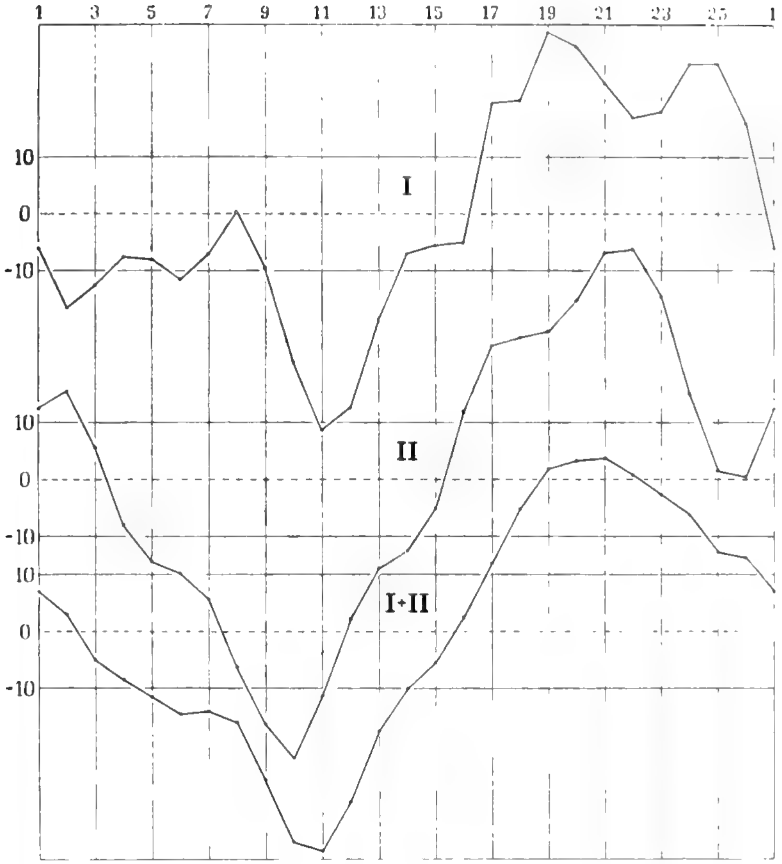
$$0.69\,(-\,118° + \tfrac{1}{2}x) = 0.69\,C$$
$$7.63\,(\,-\,73° + \tfrac{3}{2}x) = 7.63\,C \text{ etc.}$$

TABLE II.

Results of the arrangement. Average values, the general mean value being subtracted.

Number of Groups.	I	II	I+II	Three subsequent values taken together.		
				I	II	I+II
	270	240	510	270	240	510
	mm.	mm.	mm.	mm.	mm.	mm.
1	—0.016	0.034	0.036	—0.012	0.025	0.014
2	—0.055	0.047	—0.008	—0.033	0.031	0.006
3	—0.026	0.012	—0.009	—0.025	0.011	—0.010
4	0.006	—0.028	—0.011	0.015	—0.016	—0.017
5	—0.026	—0.033	0.030	—0.016	—0.029	—0.023
6	—0.028	—0.025	0.028	—0.023	—0.033	—0.029
7	—0.014	—0.042	—0.028	—0.014	—0.042	—0.028
8	0.010	—0.060	—0.029	0.001	—0.066	—0.032
9	0.015	—0.096	0.038	—0.019	—0.086	—0.052
10	—0.072	—0.103	0.088	—0.052	—0.098	—0.074
11	—0.098	—0.094	—0.097	—0.076	—0.076	—0.077
12	—0.059	—0.032	—0.047	—0.068	—0.049	—0.060
13	0.047	—0.021	—0.036	0.037	—0.031	—0.035
14	—0.004	—0.044	0.022	0.014	—0.025	—0.020
15	0.009	0.013	0.003	0.011	0.010	—0.011
16	—0.037	0.024	—0.009	—0.010	0.024	0.005
17	—0.001	0.061	0.027	0.039	0.047	0.024
18	0.054	0.058	0.055	0.040	0.050	0.043
19	0.067	0.031	0.049	0.064	0.052	0.057
20	0.071	0.069	0.069	0.059	0.063	0.060
21	0.039	0.091	0.062	0.046	0.080	0.061
22	0.029	0.079	0.051	0.034	0.081	0.055
23	0.035	0.074	0.052	0.036	0.064	0.048
24	0.046	0.038	0.041	0.053	0.030	0.041
25	0.077	—0.024	0.028	0.053	0.003	0.028
26	0.036	—0.006	0.015	0.032	0.001	0.026
Mean	0.097	0.103	0.097			

Fig. 1.



As might have been expected the result of this calculation shews little or no difference from that of the arrangement itself.

$$x = -1^\circ{,}09 \qquad C = 291^\circ \qquad T = 25.803^d.$$

As one day corresponds to $^{360^\circ}/_{25.8}$, a variation of x degrees for each group is equivalent to:

$$\frac{1.09}{30} \cdot \frac{258}{3600} = 0.003^d.$$

6. By application of the method discussed in § 2 to the differences Δ_a and Δ_b of Table I we find:

$$\Sigma M^2_x = 145.05 \qquad \Sigma M^2_y = 212.02 \qquad \Sigma M^2_{xy} = -12.44.$$

From the well known formula:

$$\text{tang } 2\varphi = \frac{2M^2_{xy}}{M^2_x - M^2_y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

for the situation of the principal axes of inertia, deduced from the condition that, when the axes of coordinates coincide with the principal axes, the moment of deviation or centrifugal force M^2_{xy} will vanish, we find:

$$\psi = -18^\circ 35'$$

and further

$$M_x^2 = 6.45 \qquad M_y^2 = 8.72 \qquad N = 0.15$$

and from formula (9)

$$r = 0.829.$$

It appears, therefore, that, in this case, all directions of the accidental quantities are equally probable, so that we are fully justified in putting:

$$r = 0.833.$$

The mean and the probable error for each group are then:

$$M = 3.89 \qquad W = 3.24$$

and the final result for each group:

1.76 mM. . . . probable error 0.810

and for each row:

0.055 mM. . . . probable error 0.027

so that the probable incertitude of the final outcome amounts to almost exactly half the amplitude.

7. The question may also be put, what will happen if the arguments of Table I are varied in such a manner, that the variations are equivalent to arrangements according to other periods slightly different from 25.8 days.

The amount of the variation is limited by the number of rows taken together in one group, which can be shifted only as a whole, and the variation ceases to have any sense as soon as the sums of each group would be sensibly affected by the actual arrangement according to the new period.

If quantities, periodical within a length of time T, are arranged according to a period T' in m columns, the value at the origin of time being represented by:

$$A \cos C,$$

the record to be inscribed in the t^{th} column of the p^{th} row (t and p counted from nought) will be:

$$A \cos \left(\frac{2\pi}{m} \cdot \frac{n}{n'} - C + 2\pi p \frac{n}{n'} \right)$$

$$n = \frac{2\pi}{T} \qquad n' = \frac{2\pi}{T'}$$

The sum of R rows is then:

$$n' - n = \delta \qquad \alpha = \frac{T\delta}{2}$$

$$A \frac{\sin R\alpha}{\sin \alpha} \cos \left[\frac{2\pi}{m} T + \frac{\delta T'}{m} T - C + (R - 1)\,\alpha \right].$$

When δ is small this expression can be simplified by putting:

$$T' = T \qquad T = \frac{m}{2}$$

in the second term under the cosine. The sum of the first, second etc. group of R rows is then:

$$A \frac{\sin R\alpha}{\sin \alpha} \cos \left(\frac{2\pi}{m} T - C + R\alpha \right) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$A \frac{\sin R\alpha}{\sin \alpha} \cos \left(\frac{2\pi}{m} T - C + 3\,R\alpha \right) \text{etc.}$$

If the oscillation is of a purely periodical description and of equal amplitudes the sum will show a principal maximum, RA, for $\alpha = 0$, and further secondary maxima for all values of α which satisfy the equation:

$$R \operatorname{tang} \alpha = \operatorname{tang} R\alpha$$

i.e., when $R = 510$, for values of α corresponding with periods of:

$$\begin{cases} 25.872^d \\ 25.728 \end{cases} \qquad \begin{cases} 25.925^d \\ 25.675 \end{cases}$$

but the amplitudes of these maxima will be resp. 5 and 8 times smaller than the principal maximum.

The amplitude will vanish whenever

$$R\alpha = \pi,\ 2\pi,\ 3\pi \text{ etc.}$$

i.e. for periods of

$$\begin{cases} 25.850^d \\ 25.750 \end{cases} \qquad \begin{cases} 25.900^d \\ 25.790 \end{cases}$$

The upper curve of fig. 2 gives an image of the fluctuations of these theoretical amplitudes.

If we put:

$$T = 25.8 \qquad T' = 25.8 \pm x$$

the amount of shifting to be given to each group corresponding with 0.01 day, is:

$$30\,\alpha = \frac{30\,.\,\pi\,.\,x}{25.8 \pm x} = 2^\circ.094.$$

x in the denominator being neglected.

The variation has been carried on, as utmost allowable limit, to

$x = \pm 0.15$, corresponding with a group-variation of about 31°. The group-amplitude is only slightly affected by this variation as:

$$\frac{\sin Ra}{\sin a} = 28.58$$

instead of 30.

When R, the total number of periods, increases, the secondary maxima will become smaller and smaller, and at the same time maxima and minima will approach nearer to the principal maximum.

TABLE III.

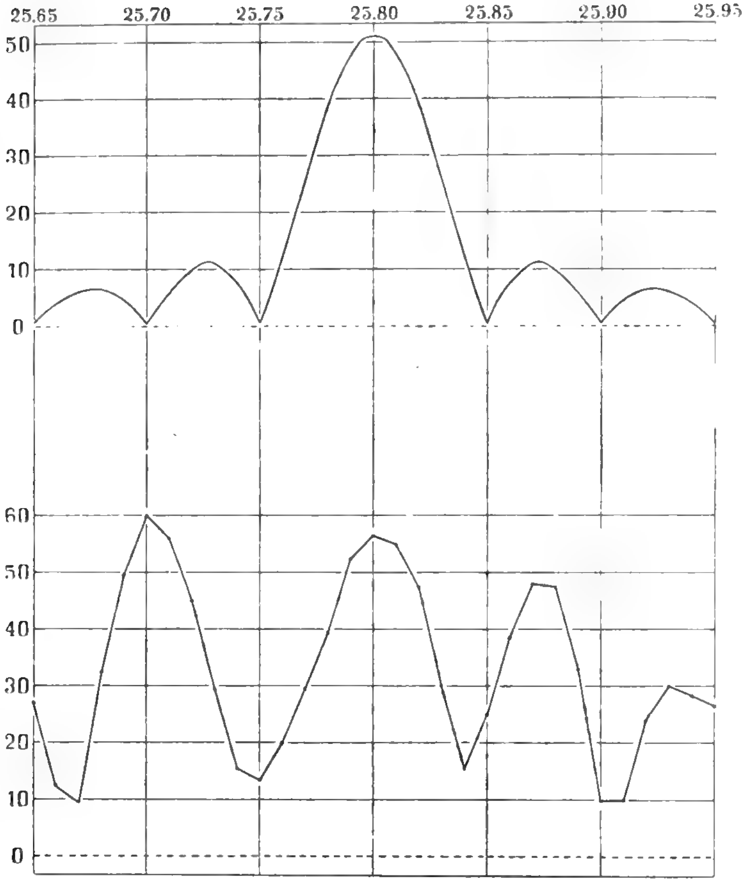
Results of the arrangement according to different periods by the shifting-process.

Period	A	C	Period	A	C
	mm.			mm.	
d. 25.65	13.4	351°	d. 25.81	27.4	247°
25.66	6.4	298°	82	23.7	217°
25.67	4.8*	148°	83	15.0	169°
25.68	16.4	76°	84	7.6*	84°
25.69	24.8	34°	85	12.6	344
25.70	30.0	345°	86	19.2	286
25.71	27.9	315°	87	24.0	244°
25.72	22.5	265°	88	23.8	207°
25.73	14.6	231°	89	16.5	174°
25.74	7.8	171°	90	5.1*	132°
25.75	6.7*	88°	91	4.9	301°
25.76	10.1	33°	92	11.9	262°
25.77	14.7	9°	93	15.0	232°
25.78	19.8	346°	94	13.6	212°
25.79	26.4	322°	95	13.3	300°
25.80	28.3	289°			

Table III exhibits the outcome of this shifting of the groups and fig. 2 shews both the theoretical and actual curves.

For the sake of comparison the data of Table III have been multiplied by 2 and the amplitude of the theoretical period has been taken equal to 0.1.

Fig. 2.



It appears then that, in fact, secondary maxima and minima occur and, at least as regards the first minima, in the right places, but that the secondary maxima, instead of being small as compared with the principal maximum, as might have been expected, are of about equal intensity and, most so on the left side, not at all agreeing with the theoretical lengths of period.

This result may be interpreted in three ways:

a. We may assume that every one of the three periods 25.80, 25.70 and 25.87 is due to a purely accidental distribution of the quantities under consideration.

b. We may concede that at least for the period 25.80 there is some indication, but that the two adventitious periods are the consequence of the unequal distribution of the group-amplitudes so that they will disappear when the arrangement is continued over a longer series of observations.

c. We can assume that the evidence is equally good for the three periods, and will be enhanced by continued arrangement.

Of course only an actual continuation of arrangement for another series of twenty years will enable us to answer these questions. The only test which at present can be applied is to form two or more groups as has been done above for the arrangement according to 25.8 days.

Period		25.70^d			25.87^d		
		A		*C*	*A*		*C*
Group	1—6	1.60	mM.	6°	1.40	mM.	252
,,	7—11	3.35	,,	292°	0.73	,,	165
,,	12—17	2.48	,,	27°	2.52	,,	253°
,,	1—9	1.11	,,	335°	1.22	,,	216
,,	10—17	2.53	,,	349°	1.88	,,	263

So far as this criterion allows a conclusion to be drawn, it appears from this result that the evidence for real existence of the periods 25.70 and 25.87 is considerably less than of the period 25.80.

In the latter case the arguments for three groups did not differ more than 25°, against differences of resp. 88° and 95° for periods of 25.70 and 25.87 days. The probabilities of mere chance, therefore, are, taking 30° and 90°:

$$\frac{1}{144} \text{ and } \frac{1}{16}$$

i. e. more than 8 times as great. If we take also into account that the amplitudes of the three groups are accordant for 25.80 and widely different for the adventitious periods, we can estimate the probability of chance at 10 times as great.

The computation of the probable error (incertitude) of the result for each group also gives an indication for this greater probability, but not in the same degree.

	Amplitude.		Probable error.
25.80	1.76	mm.	0.810
24.70	1.76	,,	0.916
25.87	1.41	,,	0.830

7. If we apply, in so far as possible, the different criteria to the data published by Prof Schuster concerning daily means of magnetic declination for Greenwich, arranged according to 26 and 27 days, we find for the sums of groups, each of which contains resp. 14 and 13.5 rows.

	$26^{d.}$		$27^{d.}$	
	A_1	C	A_1	C
Group 1— 5	6'.19	267°	3'.53	351
6—10	4.08	243°	2.19	88
11—15	3.09	351°	4.75	354
16—20	1.45	152°	7.05	203°
21—25	2.88	229°	7.56	298°

The probability, therefore, of mere chance is:

$$26 \text{ days } \ldots\ldots\ldots \left(\frac{283}{360}\right)^4 = 0.38$$

$$27 \text{ days } \ldots\ldots\ldots \left(\frac{246}{360}\right)^4 = 0{,}20.$$

and the final outcome

26 days 0'.480 . . . . prob. error 0'.343
27 ,, 0'.405 . . . . ,, ,, 0'.415

If we vary the arguments given in Table VIII of SCHUSTER's paper for a period of 26 days in such a way that the result is equivalent to an arrangement according to 25.80 days we find:

	A_1	C
Group 1— 5	10'.83	54°
6—10	5.72	104°
11—15	4.88	77°
16—20	4.61	44°
21—25	4.03	89°

As these arguments do not differ more than 60 degrees, the probability of chance is in this case:

$$\frac{1}{6^4}$$

The final result, calculated for a group of 14 rows,

1'.118 . . . . . . prob. error 0'.292.

The accurate length of the period and the most probable value of C, calculated after the method discussed sub 5, are then:

25.804 days . . . . $C = 55.°6$.

It appears from these calculations that an arrangement according to 26 and 27 days leads to results the probable incertitude of which has about the same value as the amplitude itself. On arranging according to 25.8 days we find a probable incertitude about four times less than the amplitude.

Further, from this investigation, as compared with SCHUSTER's inquiry, we may draw the conclusion, that elements of terrestrial magnetism, as observed in higher latitudes, allow a more decided judgment to be formed concerning the real existence of periodical oscillations of this kind than meteorological observations made at tropical stations.

If the outcome arrived at by the arrangement of barometric daily means for Batavia is considered to afford some evidence or indication for an oscillation periodic in 25.80 days, a much greater probability must be attached to the real existence of this fluctuation in the observations of magnetic declination made at Greenwich.

Anatomy. — *"On the Form of the Trunk-myotome."* (First Communication). By Prof. J. W. Langelaan. (Communicated by Prof. T. Place).

The segmented plan of construction of the vertebrate animals, most marked in the muscular system, has led to the conception of the myotome.

Two methods are chiefly employed in establishing the form of this myotome. The first method is based on the hypothesis of the primary connection between muscle and nerve; the second, a more direct one, is based on the dissection of the intersegmental tissue. Both methods seem equally restricted in their application, as can be concluded from the researches of Bardeen [1]); moreover there is reason to believe, that they will not always yield concordant results.

The second method is followed in this research.

1. *Trunk-myotome of Petromyzon fluviatilis.* (Fig. I).

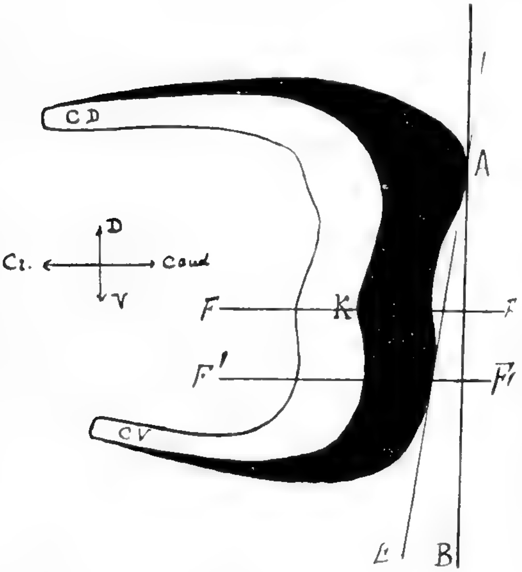


Fig II.

The trunk-myotome of the adult animal has in general the form of a crescent, the cornua being directed towards the cranial end of the body and slightly inclined to each other. The dorsal cornu (fig. II *CD*) reaches to the mid-dorsal line, while the ventral cornu (fig. II *CV*) ends at the mid-ventral line of the body. Both cornua differ in length, the dorsal being about $^1/_7$ longer than the ventral, and while both reach to the mid-plane of the body, they are slightly torquated in respect to each other.

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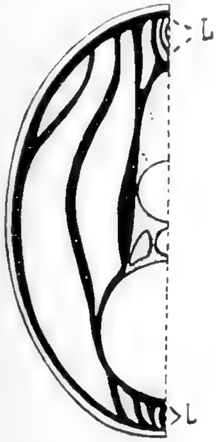
[1]) Anat. Anz. Bd. XXIII, N⁰. 10/11.

The corpus of the myotome shows a kneelike inflection (fig. II *K*), which is always situated nearer the mid-ventral line of the body than the mid-dorsal line. In transverse section (along the line *FF*, fig. II) the corpus of the myotome is rhomboidal, this rhombus being more and more flattened towards the cornua; consequently the cornua appear in transverse section as lamellae in juxtaposition (fig. III *L.L.*). These lamellae are slightly incurved.

One side of the rhombus lies in the body surface (black in fig. II). This surface is cylindrical in the middle region of the body, the transverse section being perfectly elliptical. The black-coloured surface of the myotome, must therefore be considered as cut out of this cylindrical surface.

The opposite side of the rhombus is turned towards the skeletal-axis and the abdominal cavity. In general it has the same form as the outer side, being only slightly excavated by the abdominal cavity, which in this part of the body is cylindrical, the transverse section being a perfect circle. Both the other sides of the rhombus are congruent and bound respectively, a more cranial and a more caudal myotome.

Fig. III.



Transverse section through the trunk of Petromyzon; the intersegmental tissue being black.

The position of the myotome as a whole in respect to the sagittal plane, passing through the mid-lines of the body, is such, that the corpus shows an inclination towards the caudal end of the body. Seen in transverse section (along the line *FF* fig. II) the longest axis of the rhombus makes an acute angle with the sagittal axis of the body, the vertex of the angle being turned towards the head. This caudal inclination of the myotome diminishes towards the cornua, so that the cornua are nearly normal to the surface of the body. In consequence of this caudal inclination the myotomes overlap to some extent. This muscular overlapping varies between $^1/_2$ and $^2/_3$ in the neighbourhood of the knee, diminishing towards the cornua on account of the decrease of the caudal inclination of that part of the myotome.

The position of the myotome in respect to the dorsoventral axis is variable along the body. If *AB* (fig. II) is a dorsoventral axis, at right angle to the sagittal axis, and *AE* a line tangent to the dorsum of the myotome, then we have in the angle *AEB* a measure for the ante- or retroversion of the myotome in respect to the dorsoventral axis.

The first myotomes behind the last branchial cleft, show a little anteversion, which quickly decreases, so that the 4th and 5th myotomes are strictly vertically situated. The following myotomes (as in figure II) are retroversed, this retroversion reaching a maximum of 10°. Towards the caudal end of the body this retroversion decreases and is again reversed behind the anal aperture, where the myotomes are again anteversed.

The description given here of the myotome applies only to the trunk-myotome in the middle region of the body, the branchial apparatus as well as the appearance of the dorsal fins bringing about notable changes in this form.

II. *Trunk-myotome of Acanthias vulgaris. (Fig. IV and V).*

The myotome described in this paper was situated in that region of the body which lies between the thoracic fin and the first dorsal fin. In its most general features the trunk myotome of Acanthias shows a great resemblance with that of Petromyzon, though at first view a considerable difference seems to exist.

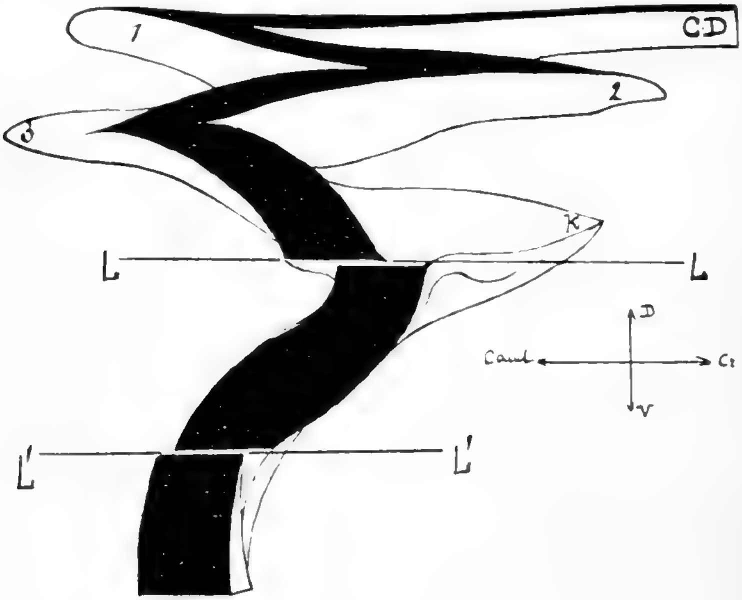


Fig. VI.

Looking at that surface of the myotome, which forms part of the surface of the body, we see it interrupted in two places.

The lines of interruption are nearly parallel to the sagittal axis of the trunk. The first line (*LL* fig. VI) coincides with the linea lateralis, the second (*L'L'* fig. VI) lies nearer the mid-ventral line of the body. At the place of interruption septa of connective tissue descend and seem to divide the myotome into three parts. One part situated between the mid-dorsal line and the line *LL* is the dorsal part of the myotome; between the lines *LL* and *L'L'* lies the lateral and between the latter and the mid-ventral line, the ventral part of the myotome is situated.

Considered at the line of interruption, the surface of the lateral part of the myotome seems to be cranially displaced in respect to the dorsal part; this displacement amounts to one half of the breadth of the myotome. The same can be observed between the surface of the lateral and the ventral part of the myotome, the lateral part being also displaced cranially in respect to the ventral part; this displacement does not surpass $^1/_3$ of the breadth of the myotome.

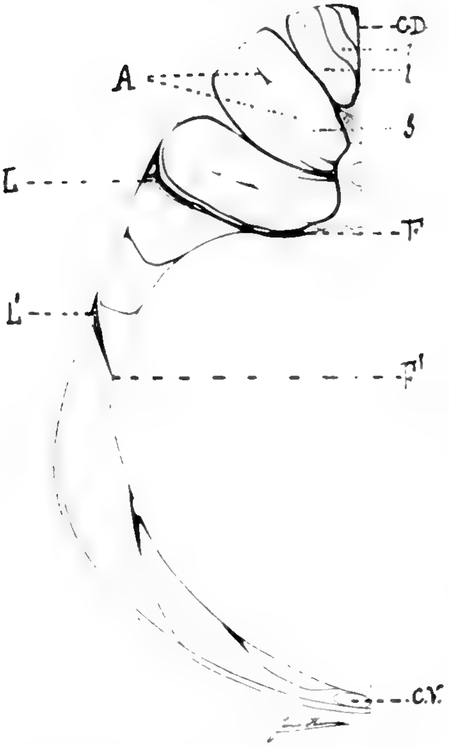
If we follow the septa of connective tissue at the line of interruption *LL*, it is easily seen, that the myotome is rolled in towards the axis of the body and then reversed till it reaches again the body surface. In most cases the continuity of the muscular tissue at the bottom of the fold is broken off, but the intersegmental tissue which covers the myotome is always continuous. If we now try to unroll the myotome as much as possible, we find that the dorsal part makes an angle with the lateral part, so that a true knee is formed. The top of the knee is directed towards the head as in Petromyzon. The line along which the myotome is folded in, is parallel to the sagittal axis of the body, and seems to run over the knee, so that the top of the knee lies at the point *K* of figure VI.

The same can be observed on following the line *L'L'* (fig. VI), the line of folding being also parallel to the sagittal axis of the trunk.

The differentiation of the myotome into three parts, ensues therefore from a process of infolding, the lines of folding being parallel to the sagittal axis of the body.

If a model of the myotome of Petromyzon is cut out of paper, and this myotome folded in along the lines *FF* and *F'F'* (fig. II), we get a precise illustration of the displacements seen in the myotome of Acanthias. The direction in which the outer-surfaces are displaced in respect to each other is a direct consequence of the form and the curvature of the myotome at the places of infolding. The difference in the extent of the displacement of the surfaces along the lines *LL* and *L'L'* (fig. VI) is due to the fact, that the fold along the line *FF* is longer in the direction from outwards to inwards in correspondence with the dimensions of the myotome. This can be seen in a transverse section through

Fig. VII.



Transverse section through the trunk of Acanthias; the intersegmental tissue black. Natural size.

the same region of the trunk of Acanthias, where *LF* (fig. VII) is the intersegmental tissue that divides the dorsal from the lateral part, while *L'F'* is the septum, that the latter separates from the ventral part of the myotome.

The further differentiation of the dorsal part of the myotome takes places by the same process: the lines of folding instead of being parallel to the sagittal axis of the body are in general at right angles to this axis.

There are three of these lines, agreeing with the number of peaks which the dorsal part of the myotome shows. These lines considered from outwards to inwards, are originally normal to the surface of the body, then curved with the convex side turned ventrally and towards the body surfaces. This curvature is most marked in the third line of folding (*A* fig. VII), reckoned from the mid-dorsal line, the first one being nearly a straight line normal to the body surface and to the sagittal axis. These lines of folding are visible on a transverse section, because septa of intersegmental tissue stretch out into the fold. The curved lines (*A* fig. VII) are the transverse sections of these septa.

The lateral part of the myotome shows no further differentiations.

The ventral part has only one line along which the folding of the myotome is well marked; consequently this part of the myotome shows only one peak turned to the caudal end of the body.

The myotome considered as a whole, as in Petromyzon, has a caudal inclination. This inclination is most marked at the knee. Considering only the dorsal part, we see this inclination diminish towards the mid-dorsal line, so that the most dorsal part of the myotome is about normal to the surface of the body. This most dorsal part is elongated into a dorsal cornu (*CD* fig. VI). In transverse section we find therefore these dorsal cornua as lamellae in juxtaposition (fig. VII *CD*).

When the direction of the myotome is reversed at a line of folding, the same happens with the sense of the inclination, so that these parts show a slight cranial inclination. The folding of the myotome together with the inclination produces the elongated and peakshaped form of the myotome at these lines of folding. The myotomes thus cover each other as hollow, pointed tubes telescoped into each other. In the transverse section (fig. VII) 1 indicates the section of the first peak directed caudally, 2 the peak turned towards the head and 3 the second peak turned to the caudal end of the body (fig. VI resp. 1, 2, 3). In consequence of the inclination of the dorsal part of the myotome, these lines of folding are not quite at right angles to the sagittal axis, but are also slightly inclined. This is the reason why we find only part of these lines in a transverse section, which is normal to the sagittal axis.

From a transverse section we can judge the extent of the muscular overlapse. Concordant with the increasing inclination from the mid-dorsal line to the first lateral line, we see the overlapse increase to about $^3/_4$. At the knee the inclination rapidly decreases. In the lateral part of the myotome the inclination is insignificant and the overlapse less than $^1/_2$. In the ventral part the inclination increases at first and then decreases towards the mid-ventral line: the muscular overlapse does not surpass $^1/_2$. The ventral part terminates at the mid-ventral line in a ventral cornu (*CV* fig. VII, fig. V) turned cranially. This ventral cornu is much shorter than the dorsal cornu.

In order to get some idea of the dimensions of the myotome I have measured the length of each of the three parts into which the myotome is divided up. These measurements have been made over the surface of the myotome and this surface was also followed where it is folded in. In this way I have found for the myotome described:

Length of the dorsal part 350 mm.; the lateral part 90 mm.; the ventral part 190 mm. The length of the whole myotome is therefore 630 mm. and of this $^{55}/_{100}$ belong to the dorsal region.

I have made the same measurements in the myotome of Petromyzon. If it be conceded that the points *K* (fig. II and fig. VI) where the knee is located in both myotomes, are corresponding points, I have found: Length of the dorsal part, from the mid-dorsal line to the knee 33 mm.; the latero-ventral part, from the knee to the mid-ventral line, 26 mm. The whole length of the myotome was therefore 59 mm., and of this also $^{55}/_{100}$ is contributed to the dorsal region.

If we compare the dorsal region in Petromyzon and in Acanthias, it is evident that this region is strongly reduced in the latter: notwithstanding this, the same part of the whole myotome belongs in both cases to the dorsal region. If this be true in general, it seems to me, that the reduction of the dorsal region is the principal moment which has led to the folding of the dorsal part of the myotome.

In figures IV and V the position of the rib, in relation to the myotome, is indicated by a crossed line. The rib is located in the intersegmental tissue that divides the dorsal from the lateral part of the myotome. The junction of the rib with the skeleton, lies a little caudally in respect to the knee of the myotome; the rib itself is turned to the caudal end of the body concordant with the caudal inclination of the myotome. In a transverse section, three successive ribs are cut through.

Geology. — *"On the direction and the starting point of the diluvial ice motion over the Netherlands."* By Prof. Eug. Dubois. (Communicated by Prof. J. M. van Bemmelen).

Referring to the *"Beschrijving van eenige nieuwe grondboringen,"* V, by Dr. J. Lorié, recently published in the "Verhandelingen der Koninklijke Akademie van Wetenschappen, 2^de^ Sectie, Deel 10, N°. 5", to which, on p. 20 and 21, the author has added a critique of some conclusions in my communication to the Academie: *"The geological structure of the Hondsrug in Drenthe and the origin of that ridge"* (Proceedings of the meeting of Saturday, June 28, 1902, Vol. V, p. 93 sqq.), I beg leave to make the following remarks.

The critique of that eminent student of the geology of the Netherlands is based on such an incorrect and incomplete statement of my conclusions and of the facts, that the reader cannot but regard those conclusions as being of a rash character, which in fact they have not.

Indeed, having said that he does well agree with my opinion regarding the structure of the Hondsrug, Dr. Lorié continues as follows [1]:

"Another case it is with a particularity mentioned on p. 4 and 5". (This refers to 12 lines on p. 96 and 97 of the Proceedings.) "In pit XLI there was found a boulder of quartzite, having a diameter of 0.35 M., cleft into two pieces, in such a manner

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[1] This quotation has been translated from the Dutch of Dr. Lorié by me.

that the upper piece, with respect to the lower one, has been pushed on $1^1/_2$ cm. in south-easterly direction. So this is a fact! The author however bases thereupon the hypothesis that the ice motion has taken place, *as a whole*, not from N.E. to S.W., such as is still generally admitted, but from N.W. to S.E., in such a way that the starting point is not to be sought for in Scandinavia but in Scotland. Now it appears to me that here is a strong disproportion between the importance of the observed fact and that of the hypothesis."

Further, at the end, he says:

"So to find the explication of the shifting of the quartzite boulder at Eksloo, over a distance of *one centimeter and a half*, we have not to admit Scotland as starting point for the ice motion, but can persist in our old opinion."

Thus far Dr. LORIÉ.

Now I wish to remind those who take an interest in the matter that it was by no means that one fact, referred to by Dr. LORIÉ, on which I based "the hypothesis" that the ice motion "took place" from N.W. to S.E., nor did I assert at all that the starting point of the ice motion is not to be sought for in Scandinavia but in Scotland. In the quoted Proceedings, to which Dr. LORIÉ refers, I do not speak of a *hypothesis*, but of a *supposition*, and this, clearly, is based upon the whole consideration of the structure and the origin of the Hondsrug ridge. Particularly this supposition is related to $2^1/_2$ pages of my communication, (the whole text being 10 pages), viz. from p. 99 (in the middle) to p. 101 (below). The only sentence bringing in relation the fact of the shifting of the pieces of the quartzite boulder, with respect to each other, to the direction of the ice motion, (p. 100, at the end of the second alinea), occurs half way the explanation of $2^1/_2$ pages and runs as follows: "Now with this supposition perfectly agrees the at first sight paradoxical direction of motion as derived from the shifted boulder of quartzite."

And concerning the starting point of the ice motion, on p. 101 of the Proceedings I most unhesitatingly admit Scandinavia to be the starting point of the ice motion, whereas I only speak of the *possibility* ("it might be possible, at least") of a deviation of the Scandinavian ice stream in south-easterly direction, caused by the Scottish ice stream.

It will be superfluous to argue that the distance over which the two pieces of the quartzite boulder are separated from one another *in the soil* ought not to be in any proportion to the large motion of the ice *over it*.

Haarlem, May 26, 1904.

Mathematics. — *"On an expression for the class of an algebraic plane curve with higher singularities."* By Mr. Fred. Schuh. (Communicated by Prof. D. J. Korteweg.)

If an *algebraic plane curve* is given by an equation in Cartesian *point-coordinates*, its *order* n can be immediately read from the equation. The *class* k of the curve is best defined as the order of the equation in *line-coordinates*. However, in the following it is my intention to restrict myself exclusively to point-coordinates and then the class can be defined as the number of *movable* points of intersection of the curve with the first polar or as the number of *proper* tangents to be drawn from an *arbitrary point* P to the curve. To obtain exclusively *different points of contact not situated in manifold points of the curve* we must understand by an *arbitrary point* a point that

1st does not lie on the curve,

2nd does not lie on one of the tangents in a *manifold point* of the curve,

3rd does not lie on a tangent in a unifold point having with the curve a contact of a higher order than the first.

A *manifold point* of the curve is a curvepoint which cannot be a single point of intersection with a straight line. The lines connecting P with the manifold points must not be counted as proper tangents.

From the above mentioned definition of the class another one can be deduced, where no single restriction is made with respect to the situation of the point P, which thus holds good for any point P.

To begin with, we make the restriction that P *may not lie on the curve.* Suppose P to lie on the tangent in a point S of the curve, where S may be a manifold point or a single point with a tangent intersecting in more than two points. If the straight line PS cuts the curve in w coinciding points S, whilst an arbitrary straight line through S cuts the curve in t coinciding points S, then S counts for $w-t$ of the k *proper* points of contact with tangents from P to the curve, in other words $w-t$ points of contact approach S when P approaches the tangent in S. It is of no importance whether the curve has one or more branches through S, touching SP, neither whether the curve has branches through S not touching SP or not.

The above mentioned follows immediately from the following:

Theorem. *Let R be a point of an algebraic curve where all branches through R have the same tangent l which intersects the curve in $t+v$ coinciding points R, whilst every other straight line through R intersects* *the curve in t points R, then R absorbs r proper points of contact with tangents from P when P lies on l outside R, and $t + r$ proper points of contact when P coincides with R.* [1]

Now, if S is such a point, where all branches have the same tangent SP, then $w = t + r$, whilst according to the above theorem S counts for $r = w - t$ points of contact with tangents from P. If besides the branches touching SP still more branches pass through S, then these latter do not give rise to any new points of contact coinciding with S; they cause however the same increase of the numbers t and w, so that they leave $w - t$ unchanged. Then too $w - t$ represents the number of points of contact, which in consequence of the singular situation of P coincide with S.

If P is not situated on one of the tangents in S, then $w = t$, so

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[1] For a branch which can be represented by *one* single PUISEUX-development this theorem can be proved i. a. out of the relation existing between the developments in point- and in line-coordinates. By addition follows immediately the same theorem for more branches having the same tangent. In a paper entitled: "An equation of reality for real and imaginary plane curves with higher singularities" (These *Proceedings* of April 23rd 1904, p. 764) I made use of the same theorem (p. 765) and referred for the deduction to STOLZ, ZEUTHEN and STEPHEN SMITH. I omitted however to mention G. HALPHEN, "Mémoire sur les points singuliers des courbes algébriques planes", *Mémoires prés. par divers savants à l'Académie des Sciences* (2), *t. 26*, (1879), n⁰. 2 (112 p.). This extensive paper was already offered to the Paris Academy in April 1874 (see: *Comptes Rendus de l'Académie des Sciences de Paris, t. 78*, p. 1105- 1108, where the autor communicates some of his results) so that this paper has the priority. HALPHEN formulates the theorem somewhat differently, namely (l. c. Théorème III, p. 42 or Théorème II, p. 50):

THÉORÈME. *La somme des ordres des contacts des branches d'une courbe avec une de ses tangentes est égale à la multiplicité du point correspondant à cette tangente dans la courbe corrélative.*

The relation between the developments of a branch in point- and in line-coordinates was first considered by A. CAYLEY ("On the Higher Singularities of a Plane Curve". *Quart. Journ. of Math., Vol. 7*, (1866), p. 212, *Collected Math. Pap., Vol. 5*, p. 520 or "Note sur les singularités supérieures des courbes planes" *Crelle's Journal, Bd. 64*, (1865), p. 369, *Coll. Math. Pap., Vol. 5*, p. 424). If $y = A x^p + B x^q + \ldots . (p > 1)$ is the development in point-coordinates then CAYLEY gives for the development in line-coordinates $Z = A' X^{\frac{p}{p-1}} + B' X^{\frac{q}{p-1}} + \ldots .$ where the general form of the exponents is $\frac{\lambda p + \mu q + \ldots}{p-1}$; here $\lambda, \mu, \ldots .$ are positive integers. Implicitly the HALPHEN-theorem is included in this. CAYLEY, however, does not enter farther into the relation between the developments and does not state the theorem.

Let me finally notice, that the theorem has also been stated by M. NÖTHER, "Ueber die singulären Werthsysteme einer algebraischen Function und die singulären Punkte einer algebraischen Curve", *Math. Annalen, Bd. 9*, (1876), p. 166 (sp. p. 182).

that then $w - t$ continues to represent the number (namely zero) of the points of contact coinciding with S.

If S is a point of contact with a tangent out of P where nothing remarkable takes place, then for that $t = 1$ and $w = 2$, so that $w - t = 1$, whilst S now also counts for *one* point of contact.

By summing up the values $w - t$ for all the points S of the curve for which $w > t$ we keep getting for sum k with respect to every point P not lying on the curve, thus

$$k = \Sigma (w_1 - t_1). \quad \ldots \ldots \quad (1)$$

We formulate this in the following way:

THEOREM I. *Let P be a point not situated on an algebraic curve and S an arbitrary point of that curve. Let us suppose that the curve cuts the straight line PS in w, an arbitrary straight line through S however in t points coinciding with S; then the class of the curve is equal to $w - t$ summed up for all the points S of the curve for which $w > t$ and for as many other curvepoints as one likes.*

To continue we suppose that P lies on the curve namely in a point of the *order* t', i.e. t' is the smallest number of coinciding points of intersection of the curve with a straight line through P. For a point S of the curve not coinciding with P the number of points of contact coinciding with S is still indicated by $w - t$. Moreover a certain number of points of contact coincides with P, namely according to the HALPHEN-theorem to the number of $t' + \Sigma r'_1$, where $\Sigma r'_1$ represents a summation with respect to the different curvetangents intersecting the curve in $t' + r'_1, t' + r'_2, \ldots$ coinciding points P. So we get

$$k = t' + \Sigma r_1' + \Sigma (w_1 - t_1), \quad \ldots \ldots \quad (2)$$

where $\Sigma (w_1 - t_1)$ represents a summation with respect to all the points S of the curve outside P.

However we can also include the point P among the points S. The line connecting P and S becomes in that case indefinite. If we take for PS a line which is not a tangent in P, then we get $w = t'$. If however we take for PS a tangent intersecting in $t' + r_1'$ points coinciding with P, then we get $w = t' + r_1'$, so $w - t' = r_1'$. So for (2) we can write

$$k = t' + \Sigma (w_1 - t_1), \quad \ldots \ldots \quad (3)$$

if only we extend the summation also to the point S lying in P itself, in which case we have but to take for PS those straight lines through P contributing to $\Sigma (w_1 - t_1)$ (thus the tangents in P) and as many other straight lines through P as one likes.

The equation (1) is a special case of (3). If namely P is not on the curve then each straight line through P has *zero* points of intersection P with the curve; in other words P is *a point of the order zero* of the curve, so $t' = 0$. So the result of all our considerations is included in equation (3).

We formulate this in the following way:

THEOREM II. *Let P be a point of the order t' of an algebraic curve (where t' may also be zero) and S an arbitrary point of the order t of that curve. Suppose the straight line PS intersects the curve in w points coinciding with S, then the class of the curve is equal to t' increased by the sum of $w - t$ over all the points S of the curve. If S is in P we have to regard all straight lines through P as the line connecting P and S.*

When speaking of *all points S* or, when S is in P, of *all straight lines through P*, we mean that we take those points or lines contributing to $\Sigma (w_1 - t_1)$ and as many other points or lines as one likes.

Theorem I is a special case ($t' = 0$) of this theorem II. The theorem always holds good for any singularities the curve may have.

Sneek, May 1904.

Geology. — "*Some considerations on the conclusions arrived at in the communication made by* Prof. EUG. DUBOIS *in the meeting of June 27, 1903, entitled: Some facts leading to trace out the motion and the origin of the underground water of our sea-provinces.*" By H. E. DE BRUYN.

(Communicated in the meeting of September 26, 1903).

In the meeting of June 27, 1903 Prof. DUBOIS made a communication dealing with a problem of great general importance, namely the presence of proper drinking-water in the province of Holland. Although readily acknowledging the many points of merit of this communication and entirely agreeing with many of its conclusions, I differ from the author on a principal point which indeed is essential, namely the origin of the fresh water in our polderland. So a speedy refutation of the author's opinion on this point seemed to me to be desirable.

In his communication Prof. DUBOIS speaks of our sea-provinces; this in my opinion ought to be Holland, since the conditions prevailing in Friesland and Zeeland are different, so that considerations which are valid for Holland cannot be applied there. So I will only consider the tract of country chiefly dealt with in the abovementioned communication, which is bounded by the dykes of the Y and the Zuiderzee at the north, by the river Vecht at the east, the Rhine from Harmelen to Katwijk at the south and the North-sea at the west.

The geological conditions of this tract inside the dunes are such as are mentioned in the communication: uppermost alluvium, then pretty generally a layer of fen (partly disappeared) under which a layer known as "old sea-clay". Under this latter the diluvium, consisting to a great depth of sand, coarser and finer, with here and there banks of clay which are not continuous however. The "old sea-clay" mentioned is called in the paper clay-containing sand and although in my opinion also that layer is permeable to water, yet I think its permeability is smaller than Mr. Dubois assumes and that it is exactly here that the cause of our difference of opinion has to be sought. In some places this layer of old sea-clay is wanting; in special cases this makes an investigation very difficult, for the general condition however, which is here dealt with, this circumstance can be neglected.

The communication consists chiefly of two parts, of facts and of conclusions drawn therefrom. The facts I will pass without commenting on them, although occasionally objections might be raised against them or rather against the remarks that accompany them.

I perfectly agree with a great many of the conclusions, e.g. with the following:

that in the diluvium fresh water is present to a certain depth;

that in deeper polders the deep groundwater moves vertically upward, in shallow polders downward;

that also in the depth a current exists from the dunes to the polders and from the shallower polders to the deeper ones;

that no important continuous subterranean current exists from the higher grounds from the east to the west.

But I cannot accept the conclusion that the fresh groundwater present in the diluvium also in our polders, owes its origin to rain fallen locally or at a relatively short distance during the wet season.

In the following refutation of this opinion I shall speak of fresh and of brackish or salt water. Of course there is no sharp division between these, but in order to avoid cumbrous definitions I shall make this distinction for simplicity's sake. I base my considerations on quantities, but since only their relative amount concerns us here, I have rounded my figures as much as possible.

I intend to show the incorrectness of the conclusion mentioned from the amount of the afflux to in the Haarlemmermeer polder. Now a paper on this amount by the member of this Academy van Diesen is found in the Versl. en Meded. der Kon. Akad. 1885[1]). I can by no means accept the amount found there. The chief reason why Mr. van Diesen arrived at an erroneous figure is that he assumes that the groundwater in the Haarlemmermeer polder which is situated at a depth of about a metre below the surface evaporates as much as water at the surface on account of the interstices between the particles of ground. This, I think, is entirely wrong; groundwater at a depth of a metre does not evaporate at all.

Now if we assume that the groundwater does not evaporate, the figures given in the paper would lead to a negative afflux, which certainly is wrong too. This is a consequence of another reason why an erroneous figure is found, namely the method of derivation. Mr. van Diesen, namely, calculates the amount of the afflux from two periods of six years, for each of which he derives the equation:

$$k = ax - b$$

in which k is the amount of the flow, x the ratio of the evaporation at the surface and the rain fallen; a and b constants, derived from the other data. So he has two equations $k = ax - b$ and $k_1 = a_1 x_1 - b_1$. Now he determines the ratio of k and k_1 from the difference in level of the water in the "bosom" [2]) and of the polderwater, a ratio naturally little differing from unity; he further assumes that the x of each period has the same average value, so he puts $x = x_1$. The two unknown quantities, k and x, can then be found from these two equations.

But x and x_1 are not exactly equal. Mr. van Diesen himself says: "evidently this value must change according to circumstances." If x_1 be equal to $x + \Delta$ we have:

$$x = \frac{\frac{k}{k_1}b_1 - b}{\frac{k}{k_1}a_1 - a} - \frac{\frac{k}{k_1}a_1 \Delta}{\frac{k}{k_1}a_1 - a}$$

Now it will entirely depend on the value of $\frac{k}{k_1}a_1$ and a whether Δ has an appreciable influence on the value of x. Since from the nature of the case $\frac{k}{k_1}a_1$ and a are great values, differing little between each other, however, a small value of Δ has a great influence on x and hence on k.

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[1]) Versl. en Meded. van de Kon. Akademie van Wetenschappen, Afd. Natuurk. 3e Reeks, Dl. I, p. 359—374.

[2]) "Bosom" is called an intermediate discharge canal or basin.

The best estimate of the afflux in the Haarlemmermeer polder is that by Mr. Elink Sterk [1]. This author bases his calculation on the assumption that the value of rain minus evaporation, averaged over many years, is practically the same for Rijnland and for the Haarlemmermeer polder. Rain is here tacitly assumed to be rain plus surface condensation, and evaporation, evaporation plus the water withdrawn by plants. From the quantity of water discharged and let in over an average of 14 years Mr. Elink Sterk then derives with the aid of the assumption mentioned that the afflux in the Haarlemmermeer polder is equal to a quantity of water corresponding to a height of 135 mm. $+ K$ (K being the afflux in Rijnland) over the whole surface.

Now he puts $K = 15$ mm. i.e. $^1/_{10}$ of the afflux in the Haarlemmermeer polder which he calls an ample estimate as I think it is; so he finds for the amount of the afflux in the Haarlemmermeer polder 150 mm.

The assumption mentioned that rain minus evaporation is equal for Rijnland and for the Haarlemmermeer polder is not quite correct of course. The rain may be taken equal, but not the evaporation. The rainfall is in my opinion more regular on the average than is indicated by our rain-gauges. Under equal meteorological conditions the rate of evaporation depends principally on water for evaporation being or not being present. In the polders having a high summer-level with regard to the land which mostly consists of meadows, evaporation will be greater than in the Haarlemmermeer polder, since water will always be present at the surface; in the dunes on the other hand it will be less. Considering the character of the grounds in Rijnland we may assume that evaporation there will be slightly greater than in the Haarlemmermeer polder. So if we apply to our figure a correction $\angle_1$, making it $150 + \angle_1$, $\angle_1$ will be negative.

Mr. Elink Sterk has left out of consideration through lack of data: 1. the quantity of water admitted into the Groot Waterschap van Woerden (having the same bosom as Rijnland); 2. The quantity of water let in by locks into Rijnland and the Groot Waterschap van Woerden. Calling these respectively $\angle_2$ and $\angle_3$, the afflux in the Haarlemmermeer polder is

$$k = 150 + \angle_1 + \angle_2 + \angle_3 \text{ mm.}$$

Now the quantities $\angle_2$ and $\angle_3$, are both small and certainly positive; probably they are together smaller than $\angle_1$. So if we omit the three corrections $\angle_1$, $\angle_2$ and $\angle_3$, the error can not be large and

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[1] Verhandelingen van het Kon. Instituut van Ingenieurs. 1897—1898. p. 63—75.

the figure for k probably becomes too great as it also becomes by putting $K = 15$ mm.

Putting the afflux of water at 150 mm. this gives for a surface of 18000 H. A. 27 million M³. This amount consists of three parts: 1. of what is let in for the higher lands behind the ringdyke through valves and syphons; 2. of the afflux through the ringdyke above the old sea-clay which I shall call the afflux *through* the alluvium: 3. of the afflux over the whole surface of the polder, moving upward through the old sea-clay on account of the greater pressure, which I shall call the afflux *from* the diluvium.

The first part which is no proper afflux, is estimated by Mr. ELINK STERK at 5 to 7 million M³ per year. Subtracting this and taking the smallest figure the afflux mentioned sub 2 and 3 becomes 22 million M³ per year. How much of this is due to each of the parts sub 2 and 3 cannot be made out, while in those places where the "old sea-clay" is absent no separation takes place. Probably 2 is the greater part, therefore I assume for the part sub 3 an amount of 10 million M³ per year; possibly it is much smaller.

These 10 million M³. the afflux *from* the diluvium must consequently either flow in as fresh water along the circumference of the polder under the old sea-clay through the upper layers of the diluvium, or rise from below as salt water. Let us for the present assume that it all flows to in the former manner. In fifty years 500 million M³. of fresh water would in this way have flowed into the diluvium. Now the quantity of fresh water present in the diluvium under the Haarlemmermeer polder is *greater*; assuming $^1/_3$ to $^1/_4$ space between the grains of sand this quantity would only correspond to a thickness of 10 metres containing fresh water, whereas this thickness is greater on the average, as is proved e.g. by borings near Sloten.

The circumference of the ringdyke being about 60.000 metres, if we assume the afflux to take place over a height of only 20 metres and the interstices between the grains of sand to be the same as above, this will give a velocity of motion of 30 metres per year and the water flowed to would, even if we neglect the loss of speed further in the polder, have penetrated into the polder only 1500 metres in 50 years and so not have reached the middle.

Moreover the assumption that all the water streaming to is fresh, is not probable, if we bear in mind the amount of salt in the Wilhelmina spring which is over 3000 mg. chlorine per litre. Hence it is certain that with a flow of 10 million M³ *from* the diluvium, part of the fresh water nowadays present in the diluvium under the

Haarlemmermeer polder was present there already 50 years ago.

Before that time conditions were very different from what they are now. Instead of the deep drainage there was bosomwater. How the fresh water then present, especially in the eastern part, had come under the Haarlemmermeer, is difficult to tell for want of data. Was the water of the Haarlem lake always so rich in chlorine as some old observations show? Certainly the difference in pressure of the deep groundwater was smaller than it is now and accordingly the quantity of water moved was also smaller, while the direction of the current in the deep groundwater e.g. near Sloten must have been exactly the reverse.

A thousand years ago when there were no dykes yet to keep out the water of rivers and of the sea, and no mills yet to drain the polders, when the dunes were so much broader at the seaside than they are now, when there were no canals in the dunes yet for sand transport and other purposes, I imagine the state of affairs in the tract of land we are considering, must have been such that fresh water was also present in the diluvium and probably more than nowadays, that in the dunes there existed a high level of groundwater by which water was driven to the diluvium, the pressure at the west side under the "old sea-clay" being greater than that of the groundwater above it. The level of the groundwater in the alluvium of the polderland was then probably much more regular and slightly higher than the average sea-level. How these conditions became prevalent I must leave to geologists to explain.

By making dykes, by enclosing polders, by draining, the level of the groundwater has gradually been lowered, now in one place, then in another. The currents in the layers of fresh water in the diluvium also had their directions changed by this; they certainly were very small, however, before the great drainages were made. In the tract we are dealing with, 3000 H.A. were drained before 1750, 10.000 H.A. between 1750 and 1850 and 26.000 H.A. between 1850 and 1900.

The dunes gradually decreased in breadth, while also the flow of water towards the land increased by canals for sand-transport etc. The height of the groundwater in the dunes will consequently also have steadily been decreasing.

Bearing in mind the figure for the amount afflux to in the Haarlemmermeer polder, we may safely assume the quantities of water which before the drainages were made, penetrated vertically downward through the old sea-clay, to have been very small compared with the amount of fresh water present. Consequently the only source of supply of fresh water to the diluvium has been the afflux from the dunes. At the same time I venture the supposition that part of the fresh water which a thousand years ago was present in the diluvium under the polderland is still present there now.

Another question arising here is whether salt water rises upward from below. About former times nothing can be stated with certainty in this respect; for the present time it is rendered probable by the circumstance that the water of the Haarlemmermeer polder contains more chlorine than can be derived from the afflux if no salt water from below is added to it. Therefore I have tried to estimate, though roughly, the quantity of chlorine, discharged by Rijnland and the quantities entering Rijnland in another way than from below, assuming that the quantity of chlorine withdrawn from the ground by plants is equal to the quantity furnished by manuring, which supposition is reasonable.

Rijnland discharges annually on the average 476 million M^3. of water; how much chlorine this contains is not known, but from the data for the percentage of chlorine of the water of the bosom [1]) a figure may be derived which is too small and another which is too large, which figures I take to be 105 and 315 mg. per litre, giving an annual discharge of 50.000 or 150.000 tons of chlorine.

The quantities of chlorine arriving into Rijnland are, besides that from the groundwater below 1. the sea-spray; assuming that this chiefly falls on the dunes we can estimate it; the dunes that discharge water into Rijnland will supply about 20 million M^3. of water annually; this water contains 40 mg. chlorine per litre, making 800 tons of chlorine; adding to this what is blown over the dunes we obtain a total of 1500 tons; 2. the fresh water which is let in, amounting on the average to 125 million M^3. per year, containing 40 mg. per litre, which makes 5000 tons; 3. the water through locks; it is difficult to estimate an average percentage of chlorine here, since one lock (Gouda) admits fresh water to the bosom, others (Spaarndam, Overtoom, etc.) water with a high percentage of chlorine; I think 2000 mg. per litre a sufficiently high estimate; putting the water let in through locks at 5 million M^3. this makes 10.000 tons; 4. what human society discharges into the bosom; this amount is difficult to estimate; putting it at 3500 tons, the total amount becomes

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[1]) Mededeelingen omtrent de Geologie van Nederland, no. 26, by Dr. J. Lorié, pp. 8—11.

20.000 tons of chlorine. Assuming that what is supplied to the bosom by all these causes is more than half this rough estimate and less than its twofold we get 10.000 or 40.000 tons of chlorine. In any case there is a deficiency amounting to something between 10.000 and 140.000 tons which has to be ascribed to a supply of salt from a greater depth. When we bear in mind that this will chiefly come from the Haarlemmermeer polder and that this latter discharges on the average about 30.000 tons of chlorine and that the supplies mentioned sub 1—4 occur there in a small degree, the supply of salt from below at the present time is pretty certain. A quantity of 35.000 tons of chlorine corresponds to that contained in two million M³. of water from the North Sea.

The motion of the deep groundwater is generally very slow.

If e. g. we consider how long it would take water to travel in a layer of sand between two impervious layers from the sea to the Haarlemmermeer polder, which is a distance of 9000 metres, the difference of pressure being 5 M., if the permeability is the same as that of dune-sand, we find that it would travel in a year (31.557.000 seconds) through a distance of

$$\frac{31.557.000 \times 5 \times 0.0006}{9000} = 10 \; M.$$

(0.0006 being the rate of filtration through 1 M. of dune-sand with a pressure of 1 M.[1]). A distance of 9000 M. would consequently require 900 years.

As to the rate with which the salt water can rise from below we find what follows. Assuming that the rise is constant and that under the Haarlemmermerer polder 5 million M³. rises annually, this gives over a surface of 18000 H.A. with a space of $^1/_3$ to $^1/_4$ between the grains of sand, a rise of about 100 mm. per year; a rise of 50 metres would then require a period of 500 years.

The question now naturally arises: since a large quantity of fresh water is present in the diluvium under our polderland and the salt water flows slowly, is it possible to withdraw this fresh water for drinking-water? The part we are considering has, after taking off the littoral margin and the country round Amsterdam which has a different formation, a surface of about 100.000 H.A.; not counting the drainages and other less suitable tracts, half of this territory contains 5000 million M³. of fresh water, if we assume an average

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[1] Report of the Committee for investigating the supply of water from the dunes to Amsterdam, 1891, supplement 16, p. 77.

of 10 M^3 of fresh water per M^2, corresponding to $^1/_3$ to $^1/_4$ space between the grains of sand over a thickness of 30 to 40 metres. A consumption of 50 million M^3 per year being sufficient with the existing dune-water conduit for the need of the population, taking its increase into account, this quantity would be able to supply water for a hundred years; now we may presume that in a hundred years science will have so much advanced that it will be practicable then to convert any water into suitable drinking-water.

The answer to our question must in my opinion be affirmative as well as negative. Affirmative with respect to supplying water to single dwellings, to a village, or to a temporary supply in war-time such as the Engineering Corps has made at Sloten; negative with respect to a lasting demand on a large scale and this because in practice pecuniary considerations would force us to withdraw the water from a limited surface which would be impossible without causing such a diminution in pressure that certainly with a lateral afflux also water from below would flow to, so that after some time brackish water would be obtained.

Hence Prof. DUBOIS' assertion, that a sufficient quantity of drinking-water is and remains available in the ground under the shallower polders, is in my opinion entirely wrong.

Geology. — *"On the origin of the fresh-water in the subsoil of a few shallow polders"*. By Prof. EUG. DUBOIS. Communicated by Prof. BAKHUIS ROOZEBOOM.

(Communicated in the Meeting of November 28, 1903).

In the meeting of the Academy of September 26 ult. Mr. H. E. DE BRUYN, although he agreed with most of the principal conclusions about the origin and the direction of motion of the groundwater in part of our lowland, contained in my communication to the Academy of June 27, gave an elaborate exposition of the grounds on account of which he cannot accept my conclusion concerning the origin of the fresh-water in the subsoil of a few shallow polders. In my opinion this has to be sought in rain, fallen on the spot or at a relatively short distance, which Mr. DE BRUYN thinks impossible on account of considerations about the amount of the afflux in the Haarlemmermeer polder which, in his opinion proves that the layers above the diluvium, especially the "old sea-clay" transmit water to a much smaller extent than is necessary in my representation. He also supposes that part of the fresh-water which was present under our polder-land a thousand years ago, is still there at the present day and that the only source from which fresh-water has been supplied to the diluvium (the subsoil) has been the dunes.

About the velocity with which water can move through our always very impure clay, which Mr. DE BRUYN rightly considers to be a cause of our difference of opinion, I will now state a few facts and at the same time point out the arguments which led me to my conception of a different origin of the deep groundwater mentioned. First however I wish to point out another possible origin which has not yet been suggested and which cannot be at once rejected, and especially a difficulty of a more serious nature even than the one objected to my representation by Mr. DE BRUYN.

If we assume the extremely slow motion ascribed to the groundwater by Mr. DE BRUYN, it might namely be that the deep fresh-water under consideration has to be considered as a remainder of what sank away there centuries ago. For not always these polders have been surrounded by brackish water only.

According to descriptions from the Roman period, Lake Flevo undoubtedly contained water from the Rhine and no salt water as the Zuiderzee does nowadays. Also the IJ was a freshwater lake communicating with the freshwater lakes Purmer, Wormer and Schermer. Moreover it is well known that the Haarlem Lake (Haarlemmermeer) arose by the union of at least four lakes: the Old Haarlem Lake, the Old Leyden Lake, the Old Lake and the Spiering Lake which were fed at least partially by one or more branches of the Katwijk Rhine. The map by Bolstra, the able land-surveyor of Rijnland, published in 1745 and incorporated in "Present state of the United Netherlands" [1]), gives us an idea of the situation of these lakes in 1531 and of their gradual union and the enlargement of the Haarlem Lake, originated in this way, down till 1740. The waves of this large lake could easily erode the steep banks, consisting of fen, as low as the same layer of clay which already formed its bottom, the circumstances for this process becoming more and more favourable, chiefly on account of the "sinking of the lands" in these parts with respect to the sea, described already a century before the draining. This erosion of land occurred at a tremendous rate at the north-east side, where the polders are situated which now have fresh-water in their underground. LE FRANCQ VAN BERKHEY [2])

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[1]) Tegenwoordige staat der Vereenigde Nederlanden. Vol. 6 p. 163. Amsterdam, I. Tirion. 1746.

[2]) J. LE FRANCQ VAN BERKHEY. Natuurlijke Historie van Holland. Vol. I. p. 227. Amsterdam 1769.

about the middle of the 18th century describes the water of the Haarlem Lake as "fresh, but in some places, where the grounds become brackish, as near Slooten and towards Amsteldam, the water of the lake is sometimes of a saltish taste. But the abundance of water from the Rhine and the supply from so many small lakes and waters which discharge themselves into it, bring about that the brackish water can by no means get the upper hand, and so the lake has on the whole good fresh-water." Meanwhile a quantity of salt amounting to 300 milligrammes per litre is according to the latest investigations not unpalatable. An analysis by G. J. MULDER [1]) of water taken from the lake near Sloten in November 1825, shows that it contained 393 mg. chlorine per litre. Now this is the season during which it will probably have been least brackish. Hence it is improbable that the water of the Haarlem Lake was on the whole really fresh. Indeed, the lake had ample opportunity to receive salt from the IJ (which had already become salt towards the middle of the 13th century) through the upper ground of the polder-land which consisted chiefly of fen and which separated the two waters in places (near Halfweg) like a true isthmus. It is also known that at any rate towards the middle of the 18th century those grounds under which fresh-water is found, were brackish. Yet fresh-water of a much earlier period might in places have remained in the underground. Water derived not only from the north and west sides, but also from the east, may have filtered into the polders mentioned at the north-east of the present Haarlem Lake. The Amstel certainly contained for centuries perfectly freshwater, derived from the Rhine. As late as 1530 the Amsterdam canals, fed by this river, had drinkable water, but soon this supply was gradually more and more reduced by natural causes.

Is now the motion of the groundwater, not only in the finer alluvium, containing much sand, but even in the coarse and gravelly diluvial sand, which transmits water much more easily, really so slow, as MR. DE BRUYN believes, that in three or four centuries the influence of the altered circumstances as to level and composition of superficial waters on the deep groundwater will scarcely be perceptible? I believe that numerous facts, of which I will mention a few in this communication, are at variance with this opinion.

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[1]) G. J. MULDER. Verhandeling over de wateren en lucht der stad Amsterdam. p. 66. Amsterdam 1827. LORIÉ, quoting from second hand, wrongly mentions this same analysis under two different headings and with different amounts of Cl. (Onze brakke, ijzerhoudende en alkalische bodemwateren, Verhandelingen der Kon. Akad. 2e Sectie, Dl. 6. N°. 8. 1899. p. 9).

In the first place the actual facts are incompatible with Mr. DE BRUYN's idea that before the draining of the Haarlem Lake, some 50 years ago, "the direction of the current of the deep groundwater e.g. at Sloten, must have been exactly the reverse" of what it is now (These Proceedings VI, p. 291) and still less I can assume this for an earlier period. For near Sloten the country was not lower, but even a little higher than the level of the Haarlem Lake and not dyked in, so that the incessant washing away of the steep fenny bank of the lake could be enormously great. According to an accurate investigation, made in 1743, it amounted yearly on the average to as much as 5 to 10 Rijnland rods (about 19 to 38 metres). It is true that the upper side of the layer of fen which now forms the Rieker polder near Sloten, lies at 1.35 metres below A. P. (Amsterdam level) but its lower side is still on a level with the bottom of the Haarlemmermeer polder, as it formerly was with the bottom of the lake, and it rests on the "old sea-clay". If we now bear in mind that fen, such as that of the Rieker polder consists, when it is completely saturated, for $^9/_{10}$ of water, as I have found to be actually the case, and that moreover the "looseness and shiftiness" of these grounds which, as it were, rose and sank with the water, were well known in the time of the lake, it is clear, how, after the draining, in half a century, by losing over $^1/_3$ of their water, they might shrink so far below A. P. and that there can be no question of an earlier current of the deep groundwater under the Haarlem lake towards the country near Sloten. The lake certainly did not allow such a current from the dunes to pass under its bottom.

Though the dunes were broader and the level of the water in them higher than nowadays, the hydrostatic pressure imparted there to the deep groundwater must have been exhausted and the horizontal current stopped by the water rising in the alluvial cover, which forms an imperfect screen, long before the opposite side had been reached. For at present the difference in pressure, owing to the water-pressure being now 5 metres less in the polder than it formerly was in the lake, is certainly not less and yet already in the middle of it only a slight upward pressure remains, although pressure is directed from all sides to the middle.

Hence in the underground we only meet water that soaked the soil from above without any considerable horizontal movement in the underground.

I quite agree with Mr. DE BRUYN (p. 291) that "part of the fresh-water now present in the diluvium under the Haarlemmermeer polder was present in it already fifty years ago", if I may consider water that contains 200 to 300 and even more milligrammes of chlorine per litre as fresh-water, as I understand he does. Only with this latter not common qualification one is entitled to say that under the Haarlemmermeer polder the diluvium has on an average more than 10 metres fresh-water, for the greater part of that polder has no fresher water in its underground than with these amounts of chlorine. Only where the higher grounds are clearly of recent origin this is different, for the rest the water in the upper diluvial layers of the Haarlemmermeer polder contains about the same amount of chlorine as the water of the former lake. Of the Wilhelmina spring, the amount of chlorine of which is over 3000 milligrammes, the depth is unknown; undoubtedly however it goes down as far as the salt water which in most places of this polder is to be found below 40.50 metres.

The most serious difficulty opposing my view of the origin of the fresh-water in the subsoil of some shallow polders is not mentioned by Mr. DE BRUYN. It is that the fresh-water in question in all seasons not only is surrounded by, but also rests on and is covered by brackish water. How can the fresh-water under these circumstances owe its origin to the rain fallen on the brackish upper ground?

The explanation of this paradoxical phenomenon I mean to have found in the peculiar hydrological condition of those polders which, like those between Amsterdam and the Haarlemmermeer polder, are themselves at a level only little below A.P. and are situated near deeper drainings. In a similar condition are the shallow polders near Purmerend and Schermerhorn. Like here towards the Haarlemmermeer polder, so yonder towards the deep polders Purmer, Wijde Wormer, Beemster and Schermer, a considerable flow exists in the coarser diluvium under the more compact alluvial cover and at the same time a vertical downward movement, while in those deeper polders the water tries to rise through the alluvial cover which forms only an imperfect screen. Consequently in boring-tubes the groundwater from the diluvium in these latter rises higher than the field, whereas in the shallow polders it remains far under it and below the level of the groundwater. These circumstances and the geological condition of the soil form in my opinion the solution of the riddle of the presence and the permanence under some shallow polders of fresh-water which on all sides is surrounded by brackish water. I arrived at this conclusion especially by studies in the Rieker polder near Sloten, in which the source for the military water-supply for the position of Amsterdam is situated. To this I was enabled by a few experimental wells which Mr. G. VAN ROYEN, 1st lieutenant-engineer, charged with the execution of the works there, was kind enough to have made for the purpose of this investigation. At my proposal seven of these experimental wells were bored to various depths in the middle of a meadow, about 300 metres south of the Sloten road and the farm "Rustvrede", within a square of three metres side. Under the lower end of the iron tubes which were open below, gravel had been poured to a depth of half a metre. By examining the water that had risen in those tubes as to level and composition one can obtain information about the state of affairs at various depths in relation with the condition of the soil.

Letter of the well.	Depth of the layer of water below the field [1]).	Layer in which the water is found.
A	1 to 1.5 M.	fen.
A'	1.7 „ 2.2 „	„
B	2.5 „ 3.0 „	Upper clay.
C	5 „ 5.5 „	Layer of sand in the clay.
C'	7.5 „ 8.0 „	Lower part of the clay.
D	10 „ 10.5 „	Between deep fen and sand
E	15 „ 15.5 „	Sand under the denser alluvium.

A well situated 30 metres to the west, 44 metres deep, IV, 13, was compared with these experimental wells.

Most of these wells were ready at the end of August ult. A' was finished about the middle of September, C' the 19th of October. The level of the water and the amount of chlorine were repeatedly examined by me. After all the wells had been left undisturbed as long as November 20, the following state of affairs was found.

	Water level in M. ÷ A.P.	Chlorine in mg. per L.
A	1.465	135
A'	1.495	202
B	1.495	617
C	1.493	780
C'	1.677	145
D	2.720	124
E	2.737	68
IV, 13	2.747	92

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[1]) The level of the field is 1.33 ÷ A.P.

Of these wells C'' may for the present be left out of account since a stationary condition has not yet established itself in it; having its lower end in the clay, the water still rises in it continually Well IV, 13 again has a higher and varying amount of chlorine; determinations at different times gave 114,92,190 mg. per litre. I believe that this increase and variation of the amount of chlorine has to be ascribed to the neighbourhood of the deep salt water in relation with fluctuations in atmospheric pressure and also with a proper motion of ebb and flood of the groundwater [1]).

In spite of the very considerable rainfall of the latest months, great variations in the percentage of chlorine did not occur; only in and near the clay, hence especially in C, the amount of chlorine decreased considerably, in C from 850 to 780 mg. per litre. This result does not verify my formerly stated supposition that perhaps during the wet season a continuous freshening of the water might take place.

Yet I could not agree with the idea that the fresh-water in the subsoil should have stayed there undisturbed for at least a few centuries. For why then is fresh-water in the diluvium under the Haarlemmermeer polder and the Lutkemeer polder only found at a distance not too far removed from the shallow polders near Sloten and Osdorp? Why does this layer of fresh-water end already before Halfweg, before the Great IJpolder is reached, south of Sloterdijk and also soon eastward of the Amstel? Why does the layer of Purmerend not extend further than a short distance under the Purmer and Beemster polders? Does not this limitation point to an autochthonous origin of the fresh-water in the underground of the shallow polders?

I think to have found the key of the riddle in the stated sudden fall in pressure, amounting to more than 1,20 metre, under the clay and the deep fen which is a consequence of the fact that the level of the groundwater in the Haarlemmermeer polder is almost 3.5 M. lower than in the Rieker polder. So this compressed deep fen, acting as a semi-permeable wall, can transmit to the deeper layers water, but no salt.

That fen in a compressed state and under similar conditions of

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[1]) On these influences, especially on the proper ebb and flood of the groundwater, see: F. WEYDE, Die Abhängigkeit des Grundwasserstandes von dem Luftdrücke, dessen Steigen und Fallen während eines Tages (Flut und Ebbe), in Meteorologische Zeitschrift of August 1903. The influence of atmospheric pressure was already pointed out in my former communication. These influences become perceptible only in deep wells, because in them the water follows more easily the changing pressure of the atmosphere and gravity than it does in the neighbourhood and so is raised or depressed.

pressure as prevail in the Rieker polder, can cause osmosis, I could prove experimentally with apparatus which Mr. A. J. Stoel Jr. at Haarlem was kind enough to make for me in his workshop and with other apparatus kindly put at my disposal by Dr. Heringa of Haarlem. The most important of these experiments is the following one.

In an iron tube of 1 M. length and 154 mm. internal diameter newly dug fen from the superficial layer in the Rieker polder was compressed by means of a lever until no further compression was observed. The pressure was gradually raised to 2,8 kilogrammes per square centimetre, a pressure equal to that which is found in a soil of sand or clay at a depth of 14 metres; the layer of fen was three centim. thick. Of water, containing a quantity of sodium chloride corresponding to an amount of chlorine of 1000 mg. per litre, this layer of fen, which on account of its slight thickness, can by no means be so perfect a semi-permeable wall as the deep layer of fen in the Rieker polder which has an average thickness of a metre, water was transmitted which contained temporarily at the utmost 750 mg. chlorine per litre; hence at least 250 milligrammes were retained.

Now the deep fen in the Rieker polder occurs as an almost coherent layer, extending from Haarlem, right through the Haarlemmermeer polder as far as Mijdrecht and from Sloten by Amsterdam as far as Zaandam and Uitdam. This layer is missed in the north-western corner of the Haarlemmermeer polder, i.e. in the place of the former Lake Spiering and farther south. The lower side of this deep layer of fen lies at about 11 to 13 metres below A.P. Still deeper at Sloten in some three borings, parts of a second old layer of fen were found and also repeatedly at Amsterdam and Zaandam. This layer must be distinguished from the former with which it was formerly identified. As a fairly coherent layer this deeper fen can be traced above the diluvium, to the north by Purmerend as far as Hoorn and Enkhuizen, to the west by Wormerveer, Beverwijk, and Velzen to IJmuiden. The upper one of these deep layers of fen can reach a thickness of about 1 M., the lower one is rarely $^1/_2$ metre thick.

So we may understand how the underground may have derived in former times and may still derive its fresh-water from the upper ground although this latter always carries brackish water itself.

But will the "layer of clay" which is 7 M. thick be permeable enough to render it possible that in the half century, elapsed after the draining of the Haarlem lake, under the polders to the north-east of this drainage a layer of fresh-water of at least 50 M. thick may have accumulated? This means a yearly increase of at least one metre, or, if we take into account the interstices between the grains of sand, of about 0.30 M. pure water a year. Now this amount is pretty much the same as of the rain that can penetrate into the earth, while also all the other surface-water can furnish fresh-water to the underground, by which also the fresh-water, flown off to the deep polder, can be accounted for. In my former communication I already pointed out that the power of clay to transmit water is commonly underrated. The clay in our alluvial grounds is generally very impure, consists mostly of very fine sand and according as the percentage of this increases, its "permeability" becomes greater. The fattest clay of the Rieker polder at Sloten lies as a thin bank immediately under the superficial layer of fen and contains 30% real clay. From the 7 M. "clay" in the Rieker polder, one has to subtract first a couple of metres of sand, the rest is also much richer in sand than the fat upper layer mentioned. Now Spring has proved that a layer of Hesbay's loam of 7 M. thickness admitted in 24 hours a movement of water of at least 0.036 to 0.045 M.[1]) which is ten to fifteen times more than the velocity calculated for the Rieker polder. A sample of loam, kindly sent me by that scientist, proved, on analysis by Dr. N. Schoorl, to contain 21.5% clay i.e. about as much as our ordinary, pretty fat alluvial clay contains on an average. Experiments with fatter clay under pressure, as it is in nature, give me a much smaller velocity which however is still sufficient to explain the hydrological condition of the Rieker polder. Of these experiments I intend to give an account on a future occasion.

I wish to draw attention to a result of the experiments of Spring already mentioned in my former communication, according to which, when the thickness of a layer of sand becomes very great with respect to the pressure-column of the water, the rate of filtration may by no means be taken inversely proportional to the thickness of the filter. On the contrary, Spring found in this case the rate independent of the thickness of the filter. I can confirm this for clay and for this substance the pressure may even be relatively great and the thickness of the layer hundreds of times smaller on account of the so much greater resistance of clay than of sand. A layer of the fattest clay, obtained in the same way as the compressed fen, by squeezing out the water, having a thickness of

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[1]) In this time namely a layer of water of 12 to 15 mm. thickness was transmitted.

15 cm., under a pressure of 80 cm. transmitted no less water than a layer of the same compressed clay of only 4 cm. thickness. Calculations like those on page 294 of Mr. DE BRUYN's communication, in which the rate of filtration through 9000 M. sand from the dunes is simply assumed to be $^1/_{9000}$ of the rate found in an experiment with 1 M. of the same sand lead consequently to erroneous conclusions. I also want to point out that in the coarse diluvial sand which forms the principal way for the horizontal movements of the water, the velocity of motion is about ten times as great as in sand from the dunes.

Under these circumstances I believe to be justified in maintaining my opinion that the water in the underground of some shallow polders is of autochthonous origin.

It is also clear now, how in many places in the Haarlemmermeer polder water can spring up which is as fresh as water from the dunes. So in the farm "het Botervat" on the Y road near the Kruisweg; in it I found as well in the driest periods as after much rain a quantity of chlorine of 35 to 37 mg. per litre, whereas in the same farm a well has been bored reaching just below the deep fen, in which the water contains an amount of chlorine of 235 mg. per litre. At numerous other spots of the Haarlemmermeer polder the presence of fresh-water in wells (which proved to be no rainwater, as I believed for some time) could be stated; it is also found at about one kilometre east of the just mentioned farm, besides on the Kruisweg between the Sloten road and the Sloter Tocht, on the Sloten road near the Slaperdijk. On the other hand the water in wells in the north-western part of that polder, in which the deep layer of fen is entirely absent, is brackish everywhere.

The water flowing under the compact alluvial cover from the higher environs of the Haarlemmermeer polder has there, as I showed in my former communication, a tendency to rise and so the salt-retaining property of the fen can here act in an opposite direction as in the shallower polders in which the vertical component of the water is directed downward.

As the old fen forms, as it were, a filter for sodium chloride, so in the shallower polders the "old sea-clay" by its high percentage of iron, keeps the water in the underground relatively free from sulphuric acid. The superficial fen in the Rieker polder contains so much compounds of sulphur that it has a very strong smell of sulphuretted hydrogen, when freshly dug. Water squeezed out from it proved on analysis by Dr. SCHOORL to contain no less than 408 mg.

SO_3 per litre, while that from a well, 44 M. deep, near the place where the fen had been taken, contained only 17 mg. SO_3 per litre. Already immediately below the clay, at a depth of ten metres below the meadow, the amount of SO_3 has become so small. In the iron-containing layer of clay, pyrites is namely formed by the well-known minerogenetic process, with previous reduction of the SO_3 compounds in the fen, which reduction takes place here with the help of sulphur-bacteria by which the freshly denuded fen is coloured yellowish.

Pyrites can indeed be shown to occur in the clay. And so this difference in the amount of SO_3 between the upper water and the deep groundwater is a proof for the origin of the latter from above instead of against it, as has been supposed.

Chemistry. — Prof. C. A. LOBRY DE BRUYN also in the name of Dr. S. TYMSTRA Bz. read a paper: "*The mechanism of the salicylacid synthese.*"

(This paper will not be published in these Proceedings).

Chemistry. — Prof. C. A. LOBRY DE BRUYN presents a paper of Dr. J. J. BLANKSMA: "*On the intramolecular oxydation of a SH-group bound to benzol by an orthostanding NO_2-group.*"

(This paper will not be published in these Proceedings).

Chemistry. — Prof. C. A. LOBRY DE BRUYN presents a paper of J. M. M. DORMAAR: "*The inversion of carron and eucarron in carvacrol and its velocity.*"

(This paper will not be published in these Proceedings).

(June 24, 1904).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday June 25, 1904.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 25 Juni 1904, Dl. XIII).

CONTENTS.

The following papers were read:

Mathematics. — Remarks on the paper of Mr. KLUYVER on page 305 of Vol VI. "*Series derived from the series* $\Sigma \frac{\mu(m)}{m}$" by EDMUND LANDAU in Berlin.

(Communicated in the meeting of May 28, 1904).

In a paper recently published[1]) Mr. KLUYVER treats the infinite series

$$\sum_{m=0}^{\infty} \frac{\mu(mb+h)}{mb+h} = \frac{\mu(h)}{h} + \frac{\mu(b-h)}{b+h} + \frac{\mu(2b-h)}{2b+h} + \ldots \ldots \quad (1)$$

where b and h are two positive integers and where h can be regarded as $\leqq b$ without limiting the generality. However, this research has to be taken only in a heuristic respect; it does not furnish the proof that series (1) converges, i. e. that for every pair of values b, h

$$\lim_{z=\infty} \sum_{m=0}^{z} \frac{\mu(mb+h)}{mb+h} \quad \ldots \ldots \ldots \ldots \quad (2)$$

exists. [2])

The methods applied by me in the paper [3]) "On the prime numbers of an arithmetical progression" ("Ueber die Primzahlen einer arithmetischen Progression") however allow such a proof to be made which will be shown in § 2—7 of this paper, after I have reminded my readers in § 1 of some theorems still known; at the same time we shall find an expression for the limit (2) i. e. the sum of the infinite series (1) in finite form. In §§ 8—9 a conclusion is drawn on the distribution of the numbers of an arithmetic progression for which $\mu(n) = +1$ resp. -1; this justifies a supposition expressed by Mr. KLUYVER at the end of his paper.

§ 1. Let $\chi_1(n)$, $\chi_2(n), \ldots, \chi_{\varphi(b)}(n)$ be the $\varphi(b)$ characters of the group of the classes of residues modulo b prime to b, of which $\chi_1(n)$ be the principal character (Hauptcharakter). If n and b have a common divisor we may understand by $\chi_1(n), \chi_2(n), \ldots, \chi_{\varphi(b)}(n)$ the value zero. Let moreover $L_\nu(s)$ for $\nu = 1, 2, \ldots, \varphi(b)$ denote the analytic function determined by the DIRICHLET series

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[1]) These Proc. VI p. 305.

[2]) Only for the case $b=1$, $h=1$ this was already known and from this ensues directly, as Mr. KLUYVER states at the beginning of his paper, the correctness of the statement for any b and $h=b$, but not for the general case.

[3]) Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wien, mathematisch-naturwissenschaftliche Klasse, Bd. 112, Abt. 2a, 1903, S. 493—535.

$$\sum_{n=1}^{\infty} \frac{\chi_\nu(n)}{n^s}$$

As is known this series converges, in case $\nu = 1$, for $\Re(s) > 1$, and in case $\nu = 2, \ldots, \varphi(b)$, for $\Re(s) > 0$.

The equation holding good for $\Re(s) > 1$ and every $\nu (= 1, \ldots, \varphi(b))$

$$L_\nu(s) = \sum_{n=1}^{\infty} \frac{\chi_\nu(n)}{n^s} = \prod_p \frac{1}{1 - \frac{\chi_\nu(p)}{p^s}}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where p passes through all prime numbers, shows that no $L_\nu(s)$ possesses a zero with real part > 1. The equation (3) gives for $\nu = 1$

$$L_1(s) = \prod_p \frac{1}{1 - \frac{1}{p^s}} \prod_{p/b} \left(1 - \frac{1}{p^s}\right) = \zeta(s) \prod_{p/b} \left(1 - \frac{1}{p^s}\right), \quad (4)$$

where p passes through all prime factors of b. From (4) it follows that $L_1(s)$ may be continued across the right line $\Re(s) = 1$ and that it possesses in $s = 1$ a pole, so that

$$\lim_{s=1} \frac{1}{L_1(s)} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Further DIRICHLET [1]) has expressed the quantities

$$L_2(1) = \sum_{n=1}^{\infty} \frac{\chi_2(n)}{n}, \quad \ldots, \quad L_{\varphi(b)}(1) = \sum_{n=1}^{\infty} \frac{\chi_{\varphi(b)}(n)}{n}$$

in finite form by logarithms and trigonometric functions and proved moreover — what did not at all ensue from it — that each of the afore mentioned $\varphi(b) - 1$ quantities is different from zero. So the limits

$$\lim_{s=1} \frac{1}{L_2(s)} = \frac{1}{L_2(1)}, \ldots, \lim_{s=1} \frac{1}{L_{\varphi(b)}(s)} = \frac{1}{L_{\varphi(b)}(1)} \quad . \quad . \quad . \quad (6)$$

do exist.

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[1]) "Proof of the theorem that every unlimited arithmetical progression of which the first term and difference are integers without common factor, contains an infinite number of prime numbers," Transactions of the Royal Prussian Academy of Sciences at Berlin, 1837, p. 45—71; Works, Vol. 1, 1889, p. 313—342.

(„Beweis des Satzes, dass jede unbegrenzte arithmetische Progression, deren erstes Glied und Differenz ganze Zahlen ohne gemeinschaftlichen Factor sind, unendlich viele Primzahlen enthält", Abhandlungen der Königlich Preussischen Akademie der Wissenschaften zu Berlin, 1837, S. 45—71; Werke, Bd. 1, 1889, S. 313—342).

Mrs. Hadamard and de la Vallée Poussin have proved that no $L_\nu(s)$ possesses on the right line $\Re(s)=1$ a zero, so that $\frac{1}{L_\nu(s)}$ is regular for every ν on the right line $\Re(s)=1$. In the quoted paper I have proved [1]) the more general theorem: There is a positive number α so that, when $s=\sigma+ti$, in the region

$$t \geqq 3,\ 1-\frac{1}{\log^\alpha t} \leqq \sigma \leqq 2$$

each of the $\varphi(b)$ functions $L_\nu(s)$ differs from zero and fulfills the inequality

$$\left|\frac{1}{L_\nu(s)}\right| < \log^\alpha t.$$

§ 2. Now I denote by $M_{b,h}(s)$ that analytic function which is determined by the Dirichlet series

$$\sum_{m=0}^{\infty} \frac{\mu(mb+h)}{(mb+h)^s},$$

convergent at least for $\sigma=\Re(s)>1$ and I shall show that $M_{b,h}(s)$ can be brought in a very simple connexion with the functions $L_\nu(s)$.

Let the greatest common factor (b,h) of b and h be put equal to d. Without limiting the generality d can be regarded as being without quadratic factor; for in the other case $\mu(mb+h)=0$, so every member of the infinite series (1) is equal to zero.

I. Let then be $d=1$, so h prime to b. Then there is an integer h_1, (determinate modulo b) for which

$$h_1 h \equiv 1 \ (mod.\ b).$$

Now ensues from (3) for $\sigma=\Re(s)>1$

$$\frac{1}{L_\nu(s)}=\prod_p\left(1-\frac{\chi_\nu(p)}{p^s}\right)=\sum_{n=1}^{\infty}\frac{\chi_\nu(n)\mu(n)}{n^s} \quad . \quad . \quad . \quad . \quad (7)$$

If we multiply (7) by $\chi_\nu(h_1)$ and sum up with respect to all values of ν we get

$$\sum_{\nu=1}^{\varphi(b)}\frac{\chi_\nu(h_1)}{L_\nu(s)}=\sum_{\nu=1}^{\varphi(b)}\chi_\nu(h_1)\sum_{n=1}^{\infty}\frac{\chi_\nu(n)\mu(n)}{n^s}=\sum_{n=1}^{\infty}\frac{\mu(n)}{n^s}\sum_{\nu=1}^{\varphi(b)}\chi_\nu(h_1 n). \quad . \quad (8)$$

Now according to the fundamental property of the characters the sum $\sum\limits_{\nu=1}^{\varphi(b)}\chi_\nu(l)$ differs from zero only, and then is equal to $\varphi(b)$, when $l\equiv 1$ (mod. b); hence

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[1]) l. c., page 521. Here I put the greater of the two numbers c_{21} and $c_{31}=\alpha$.

$$\sum_{\nu=1}^{\varphi(b)} \chi^{\nu}(h_1 n) \begin{cases} = \varphi(b), \text{ if } h_1 n \equiv 1, \text{ i. e. } n \equiv h \ (mod.\ b) \\ = 0, \text{ if } h_1 n \not\equiv 1, \text{ i. e. } n \not\equiv h \ (mod.\ b) \end{cases}$$

So (8) changes into

$$\sum_{\nu=1}^{\varphi(b)} \frac{\chi_\nu(h_1)}{L_\nu(s)} = \varphi(b) \sum_{m=0}^{\infty} \frac{\mu(mb+h)}{(mb+h)^s} = \varphi(b)\, M_{b,h}(s);$$

when with the aid of

$$\chi_\nu(h_1)\, \chi_\nu(h) = \chi_\nu(h_1 h) = \chi_\nu(1) = 1$$

we eliminate h_1, we get

$$M_{b,h}(s) = \frac{1}{\varphi(b)} \sum_{\nu=1}^{\varphi(b)} \frac{1}{\chi_\nu(h) L_\nu(s)} \quad \ldots\ldots \quad (9)$$

II. Let d be > 1 and let b be put equal to dB, h to dH, so that B and H are prime to each other. Evidently

$$\mu(mb+h) = \mu\Big(d(mB+H)\Big) \begin{cases} = \mu(d)\, \mu(mB+H) \\ \text{or} = 0, \end{cases}$$

according to $mB+H$ being prime to d or not. Hence

$$M_{b,h}(s) = \sum_{m=0}^{\infty} \frac{\mu(mb+h)}{(mb+h)^s} = \frac{\mu(d)}{d^s} \sum_{m=0}^{\infty}{}' \frac{\mu(mB+H)}{(mB+H)^s}, \quad \ldots \quad (10)$$

where the sign Σ' denotes that m assumes only those values, for which $mB+H$ is prime to d. If $m_1 \equiv m_2$ (mod. d), then it is evident that $m_1 B + H$ and $m_2 B + H$ are simultaneously prime to d or not. So those m distribute themselves in certain arithmetical progressions modulo d; i.e. among the d progressions $m \equiv 0, 1, \ldots, d-1$ (mod. d) m has in certain progressions, let the number be ϱ, to pass through all numbers $\geqq 0$. This ϱ is the number of those among the d numbers in $mB+H$, $(m = 0, 1, \ldots, d-1)$, which are prime to d; this number is known to be $\dfrac{(B,d)\varphi(d)}{\varphi(B,d)}$. When the corresponding values of m are denoted by $m_1, \ldots, m_\lambda, \ldots, m_\varrho$ and $m_\lambda B + H$ is put equal to h_λ, $(\lambda = 1, \ldots, \varrho)$, then every h_λ is prime to d and — on account of $(B, H) = 1$ — to B, so to $b = dB$ and situated between 0 (excl.) and b (excl.) (as

$$0 < H \leqq h_\lambda = m_\lambda B + H \leqq (d-1) B + H = b - B + H \leqq b$$

and b itself is not prime to b). The corresponding values of $mB+H$ are

$$(m_\lambda + ld) B + H = lb + h_\lambda,$$

where l assumes all integer values $\geqq 0$. In other words on the rightside of (10), when it is written short

$$\frac{\mu(d)}{d^s}\sum_{k=1}^{\infty}\frac{\mu(k)}{k^s}.$$

k assumes all positive numbers belonging to certain ϱ progressions of the form $lb + h_\lambda$, $(\lambda = 1, 2, \ldots, \varrho)$, where $0 < h_\lambda < b$ and $(b, h_\lambda) = 1$; so

$$M_{b,h}(s) = \frac{\mu(d)}{d^s}\sum_{\lambda=1}^{\varrho} M_{b,h_\lambda}(s). \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and from the result (9) of the case (I) follows after application to the single members on the right side of (11)

$$M_{b,h}(s) = \frac{1}{\varphi(b)}\frac{\mu(d)}{d^s}\sum_{\lambda=1}^{\varrho}\sum_{\chi=1}^{\varphi(b)}\frac{1}{\chi(h_\lambda)L_\chi(s)} \quad . \quad . \quad . \quad . \quad (12)$$

Of (12) the equation (9) is a special case, as for $d = 1$

$$B = b, \ H = h, \ \varrho = 1, \ h_1 = h.$$

In the following the equation (12) may always be taken as basis.

§ 3. The equation (12) proved above for $\sigma > 1$ furnishes in connection with the properties of the functions $L_\chi(s)$ quoted in § 1 firstly the analytic continuation of $M_{b,h}(s)$ across the right line $\sigma = 1$. It teaches us that all points of the right line, $s = 1$ included, are regular places. From the theorem quoted at the end of § 1 follows more accurately that for $t \geqq 3$ and $1 - \frac{1}{log^\alpha t} \leqq \sigma \leqq 2$ the function $M_{b,h}(s)$ is regular and satisfies there the inequality

$$M_{b,h}(s) \leqq \frac{1}{\varphi(b)}\frac{1}{d^\sigma}\sum_{\lambda=1}^{\varrho}\sum_{\chi=1}^{\varphi(b)}\frac{1}{|L_\chi(s)|} < \frac{1}{\varphi(b)} \cdot 1 \cdot \varrho \cdot \varphi(b)\, log^\alpha t = \varrho\, log^\alpha t.$$

Let now a number $a > \alpha$ be chosen in such a way that in the first place for any $t \geqq 3$ we have

$$\varrho\, log^\alpha t < log^a t$$

and in the second place $\frac{1}{log^a 3}$ is smaller than the distance of the right line $\sigma = 1$ from any singular point of $M_{b,h}(s)$, the imaginary part of which lies between $-3i$ and $3i$. If moreover the equation

$$|M_{b,h}(\sigma + ti)| = |M_{b,h}(\sigma - ti)|$$

is paid attention to, then ensues from the preceding:

The function $M_{b,h}(s)$ is regular in that part of the plane lying on the right side of the continuous curve (incl. the curve itself)

$$\begin{cases} \sigma = 1 - \dfrac{1}{\log^a t} & \text{for } t \geqq 3, \\ \sigma = 1 - \dfrac{1}{\log^a 3} & \text{for } -3 \leqq t \leqq 3, \\ \sigma = 1 - \dfrac{1}{\log^a (-t)} & \text{for } t \leqq -3 \end{cases}$$

and for $t \geqq 3,\ 1 - \dfrac{1}{\log^a t} \leqq \sigma \leqq 2$ it is

$$|M_{b,h}(\sigma + ti)| = |M_{b,h}(\sigma - ti)| < \log^a t\,. \quad . \quad . \quad . \quad . \qquad (13)$$

§ 4. In § 2 of my paper [1] "On the function $\mu(k)$ occurring in the theory of numbers" ("Ueber die zahlentheoretische Funktion $\mu(k)$") the relation

$$\sum_{k=1}^{x} \mu(k) \log \frac{x}{k} = \frac{1}{2\pi i} \int_{2-x^2 i}^{2+x^2 i} \frac{x^s}{s^2} \sum_{k=1}^{\infty} \frac{\mu(k)}{k^s}\, ds + O(1)$$

is developed, where the integral is taken along the straight line. In like manner we find here, when the sign Σ' means that k has but to assume all those numbers of the interval of summation which are $\equiv h$ (mod. b),

$$\sum_{k=1}^{x}{}' \mu(k) \log \frac{x}{k} = \frac{1}{2\pi i} \int_{2-x^2 i}^{2+x^2 i} \frac{x^s}{s^2} \sum_{k=1}^{\infty}{}' \frac{\mu(k)}{k^s}\, ds + O(1)$$

$$= \frac{1}{2\pi i} \int_{2-x^2 i}^{2+x^2 i} \frac{x^s}{s^2} M_{b,h}(s)\, ds + O(1)\,. \quad . \quad . \qquad (14)$$

§ 5. We now apply CAUCHY's theorem to the integral $\int \frac{x^s}{s^2} M_{b,h}(s)\, ds$ taken along the closed path $ABCDEFA$, where $A = 2 - x^2 i$, $B = 2 + x^2 i$, $C = 1 - \dfrac{1}{\log^a (x^2)} + x^2 i$, $D = 1 - \dfrac{1}{\log^a 3} + 3i$, $E = 1 - \dfrac{1}{\log^a 3} - 3i$, and $F = 1 - \dfrac{1}{\log^a (x^2)} - x^2 i$, where the segments AB, BC, DE, FA are rectilinear, CD denotes the arc of the curve

$$s = 1 - \frac{1}{\log^a t} + ti \qquad (x^2 \geqq t \geqq 3)$$

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[1] Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wien, math.-naturw. Klasse, Bd. 112, Abt. 2a, 1903, S. 537—570.

and EF the arc of the curve

$$s = 1 - \frac{1}{\log^a(-t)} + ti \qquad (-3 \geqq t \geqq -x^2)$$

As according to § 3 in this closed region and on the boundary the function to be integrated is regular, the CAUCHY theorem furnishes for the integral appearing in (14)

$$\int\limits_{2-x^2 i}^{2+x^2 i} \frac{x^s}{s^2} M_{b,h}(s)\,ds = \int\limits_{AB} = \int\limits_{AF} + \int\limits_{FE} + \int\limits_{ED} + \int\limits_{DC} + \int\limits_{CB} \quad . \quad . \quad (15)$$

Now I have proved in § 10 of my paper on the arithmetic progression for a certain function $K(s)$ that, when integrating $\frac{x^s}{s^2} K(s)$ along the same given path, we have

$$\int\limits_{AF} + \int\limits_{FE} + \int\limits_{ED} + \int\limits_{DC} + \int\limits_{CB} = O\left(xe^{-\sqrt[c]{\log x}}\right)$$

where c denotes a positive constant[1]). Concerning that function $K(s)$ I have made use l. c. only of the fact that it is regular on the path of integration and satisfies for $t \geqq 3$, $1 - \frac{1}{\log^a t} \leqq \sigma \leqq 2$ the inequality

$$|K(\sigma + ti)| = |K(\sigma - ti)| < \log^a t.$$

As now according to (13) the function $M_{b,h}(s)$ has exactly these properties, we have for the present case the expression (15)

$$= O\left(xe^{-\sqrt[c]{\log x}}\right).$$

This gives after substitution in (14)

$$\sum_{k=1}^{x}{}' \mu(k) \log \frac{x}{k} = O\left(xe^{-\sqrt[c]{\log x}}\right) \quad . \quad . \quad . \quad . \quad . \quad (16)$$

§ 6. Just as in § 4 of my paper on the function $\mu(k)$ it could be concluded from

$$\sum_{k=1}^{x} \mu(k) \log \frac{x}{k} = O\left(xe^{-\sqrt[11]{\log x}}\right)$$

that

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[1]) May be $c = 3a$.

$$\sum_{k=1}^{x} \mu(k) = O\left(xe^{-\sqrt[12]{\log x}}\right)$$

we find here out of (16)

$$\sum_{k=1}^{x}{}' \mu(k) = O\left(xe^{-\sqrt[\gamma]{\log x}}\right)$$

where γ denotes a certain positive constant [1]).

Thus for every n we find

$$\lim_{x=\infty} \frac{\log^n x}{x} \sum_{k=1}^{x}{}' \mu(k) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

§ 7. In § 5 l.c. we found out of

$$\lim_{x=\infty} \frac{\log^n x}{x} \sum_{k=1}^{x} \mu(k) = 0$$

that the infinite series

$$\sum_{k=1}^{\infty} \frac{\mu(k) \log^n k}{k^{1+ti}}$$

converges for every pair of real values n, t; in the same way we find out of (17): the infinite series

$$\sum_{k=1}^{\infty}{}' \frac{\mu(k) \log^n k}{k^{1+ti}} = \sum_{m=0}^{\infty} \frac{\mu(mb+h) \log^n (mb+h)}{(mb+h)^{1+ti}}$$

converges for every pair of real values n, t. Here is proved in particular for $n=0$, $t=0$ the convergence supposed by Mr. Kluyver of the infinite series

$$\sum_{m=0}^{\infty} \frac{\mu(mb+h)}{mb+h},$$

i. e. the existence of the quantity designated by him as $T_{b,h}$.

As now its existence is proved, it is easy to express its value in finite form. As is known it follows from the convergence of $\sum\limits_{n=1}^{\infty} \frac{u_n}{n}$, that

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[1]) May be $\gamma = c + 1$.

approaching from the right side $\lim\limits_{s=1} \sum\limits_{n=1}^{\infty} \frac{u_n}{n^s}$ exists and is equal to $\sum\limits_{n=1}^{\infty} \frac{u_n}{n}$. Making use of (12), (5) and (6) we find therefore

$$T_{b\,h} = \sum_{m=0}^{\infty} \frac{\mu\,(mb+h)}{mb+h} = \lim_{s=1} \sum_{m=0}^{\infty} \frac{\mu\,(mb+h)}{(mb+h)^s} = \lim_{s=1} M_{b,h}\,(s)$$

$$= \frac{1}{\varphi\,(b)} \frac{\mu\,(d)}{d} \sum_{\lambda=1}^{\rho} \sum_{\nu=2}^{\varphi(b)} \frac{1}{\chi_\nu\,(h_\lambda)\, L_\nu\,(1)}\,.$$

§ 8. In this paragraph must be proved the lemma:

When $Q_{b,h}\,(x)$ denotes the number of the integers without quadratic factors $\leqq x$ belonging to the linear form $mb+h$ (where $(b,h)=d$ is supposed to be without quadratic factors [1])), then

$$\lim_{x=\infty} \frac{Q_{b,h}\,(x)}{x}$$

exists and has a value differing from zero.

I. Let us suppose $(b,h)=d=1$ first. Let $A_{b,h,n}(x)$ denote the number of those integers m which fulfill the congruence

$$mb+h \equiv 0\ (mod.\ n)$$

and the unequalities

$$0 \leqq m \leqq \frac{x-h}{b}$$

(i. e. $1 \leqq mb+h \leqq x$). Then it is evident when n possesses with b a common factor that on account of $(b,h)=1$ the congruence cannot be solved; so

$$A_{b,h,n}\,(x) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

When however $(n,b)=1$ the congruence has modulo n exactly one root; so the number of roots between 0 and $\frac{x-h}{b}$ is equal to $\left[\frac{x-h+b}{bn}\right]$ or $\left[\frac{x-h+b}{bn}\right]+1$, i. e.

$$A_{b,h,n}\,(x) = \frac{x}{bn} + \vartheta \qquad (-1 < \vartheta < 2). \quad . \quad . \quad . \quad . \quad (19)$$

Now it is evident that when k passes through every number the

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[1]) In the opposite case $Q_{b,h}\,(x)=0$.

square of which divides l

$$\Sigma\, \mu(k) = 1 \text{ or } 0,$$

according to l being without or with quadratic factor; for those k's are the divisors of the greatest number g the square of which divides l, so that

$$\Sigma\, \mu(k) = \sum_{k/g} \mu(k) = 1 \text{ or } = 0$$

according to $g = 1$, i. e. l being with or without quadratic factors. Hence

$$Q_{b,h}(x) = \sum_{m=0}^{\left[\frac{x-h}{b}\right]} \sum \mu(k),$$

where k passes through every integer the square of which divides $mb + h$. If we invert the order of summation, k passes from 1 to $[\sqrt{x}]$, and every $\mu(k)$ appears as often as there are multiples of k^2 in the progression $mb + h$ between 1 and x, i. e. $A_{b,h,k^2}(x)$ times. So according to (18) and (19)

$$Q_{b,h}(x) = \sum_{k=1}^{[\sqrt{x}]} \mu(k)\, A_{b,h,k^2}(x) = \sum_{k=1}^{[\sqrt{x}]}{}' \mu(k) \left(\frac{x}{bk^2} + \vartheta\right),$$

where the sign Σ' indicates that k has but to pass through the numbers $\leqq \sqrt{x}$ prime to b. Hence

$$Q_{b,h}(x) = \frac{x}{b} \sum_{k=1}^{[\sqrt{x}]}{}' \frac{\mu(k)}{k^2} + O(\sqrt{x}) = \frac{x}{b}\left(\sum_{k=1}^{\infty}{}' \frac{\mu(k)}{k^2} + O\left(\frac{1}{\sqrt{x}}\right)\right) + O(\sqrt{x})$$

$$= \frac{x}{b} \sum_{k=1}^{\infty}{}' \frac{\mu(k)}{k^2} + O(\sqrt{x}) = \frac{x}{b} \prod_{p}{}' \left(1 - \frac{1}{p^2}\right) + O(\sqrt{x}),$$

where p passes through every prime number not dividing b; on account of

$$\prod_{p} \left(1 - \frac{1}{p^2}\right) = \frac{1}{\zeta(2)} = \frac{6}{\pi^2}$$

we find

$$Q_{b,h}(x) = x \frac{6}{\pi^2} \frac{1}{b \prod\limits_{p/b} \left(1 - \frac{1}{p^2}\right)} + O(\sqrt{x}), \quad . \quad . \quad . \quad (20)$$

where p passes through the prime factors of b, so

$$\lim_{x=\infty} \frac{Q_{b,h}(x)}{x} = \frac{6}{\pi^2} \frac{1}{b \prod\limits_{p/b} \left(1 - \frac{1}{p^2}\right)} > 0. \quad . \quad . \quad . \quad . \quad (21)$$

It is worth noticing that this limit is independent of h.

II. When $d > 1$, then b being equal to dB and h to dH the numbers $mb + h \leqq x$ without a quadratic factor are identical with the numbers $d(mB + H) \leqq x$, where $mB + H$ is without quadratic factor and prime to d. Now the numbers $mB + H$ (comp. § 2) prime to d break up into $\varrho = \frac{(B,d)\varphi(d)}{\varphi(B,d)}$ arithmetic progressions with the difference b and the first term h_λ, $(\lambda = 1, 2, \ldots, \varrho)$, h_λ being prime to b; the number of the integers without quadratic factors $\leqq \frac{x}{d}$ in each of these progressions amounts according to (20) to

$$Q_{b,h_\lambda}\left(\frac{x}{d}\right) = \frac{x}{d} \frac{6}{\pi^2} \frac{1}{b \prod\limits_{p/b} \left(1 - \frac{1}{p^2}\right)} + O(\sqrt{x});$$

hence

$$Q_{b,h}(x) = \sum_{\lambda=1}^{\varrho} Q_{b,h_\lambda}\left(\frac{x}{d}\right) = x \, . \, \frac{6}{\pi^2} \frac{(B,d)\,\varphi\,(d)}{db \prod\limits_{p/b} \left(1 - \frac{1}{p^2}\right) \varphi(B,d)} + O(\sqrt{x}),$$

$$\lim_{x=\infty} \frac{Q_{b,h}(x)}{x} = \frac{6}{\pi^2} \frac{(B,d)\,\varphi\,(d)}{db \prod\limits_{p/b} \left(1 - \frac{1}{p^2}\right) \varphi(B,d)} > 0. \quad . \quad . \quad (22)$$

§ 9. We now denote by $R_{b,h}(x)$ resp. by $S_{b,h}(x)$ the number of integers $mb + h \leqq x$ containing an even, resp. an odd number of distinct prime factors and we put

$$P_{b,h}(x) = \sum_{k=1}^{x}{}' \mu(k),$$

where Σ' denotes that k passes through every number $mb + h \leqq x$. Then it is evident that

$$R_{b,h}(x) - S_{b,h}(x) = \sum_{k=1}^{x}{}' \mu(k) = P_{b,h}(x)$$

and

$$R_{b,h}(x) + S_{b,h}(x) = \sum_{k=1}^{x}{}' \mu^2(k) = Q_{b,h}(x),$$

so

$$\frac{R_{b,h}(x)}{x} = \frac{1}{2}\left(\frac{Q_{b,h}(x)}{x} + \frac{P_{b,h}(x)}{x}\right) \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and

$$\frac{S_{b,h}(x)}{x} = \frac{1}{2}\left(\frac{Q_{b,h}(x)}{x} - \frac{P_{b,h}(x)}{x}\right) \quad . \quad . \quad . \quad . \quad . \quad (24)$$

As now according to (17) (after substitution of $n=0$)

$$\lim_{x=\infty} \frac{P_{b,h}(x)}{x} = 0$$

and on the other hand according to (21) and (22) when the limit is put equal to $L_{b,h}$,

$$\lim_{x=\infty} \frac{Q_{b,h}(x)}{x} = L_{b,h} > 0,$$

we find from (23) and (24)

$$\lim_{x=\infty} \frac{R_{b,h}(x)}{x} = \frac{1}{2} L_{b,h},$$

$$\lim_{x=\infty} \frac{S_{b,h}(x)}{x} = \frac{1}{2} L_{b,h},$$

so

$$\lim_{x=\infty} \frac{R_{b,h}(x)}{S_{b,h}(x)} = 1.$$

This confirms the supposition expressed by Mr. KLUYVER at the conclusion of his paper:

If we divide the integers $mb+h$ without quadratic factors into two classes according to their consisting of an even or an odd number of prime factors, the ratio of the numbers of integers minor to x of both classes converges for $x=\infty$ towards the limit unity.

Berlin, May 23rd 1904.

Crystallography. — *"On Benzylphtalimide and Benzylphtal-iso-imide."* By Dr. F. M. JAEGER. (Communicated by Professor A. P. N. FRANCHIMONT.

(Communicated in the meeting of May 28, 1904).

Some time ago a preparation was forwarded to me by Prof. Dr. GABRIËL of Berlin, of a *Benzylphtalimide*[1]: $C_6H_4.(CO)_2.N(CH_2.C_6H_5)$ melting point 115°,5, which he had obtained by synthesis. A short time afterwards, through the kindness of Prof. HOOGEWERFF, at Delft,

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[1] Berl. Ber. **20.** 2227.

I obtained some crystals of *Benzylphtal-iso-imide*[1]) melting point 82°,5. As both isomeric compounds are, structurally, closely related, I thought it a matter of importance to investigate their crystallographical symmetry.

a). *Benzylphtalimide.* (m.p. $115\frac{1}{2}$°).

From a mixture of ether and alcohol I obtained this compound in large, very transparent and lustrous crystals of a somewhat rhombohedric habitus. In many cases they are more flattened. The power of crystallising from the said solvent is extraordinarily great.

The symmetry is *triclino-pinacoidal:* the axial elements are:

$$a : b : c = 0{,}8443 : 1 : 1{,}3600$$

$A = 101° \; 51'$. $\qquad \alpha = 108° \; 24'$.

$B = 116 \; 51\frac{1}{2}'$. $\qquad \beta = 120° \; 7'$.

$C = \; 80° \; 45\frac{1}{2}'$. $\qquad \gamma = \; 73° \; 8'$.

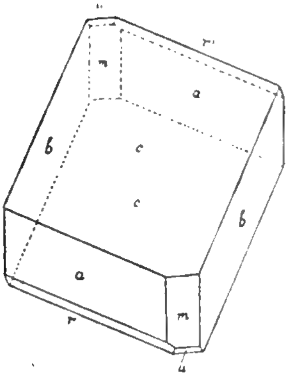

Fig. 1.

Forms observed are $c = \{001\}$, predominating; $a = \{100\}$ and $b = \{010\}$, about equally much developed; $m = \{110\}$, narrow; $r' = \{\bar{1}01\}$ small and narrow, sometimes a little broader; $u = \{\bar{1}11\}$, small and much less conspicuous.

The crystals are represented in fig. 1; the measured and calculated angles are annexed:

	Measured :	Calculated :
*$a : b = (100) : 010$	$= 99 \; 14\frac{1}{2}'$	--
*$a : c = (100) : (001)$	$= 63 \; 8\frac{1}{2}$	—
*$b : c = (010) : (001)$	$= 78 \; 9$	—
*$m : b = (110) : (010)$	$= 58 \; 19\frac{1}{2}$	—
*$c : r' = (001) : (\bar{1}01)$	$= 78 \; 59$	—
$a : m = (100) : (110)$	$= 40 \; 55$	$40° \; 55'$
$c : m = (001) : (110)$	$= 58 \; 22\frac{1}{2}$	$58 \; 17$
$a : r' = (100) : (10\bar{1})$	$= 37 \; 55$	$37 \; 55$
$b : r' = (010) : (\bar{1}01)$	$= 71 \; 35$	$71 \; 28$
$m : r' = (110) : (10\bar{1})$	$= 61 \; 53$	$62 \; 1$

The crystals cleave quite parallel {100} and {010}.

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[1]) Receuil d. Trav. Chim. d. Pays-Bas, T. **XIII**. 99.

When recrystallised from ether, very strongly refractive, hexagonally bounded little plates are obtained. On investigation it appears that these are *twin* crystals: $\{001\}$ is the twin-plane with a twin-axis standing normally on it.

In addition to $c = \{001\}$, $b = \{010\}$, $r' = \{\bar{1}01\}$ and $u' = \{1\bar{1}\bar{1}\}$, I noticed a form $q = \{01\bar{1}\}$; c is strongly developed, b and q are narrow, r' and u' are equally broad and well-formed. The planes of cleavage are the same as above.

There were also measured:

$q : b = (01\bar{1})_{(2)} : (010)_{(1)} = 23°58'$; calculated : $23°42'$.
$b : b = (010)_{(1)} : (010)_{(2)} = -19°23'$; calculated : $-19°28'$.
$r : r = (10\bar{1})_{(1)} : (10\bar{1})_{(2)} = 21°45'$; calculated : $22°2'$.
$c : q = (00\bar{1}) : (01\bar{1}) = 58°21'$; calculated : $58°9'$.

The nature of the twin-formation has, therefore, been sufficiently explained.

On $\{001\}$, the direction of the optical elasticity-axis is orientated nearly perpendicularly on the sides $(001) : (010)$; an axial image could not be observed.

The specific gravity of the crystals was determined by means of a **Thoulet**'s solution; $d = 1{,}343$, at $16°$ and consequently the topical axes, calculated according to the formule:

$$\chi = \left(\frac{a^2\ V}{c \sin\beta \sin\gamma \sin A}\right)^{1/3};\ \psi = \left(\frac{V}{ac \sin\beta \sin\gamma \sin A}\right)^{1/3};$$

$$\omega = \left(\frac{c^2\ V}{a \sin\beta \sin\gamma \sin A}\right)^{1/3},$$

in which $V = \frac{M}{d}$, if M represents the molecular weight, are equal to:

$$\chi : \psi : \omega = 4{,}8513 : 5{,}7458 : 7{,}8145.$$

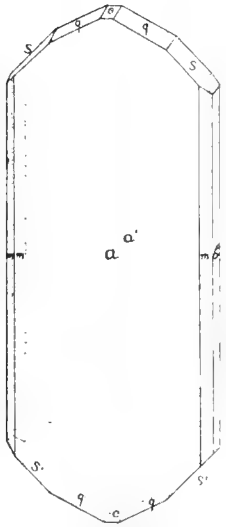

Fig. 2.

b.) During a cold winter night, I once obtained from a solution of the compound in *benzene* a second, *less stable* modification.

There were formed transparent hexagonal bounded little plates; the crystals were single and not twin crystals as in the former case. The melting point was situated at 115°; the little crystals, however, soon became opaque so that on warming a molecular transformation probably takes place. But I have only once succeeded in obtaining this modification.

It is *monoclino-prismatic*; the crystal parameters were calculated to be:

$$a : b : c = 0{,}8476 : 1 : 0{,}5092$$
$$\beta = 70^\circ 42'.$$

Forms observed: $a = \{100\}$, strongly predominating; $m = \{110\}$ and $b = \{010\}$, very narrow; $c = \{001\}$, very small and less conspicuous; $q = \{011\}$ and $s = \{021\}$ equally broadly developed.

$^*a : m = (100) : (110) =$	$38^\circ\ 39\frac{1}{2}'$	—
$^*a : q = (100) : (011) =$	$72\ \ 40$	—
$^*c : q = (001) : (011) =$	$25\ \ 40$	—
$s : q = (021) : (011) =$	$18\ \ 18$	$18^\circ\ 12'$
$b : m = (010) : (110) =$	$51\ \ 20$	$51\ \ 20\frac{1}{2}$.

A distinct cleavability was not found.

Therefore, *benzylphtalimide* is *dimorphous*. As regards the remarkable connection of this β-modification with the crystalline form of the *iso-imide* and with that of the α-modification, see the end of this article.

c). *Benzylphtal-iso-imide*. (m.p. $82\frac{1}{2}^\circ$).

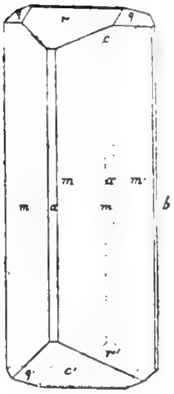

Fig. 3.

The crystals represented in Fig. 3 have been obtained from *anhydrous* ether; they are long-prismatic and here and there of a porcelain white. After some time, even if kept in the dark, they become quite opaque and look as if they were effloresced. The crystals, however, do not contain any co-crystallised solvent; probably some transformation as yet unknown, has taken place here.

The symmetry is *monoclino-prismatic*; the axial elements, when choosing the following elementary forms, are calculated to be:

$$a : b : c = 1{,}2303 : 1 : 0{,}5932$$
$$\beta = 71^\circ 46'.$$

Forms observed: $m = \{110\}$, strongly predominating; $c = \{\bar{2}01\}$, also well developed; $r = \{001\}$, fairly strongly; $q = \{011\}$, very plain; $a = \{100\}$ narrower; $b = \{010\}$ very narrow; between r and c there is still an orthodoma $\{h0k\}$, which was very little developed and could not be measured. I have retained the above letters for the notation of the forms, because the habitus of the crystal renders, at first sight, the use of $c=\{001\}$, $r=\{\bar{2}01\}$ and $q=\{\bar{2}11\}$, in many respects more obvious.

	Measured:	*Calculated:*
$^{*}a : m = (100):(110)$	$= 49^\circ\ 26^{2}/_{3}{}'$	—
$^{*}c : m = (\bar{2}01):(110)$	$= 68\ \ 25^{1}/_{2}$	—
$^{*}q : q = (011):(0\bar{1}1)$	$= 58\ \ 47^{1}/_{2}$	—
$c : r = (\bar{2}01):(001)$	$= 52\ \ 32^{1}/_{2}$	$52^\circ\ 40^{1}/_{2}{}'$
$c : a = (\bar{2}01):(100)$	$= 55\ \ 42^{1}/_{2}$	$55\ \ 33^{1}/_{2}$
$r : a = (001):(100)$	$= 71\ \ 44$	$71\ \ 46$
$c : q = (\bar{2}01):(011)$	$= 58\ \ \ 9^{1}/_{2}$	$58\ \ \ 7$
$q : r = (011):(001)$	$= 29\ \ 24$	$29\ \ 24$
$m : b = (110):(010)$	$= 40\ \ 49$	$40\ \ 33$
$m : m = (110):(\bar{1}10)$	$= 81\ \ \ 7$	$81\ \ \ 7$
$q : m = (011):(\bar{1}10)$	$= 53\ \ 34$	$53\ \ 28$

A distinct cleavability was not found; perhaps q is a plane of cleavage. The symmetrical extinction on the planes of $\{110\}$ amounts to about 3° with regard to the vertical axis; a further optical investigation was excluded.

The density of the crystals is *approximately*[1] 1,145; by putting in the above formula γ and $A = 90^\circ$ we obtain for the proportion of the topical axes:

$$\chi : \psi : \omega = 8.2234 : 6.6840 : 3.9650.$$

If we compare the crystal parameters of the two heteromorphous modifications of benzylphthalimide with the parameters of *benzylphtal-iso-imide* we at once notice an interesting relation between the crystalline forms of these substances.

Compound:	*Symmetry:*	*Crystal-parameters:*
α-Benzylphtalimide.	Triclino-pinacoidal.	$a:b:c = 0{,}8443:1:1{,}3600.(\alpha,\beta,\gamma;$ s.a.)
β-Benzylphtalimide.	Monoclino-prismatic.	$a:b:c = 0{,}8476:1:0{,}5092.\ \beta = 70^\circ 42'$
Benzylphtal-iso-imide.	Monoclino-prismatic.	$a:b:c = 1{,}2303$[2]$:1:0{,}5932.\ \beta = 71^\circ 46'$

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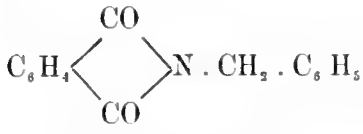
[1] *Approximately*, because the opaque crystals did not give a sufficient guarantee of *homogeneity* and because the substance is attacked on the surface by contact with THOULET's solution.

[2] It may be observed that the proportion $a:b$ would become for m $\{230$ 0,8202 : 1.

First of all the proportion $a : b$ is the same in both the α- and β-modification; a proof that these crystallographical forms are closely related to each other as regards their internal structure. I have noticed more than once this equality of two parameters in different modifications of a same compound; I met lately with a striking instance in the case of the red α- and the less stable yellow β-modification of the 1-3-4-*Dinitrodiethylaniline* notwithstanding the difference in the degree of symmetry. From a crystallographical point of view such modifications *must* always be dependent on each other, although that dependence may not always be immediately noticed.

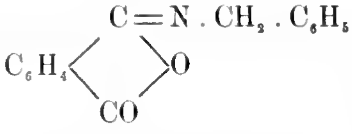
But then the very close relationship between the less stable β-modification and the crystalline form of the *iso-imide*, as is plainly shown from the analogous values for the angle β and the proportion $b : c$ is surprising in a high degree.

According to Drs. HOOGEWERFF and VAN DORP [1]) the isomerism of *imides* and *iso-imides* is based on a difference in the way of combination of the N-atom on the one side and the O-atom on the other:



Benzylphtalimide.

and



Benzylphtal-iso-imide.

The heteromorphous β-modification of the first substance now appears to be extremely closely related to the crystalline form of the first one owing to desmotropical change. Both phenomena, dimorphism and desmotropism therefore cause, respectively, an analogous change in the crystal-symmetry of α-benzylphthalimide.

The presumption raised by me some time ago that *crystallographic polymorphism* in a number of organic compounds might be caused by a *chemical isomerism* [2]), which would then account for the temporary existence of more stable atom-configurations is again a little more justified by the fact that above connection has been found.

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[1]) loco cit.

[2]) Kristallografische en Molekulaire Symmetrie van plaatsings-isomere Benzolderivaten. Proefschrift, Leiden, 1904, pag. 120, 121. Z. f. Kryst. 38. 600. (1904).

Botany. — *"On the development of the perithecium of Monascus purpureus Went and Monascus Barkeri Dang."* By Mr. H. P. KUYPER. Communicated by Prof. F. A. F. C. WENT.

(Communicated in the meeting of May 28, 1904).

With a view to the conflicting results obtained by WENT [1]), UYEDA [2]), BARKER [3]), IKENO [4]) and DANGEARD [5]) in their investigations concerning the development of the perithecium in the genus Monascus, it seemed desirable to study once more the forms investigated by them.

The results of an investigation of Monascus purpureus and Monascus Barkeri will be briefly communicated here; a more extensive article on the same subject will soon be published elsewhere.

Monascus purpureus was obtained by placing externally sterilised ang-cac grains in boxes containing a sterile nutrient, after which the mycelium developed in a few days.

Mr. BARKER had the very great kindness to send me a culture of the Samsu fungus, studied by him.

Both moulds were cultivated on sterilised bread or on thin plates of malt-gelatine. In the latter case the gelatine was dissolved in water of about 30° C. and the remaining mycelium, as well as the bread, fixed in KEISER's bichloride of mercury-acetic acid.

Microtomic sections 2—5 μ thick, of the material melted in paraffine, were stained with HEIDENHAIN's ferro-haematoxilin [6]) and partly restained for 1 or 2 minutes with a saturated aqueous solution of orange-G. In this case the slides were at once washed in absolute alcohol and then inclosed in canada balsam, as in the former case.

Monascus purpureus.

The two hyphae whose appearance precedes the development of a perithecium [7]), the pollinodium (le premier filament couvrant) [8]) and the ascogonium, do not seem to me to enter into open communication. The ascogonium divides into two cells, the anterior one of which soon becomes irrecognisable in later stages of development. This division of the ascogonium in some cases takes place at a

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[1]) Ann. des sc. nat. Bot. Ser. 8 T. I. 1895, p. 1.

[2]) The Bot. Magaz. vol. XV, 1902.

[3]) Ann. of Bot. vol. XVII, 1903, p. 167.

[4]) Ber. d. deutschen bot. Ges. Band XXI, 1903, p. 259.

[5]) Comptes rendus, Acad. Sc. T. CXXXVI, 1903, p. 1281.

[6]) 48—60 hours.

[7]) WENT l. c.

[8]) WENT l. c. pag. 3.

time, when it is entirely free from the pollinodium, whereas in other cases the division only occurs when the somewhat tapering and curved tip of the ascogonium lies alongside the pollinodium.

The posterior cell of the divided ascogonium, the final ascogonium, increases in size and is surrounded by a number of hyphae, having their origin under the ascogonium. The number of nuclei of the ascogonium increases at this stage; they lie spread in the foamy protoplasm.

Round a number of pairs of nuclei protoplasm accumulates so that free cells arise, having two nuclei each. The remaining protoplasm with the nuclei that have formed no cells, appears chiefly as a wall-layer. The nuclei of the free cells are bigger than those in the remaining protoplasm. The optic section of the free cells is often elliptic, sometimes also slightly bent in the middle of the major axis. The nucleus of the free cells consists of a grain which stains very strongly and which in some cases is surrounded by a zone of a lighter tint than the dense protoplasm of the cell.

Sometimes one finds in one cell more than two nuclei, mostly three, two of which are then bigger than the third.

From the examination of a number of preparations of various stages, I infer that the two nuclei of the free cells fuse, thus giving rise to one nucleus which is bigger than its components.

The development now proceeds fairly quickly, as a result of which one finds the uninucleate stage of the free cells pretty rarely in comparison with the binucleate. The development of all cells in an ascogonium is by no means simultaneous.

In a following stage the cell has grown and its protoplasm is less dense. It now contains a great number of very small nuclei. Next, some parts in the cell differentiate which apparently have no nuclei and consist of a homogeneous substance. These spots occupy the greater part of the cell-space and the small nuclei, which I would call chromatine grains, are pushed back into the layers of protoplasm between the unnucleate parts.

After this one sees one nucleus in the middle of the homogeneous, elliptic spots, which themselves are divided into a central part with the nucleus and a margin, having a lighter tint. This stage represents the first occurrence of spores in the free cells, mostly numbering from 6 to 8.

Between the spores one finds what Ikeno calls the "Wabenwände" [1], chokeful of chromatine grains, which can be distinctly seen separately.

These chromatine grains, now, soon disappear, while the nucleus of the spore divides, so that we find spores with 2, 4 and 8 nuclei.

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[1] Ikens l. c. p, 265.

Finally, probably by further division, the spore is entirely filled up with a granular, strongly staining mass.

In the meantime the wall of the spore has become more prominent. The number of spores, as was said above, is not constant and sometimes one finds only a single spore in one cell; in some cases however about 16 are counted, which then are smaller than the normal ones. When the spores are ripe, the free cell, as a unit, falls asunder and the spores become free in the ascogonium, the contents of which are further formed by the epiplasm of the free cells and the remainders of the protoplasm which in the beginning did not take part in the formation of free cells.

The spores do not fill up the ascogonium entirely but form together a peripheral layer. Between the spores one finds an intermediate substance, which is strongly stained by orange-G. So Ikeno's opinion that the polygonal appearance of the spores is an optic illusion, is correct [1])

Monascus Barkeri.

The first stages of the development of the perithecium of this form agree with those of the first species dealt with. Here also I have not been able to state an open communication between pollinodium and ascogonium. The latter, which here lies more parellel to the pollinodium, is also divided by a cell-wall into two cells, the posterior of which forms the final ascogonium. Only after it has become surrounded, at first rather loosely, by hyphae, it greatly increases in size. As long as it is small, sections of the whole perithecium — ascogonium with enveloping hyphae — show much resemblance with figures 17, 18 and 25 by Barker [2]). Together with the volume of the ascogonium the number of nuclei also increases. The ascogonium is now rich in protoplasm with many vacuoles. A first indication of a division of the protoplasm into parts — especially concerning the central part — is observed by the occasional appearance of long-stretched vacuoles. The nuclei are here and there seen in couples and also a few bigger nuclei are seen, which I presume to have been formed by the fusion of two of the smaller ones.

In a following stage free cells have formed, each with a single pretty large nucleus. This stage strongly reminds us of the corresponding one with M. purpureus. The protoplasm of the free cells is in most cases much denser than in former stages; in few cases

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1) Ikeno l. c. pag. 267.

2) Barker l. c.

only it is still foamy. It very often occurs that the free cells have assembled on one side of the ascogonium. Besides this one finds then in the ascogonium a fairly strongly developed lining layer of protoplasm and one or a few very large vacuoles. This condition reminds us of figs. 22 and 29 of BARKER. The protoplasm which has taken no part in the formation of free cells contains very few or no nuclei, so that it is probable that several nuclei soon degenerate.

The single nucleus of a free cell now successively undergoes three divisions, so that at last eight nuclei are present. The two nuclei after the first division and the four after the second, do not always divide at the same moment, so that also cells with 3, 5, 6 and 7 nuclei are found, but then in the first case e.g. one of the three nuclei is bigger than the other two.

When two divisional nuclei — here again consisting of a strongly staining grain — have arrived at a certain distance from each other, one often finds between them a more or less complete band of a somewhat lighter colour than the nuclei themselves but darker than the protoplasm of the free cell. These divisional figures agree pretty well with IKENO's representations for Taphrina Cerasi [1]).

After the eight nuclei have formed, spores arise with the nuclei as centres. These spores become free in the ascogonium and further behave like those of Monascus purpureus.

The manner in which in the two forms described, the nuclei for the spores are developed, differs in important points, but agrees in a remarkable degree with what has been described by IKENO for Taphrina Kusanoi and T. Cerasi [2]).

Both forms agree in this respect that in the ascogonium free cells are formed with originally two nuclei, which fuse into one, from which single nucleus the nuclei of the spores arise. This has induced me to see in the free cells in the ascogonium of the genus Monascus the homologon of an ascus, especially on account of DANGEARD's investigations on the Ascomycetes [3]).

With the remaining Ascomycetes, e.g. Pyronema confluens [4]) and Ascobolus [5]) the fusing of the nuclei would, according to this representation, only be shifted in time and place compared with Monascus

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[1]) Flora Band 92 p. 1 (fig. 24 and 27).

[2]) Flora Band 92 p. 1 (fig. 24 and 27).

[3]) Le Botaniste 4 Serie, pag. 21—58, 1894—1895.

[4]) HARPER, Ann. of Bot. vol. XIV, 1900.

[5]) HARPER, Jahrb. f. wiss. Bot. Band XXIX, 1896.

and take place in hyphae, growing out from the ascogonium and into which part of the contents of the ascogonium would be transformed.

In accordance with this representation I would place Monascus in a new order, that of the Endascineae.

Anatomy. — *"On the genital cords of Phalangista vulpina."* By Mr. A. J. P. VAN DEN BROEK. (Communicated by Prof. L. BOLK).

(Communicated in the meeting of May 28, 1904.)

In the course of an investigation concerning the structure and development of the female genital organs of marsupials, the result of which will be more extensively published elsewhere, I had an opportunity of studying a series of transverse sections through a young female specimen taken from the marsupium of Phalangista vulpina, measuring 16.7 mm.

An examination of the genital cords and of the Wolffian and Müllerian ducts enclosed in them, revealed a relation differing from what is noticed in the genital cords and the above-mentioned ducts both in Monotremes and in monodelphic mammals and which appears to be connected with the peculiar anatomical details of the genital system of the marsupials.

In following up the genital cords, after they have issued from the tissue of the primitive kidney, in a caudal direction, it is noticed that the cords from both sides approach each other, unite into a single cord along a short distance, then separate again and are continued in a caudo-lateral direction as far as the wall of the uro-genital sinus. In this manner a short bridge is formed, connecting the two genital cords. On reconstructing the successive cross-sections, we obtain what is schematically represented in fig. 1, where the genital apparatus is represented as seen from the dorsal side.

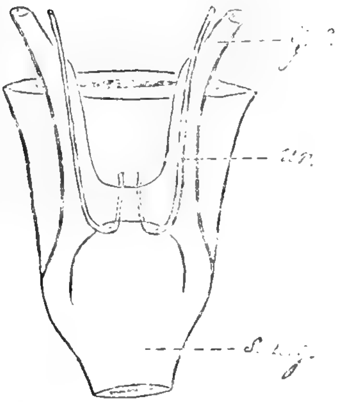

Fig. 1. Genital cords and ureters of a marsupial young one of Phalangista vulpina, seen from the dorsal side.

g. s. Genital cord. *ur.* Ureter.
s. u. g. Sinus uro-genitalis.

The course of the ureters is very peculiar. After having passed behind the connecting bridge just-mentioned which connects the two genital cords, they bend round the caudal edge of this and, continuing their course again in a cranial direction, pierce the posterior wall of the bladder in an oblique, caudo-cranial direction and open into this organ on two adjacent papillae with ostia, which are turned towards the fundus of the bladder. It is very remarkable that the course of the ureters at this stage already agrees completely with the adult condition. The question as to the cause of the hook-shaped bend in the ureters of marsupials, which has already long been known, and which, in my opinion, must exactly be sought in the above-mentioned bridge between the two genital cords, will be briefly discussed later on.

With regard to the mutual relation of the Wolffian and Müllerian ducts, we have to offer the following remarks. At the level of the caudal pole of the primitive kidney, the Müllerian duct lies ventrally and a little laterally of the Wolffian. In a caudal direction this relation is changed, the Müllerian duct being gradually shifted towards the ventro-medial side of the Wolffian duct. This topographical relation exists until near the place where they enter the uro-genital sinus. In their course they follow the genital cords and, in doing so, bend medially, then caudo-laterally and finally, in the last part of their course, show very peculiar characteristics.

The Müllerian duct suddenly bends ventrally and medially, describes a caudally slightly convex arc and then opens into the uro-genital sinus.

The Wolffian duct, at first situated dorso-laterally of that of Müller, describes like this latter in its terminal portion a caudally convex arc and so becomes placed caudally of the Müllerian duct. Next it bends medially and lays itself against the medial wall of the Müllerian duct, after which it opens into the uro-genital sinus, cranially of the latter.

Hence it appears that the Wolffian duct in the last part of its course describes almost a complete spiral revolution round the Müllerian being successively dorso-lateral, caudal (dorsal), medial and cranial. This course I have schematically represented in figure 2, seen from the front and somewhat from above. The bladder has in the figure been imagined cut off exactly at the level where the Wolffian duct enters.

F. Keibel[1]) has suggested that in marsupials the ureters enter into communication with the bladder already at the stage in which they appear as sprouts of the dorso-medial wall of the Wolffian

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[1]) F. Keibel. Zur Entwicklungsgeschichte des menschlichen Uro-genitalapparates Archiv für Anatomie und Entwicklungsgeschichte. 1896. p. 55.

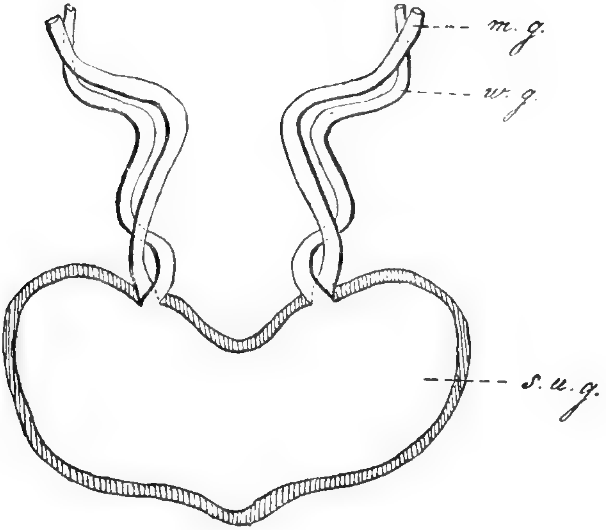

Fig. 2. Course of Wolffian and Müllerian ducts in a marsupial young one of Phalangista vulpina.
w. g. Wolffian duct. *m. g.* Müllerian duct. *s. u. g.* Sinus uro-genitalis.

duct i. e. at a stage, which occurs as a temporary condition in the monodelphic mammals, at any rate in so far as these have been examined, while in the latter they move, before the terminal piece of the Wolffian duct has been incorporated in the wall of the bladder, towards the dorso-lateral wall of that passage, so that in the adult condition they are found laterally of the Wolffian and the Müllerian duct. Although I have not been able to test this theoretical consideration by observations of my own, yet it seems to me that besides the cause, postulated by KEIBEL for the course of the ureters medially of the Müllerian duct, the spiral course of the Wolffian duct and the consequent torsion of this canal, must certainly have an influence and probably a not inconsiderable one on the origin of this course.

A notable fact in this respect is that in male marsupials a masculine uterus is absent, that no remnants have been found of the caudal terminals of the Müllerian ducts, as is expressly stated by WEBER[1]) and DISSELHORST[2]). Only Hypsiprymnus would be an exception to this, according to OWEN.

At the stage, observed by me, the terminals of the Müllerian

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[1]) M. WEBER. Die Säugetiere. Jená. G. FISCHER 1904.

[2]) R. DISSELHORST. Ausführapparat und Anhangsdrüsen der männlichen Geschlechtsorganen in: Lehrbuch der vergleichend mikroskopischen Anatomie der Wirbeltiere, herausgegeben von A. OPPEL. 4er Teil.

ducts are lateral (and caudal) of the Wolffian. Now it is obvious that if my observation holds for marsupials generally, no masculine uterus can arise, because between the two Müllerian ducts those of Wolff are found. Eventual remnants of Müllerian ducts will have to be sought for in the male sex laterally of the terminal opening of the vasa deferentia. I have not yet been able to make observations of my own concerning this point.

As I have already stated, the ureters, at the stage I observed, lie at the medial side of the genital cords. Only those parts of the female genital apparatus of the marsupials which lie at the lateral side of the ureters, can, as I shall try to prove more fully elsewhere, have their homologa in the female genital system of the monodelphic mammals. The vaginal caecal sac developing phylogenetically in the marsupial group, has no homologon in the female sexual organ of the Monodelphia.

Finally, I think, my observation contains an explanation of the peculiar hook-shaped course of the terminals of the ureters of marsupials.

Either as a consequence of the spiral course of the Wolffian ducts, or for some other cause, the ureters at a certain stage of development lie medially of the Wolffian ducts (and of the genital cords) in a dorso-cranial direction towards the primitive kidney.

Marsupials possess a milk-nutrition (intestinal) at such an early stage of development as is known of no other mammal. This milk-nutrition will have a great influence on the development of the bladder which I found as a very voluminous organ in the marsupial young one described, as well as in other specimens (Didelphis) examined by me. With the rapid growth of the bladder the orifices of the ureters are at the same time displaced cranially. The above-mentioned cross-connection between the two genital cords is an obstacle to the cranial displacement of the ureters, the natural consequence of which is that the ureters have always to go round the caudal end of this bridge, while their orifices are further displaced cranially, the result of which is the pronounced hook-shaped course.

Zoology. — *"An interesting Case of Reversion."* By Dr. P. P. C. Hoek.

Pollicipes and *Scalpellum* are two nearly related genera of pedunculate Cirripedes mainly differing from one another, by the one having in its capitulum a restricted number of valves (*Scalpellum*) and by the other having a much larger number of such calcareous parts (*Pollicipes*).

Darwin pointed out the resemblance of these two genera already in 1851[1]). That resemblance is greatest in those species of *Scalpellum* in which the carina is not bowed or angularly bent, but straight or nearly straight. Darwin gave as an interesting case of such a species a description of *Sc. villosum* (fig. 2 of the accompanying plate). He was so struck by its general likeness to *Pollicipes*, that he wrote (l.c. p. 278): "*Sc. villosum* most closely resembles or rather is identical with *Pollicipes*. Had it not been for the fewness of the valves forming the capitulum, and from the presence of complemental males, I should have placed this species alongside of *Pollicipes spinosus* and *sertus*." And under *Pollicipes* (l.c. p. 294): "We have seen under *Scalpellum villosum* that the addition of a few small valves to the lower whorl, would convert it into a Pollicipes" etc. Compare fig. 3 of the accompanying plate.

The genus *Scalpellum* is represented under the deepsea animals by numerous species. Those of *Pollicipes* are shallow water forms only. The English "Challenger" Expedition collected during a four years' cruise over all the oceans of the world, specimens of 42 different species of *Scalpellum*, 41 of which were new to science. Only two of these were found in depths of less than 200 m.: all the others were true deep-sea species. H.M. "Siboga" collected in the Malay Archipelago, during a cruise of one year's duration, specimens of 38 different species of *Scalpellum*. Of these, 32 must be considered as new to science; 34 of these species are deepsea animals, 4 shallow-water forms.

The genus *Pollicipes* was not represented under the Cirripedia of the Challenger and by one species only under those of the Siboga: *Pollicipes mitella* a common littoral form of tropical seas. Whereas the number of known living species of *Scalpellum* was 6 in 1851 and is at least 125 at the present time (so far as I know [2])), of the genus *Pollicipes* which figures in Darwin's book with 6 species also, only a seventh species has been described since the appearance of the said monograph. When Darwin wrote that book the mysteries of the oceanic abysses were not unveiled to him of course, but his

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[1]) Darwin, C., A Monograph on the Subclass Cirripedia. I. The Lepadidae or pedunculated Cirripedes. 1851.

[2]) Including the species collected by the Siboga. A. Gruvel, who described the species collected by the French expeditions with the Travailleur and the Talisman, and C. Aurivillius, who studied the Cirripedia of Swedish collections and published provisional descriptions of the Cirripedia collected by the Prince of Monaco during his numerous cruises have, with the present author contributed most to our knowledge of the species of this genus.

knowledge of the existing shallow-water forms of Cirripedia was fairly complete.

Returning to the interesting species *Sc. villosum,* the near affinity of which to *Pollicipes* was pointed out by **Darwin**, I may mention first, that in my Report on the Cirripedia of the Challenger I was able to describe a species (*Sc. trispinosum*) belonging to the same division of the genus. It was collected in the Philippine Archipelago at a depth of 150 (perhaps 180 meters). Next, that the Siboga was successful in finding two more of them and that these will bear the names of *Sc. pollicipedoides* and *Sc. aries.* Though the capitulum of both species resembles the common form of *Scalpellum* (compare fig. 1) more than that of either *Sc. trispinosum* or *Sc. villosum,* the shape of the carina shows their affinity to the last named species at once.

These species were also taken in rather shallow water: in depths varying between 57 and 94 meters. The depth at which *Sc. villosum* lives is not so well known, but it cannot be important. **Darwin** says that the specimens were found attached to shells and rocks: they were taken no doubt during shore-exploration.

So we can say that those species of *Scalpellum* which resemble *Pollicipes* most closely, like all known species of that genus itself, are inhabitants of shallow water. *Pollicipes* as is well known, embraces the oldest known Cirripeds and the genus *Scalpellum* is the second in age. The structure of *Sc. villosum* makes it highly probable that the genus *Scalpellum* descended from *Pollicipes.* This supposition finds very striking confirmation in a peculiarity of one of the specimens of *Sc. pollicipedoides,* which peculiarity I shall briefly describe here.

The said species is represented in the Siboga-collection by six specimens. It was found at Station 274 near the Jedan Islands, south of New Guinea, at a depth of 57 meter. Its capitulum has 15 valves: two scuta of triangular, two terga of rhomboid shape; a nearly straight carina, two rather small upper latera and eight valves of the lower whorl. Of these the rostrum and the subcarina have the umbo pointing transversely outwards; of the three pair of latera which, with rostrum and subcarina form the lower whorl, those of the middle pair are by far the smallest. The shape of all these valves is triangular with the umbo at the apex. Whereas the scutum and the tergum stand rather close together, the other valves are far apart, being separated from one another by chitinous membrane.

Though, as I pointed out above, the general shape of the capitulum is more like a normal *Scalpellum*, in having one pair of latera more than *Sc. villosum* or *Sc. trispinosum*, *Sc. pollicipedoides* comes nearer to *Pollicipes* even than those species.

Looking over the six specimens of this new species, I was struck by finding that one of the specimens, though in other regards similar to the other five, differed from them by having in the lower whorl of valves two latera in addition to the three which all the specimens possess. In fig. 4 the left side of a normal, in fig. 5 the same side of the abnormal specimen is represented. (At the right side only one of the additional valves is developed.) In fact, the few small valves which according to DARWIN were wanting in the lower whorl of *Sc. villosum* to convert it into a *Pollicipes* occur in one of the specimens of this new species. By calling it a case of reversion I would indicate the high importance, which from an evolutionary point of view I attach to this abnormality. We need not go so far as to consider this species as representing exactly the "missing link" between the genera *Pollicipes* and *Scalpellum*, but I think the case shows clearly that a form with more numerous calcareous parts in its capitulum (like *Pollicipes*) is the older, the form with fewer (like *Scalpellum*) the younger one; moreover, that the *Scalpellum*-species with straight carinae, inhabitants of shallow water, must be considered as the oldest, i. e. the species most resembling the primitive form of *Scalpellum*.

(It is perhaps not quite superfluous to remark here, that 80 of the 125 species of *Scalpellum* have been studied and described by myself and I never saw before such an augmentation of valves in the lower whorl (or in the capitulum in general). Nor can I remember to have met with descriptions of such cases in literature. DARWIN for the classification of the genera of Cirripedia made use of the number, the shape and the mode of growth of the valves. That he was right in doing so is proved by the fact that later authors never put in doubt the value of these characteristics).

A full description of this and of the other new species of *Scalpellum* will be given in the forthcoming report on the Cirripedia of the Siboga-Expedition. I wish however to point out here, that *Sc. pollicipedoides* by the presence of a complemental male (Fig. 6) shows itself to be a true *Scalpellum* and that it has rudimentary caudal appendages which occur in *Pollicipes* also, but which curiously enough according to DARWIN are wanting in *Scalpellum villosum*.

EXPLANATION OF FIGURES.

Fig. 1. *Scalpellum rostratum*, Darwin. Seen from the right side.
" 2. *Scalpellum villosum*, Leach. Seen from the right side.
" 3. *Pollicipes sertus*, Darwin. Seen from the right side.
(Fig. 1—3 after Darwin, Monograph on the Cirripedia. Lepadidae. 1851).
" 4. *Scalpellum pollicipedoides*, n. sp. Seen from the left side. Magnified 11 diameters.
" 5. Same species, abnormal specimen. *a* the additional values. *b* the complemental male. Magnified 11 diameters.
" 6. The complemental male of *Sc. pollicipedoides*. Magnified 180 diameters.

Physics. — "*On the function* $\frac{a}{b}$ *for multiple mixtures.*" By Mr. B. M. VAN DALFSEN. (Communicated by Prof. J. D. VAN DER WAALS).

The quantities a and b appearing in this quotient are the constant quantities of the equation of condition of VAN DER WAALS, applied to a multiple mixture. The quantity $\frac{a}{b}$ then represents an expression proportional to the critical temperature of the undivided mixture. We imagine the mixture determined by the molecular fractions $x_1, x_2, \ldots, x_n$, where $x_1 + x_2 + \ldots + x_n = 1$ and all x's are positive quantities. Further we assume for a and b homogeneous quadratic functions of the x's, so that

$$a = \sum_{p=1}^{p=n} \sum_{q=1}^{q=n} a_{pq}\, x_p\, x_q$$

and

$$b = \sum_{p=1}^{p=n} \sum_{q=1}^{q=n} b_{pq}\, x_p\, x_q .$$ [1])

For the quantity a we must arrive, it is clear, at a quadratic function, as we have to do with attraction of the molecules two by two; for b we can suffice [2]) with a quadratic function as long as simultaneous collisions of more molecules are neglected.

Our particular business now is to find out whether there are mixtures for which $\frac{a}{b}$ is stationary.

The constitutions of those mixtures we find out of

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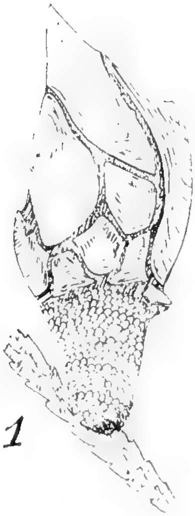
[1]) Here $a_{pq} = a_{qp}$ and $b_{pq} = b_{qp}$. For a_{pp} and b_{pp} we put in the sequel ordinarily a_p and b_p.

[2]) Comp. H. A. LORENTZ, Wied. Ann. 12, p. 134.

P. P. C. HOEK. “An interesting case of reversion.”


1


2


3


6


4

5

$$\frac{a}{b} = \frac{\frac{\partial a}{\partial x_1}}{\frac{\partial b}{\partial x_1}} = \frac{\frac{\partial a}{\partial x_2}}{\frac{\partial b}{\partial x_2}} = \ldots\ldots\ldots = \frac{\frac{\partial a}{\partial x_n}}{\frac{\partial b}{\partial x_n}} = \lambda\,;$$

thus out of the system of linear equations

$$\begin{cases} \dfrac{\partial a}{\partial x_1} - \lambda \dfrac{\partial b}{\partial x_1} = 0 \\ \dfrac{\partial a}{\partial x_2} - \lambda \dfrac{\partial b}{\partial x_2} = 0, \quad \text{besides} \quad x_1 + x_2 + \ldots + x_n = 1 \\ \vdots \\ \dfrac{\partial a}{\partial x_n} - \lambda \dfrac{\partial b}{\partial x_n} = 0 \end{cases}$$

or explicitly

$$(V) \quad \begin{cases} (a_1 - \lambda b_1)\, x_1 + (a_{12} - \lambda b_{12})\, x_2 + \ldots\ldots + (a_{1n} - \lambda b_{1n})\, x_n = 0 \\ (a_{21} - \lambda b_{21})\, x_1 + (a_2 - \lambda b_2)\, x_2 + \ldots\ldots + (a_{2n} - \lambda b_{2n})\, x_n = 0 \\ \vdots \\ (a_{n1} - \lambda b_{n1})\, x_1 + (a_{n2} - \lambda b_{n2})\, x_2 + \ldots\ldots + (a_n - \lambda b_n)\, x_n = 0 \end{cases}$$

and

$$x_1 + x_2 + \ldots + x_n = 1.$$

In these equations $b_{pq} = b_{qp}$ and $a_{pq} = a_{qp}$; they are the same quantities appearing in the theory of the binary mixtures. All a's and b's are essentially positive.

Out of the system (V) can be deduced that — for the mixtures sought for — $\frac{a}{b}$ or λ can be found out of an equation of degree n:

$$\Delta_n \equiv \begin{vmatrix} a_1 - \lambda b_1 & a_{12} - \lambda b_{12} & \ldots\ldots & a_{1n} - \lambda b_{1n} \\ a_{21} - \lambda b_{21} & a_2 - \lambda b_2 & & a_{2n} - \lambda b_{2n} \\ \vdots & & & \\ a_{n1} - \lambda b_{n1} & a_{n2} - \lambda b_{n2} & \ldots\ldots & a_n - \lambda b_n \end{vmatrix} = 0.$$

Algebraically there are thus n solutions — the values of x belonging to the obtained values of λ are found out of

$$x_1 = \frac{M_{11}}{\sum\limits_{s=1}^{s=n} M_{1s}} \qquad x_2 = \frac{M_{12}}{\sum\limits_{s=1}^{s=n} M_{1s}} \quad \ldots\ldots \quad x_n = \frac{M_{1n}}{\sum\limits_{s=1}^{s=n} M_{1s}}.$$

Here M_{pq} represents the coefficient of $a_{pq} - \lambda b_{pq}$ in the development of Δ_n according to the elements of the p^{th} row whilst in these expressions we must substitute successively for λ the roots of $\Delta_n = 0$.

If such a mixture is to be realized we must find for the molecular fractions positive values so that one of the two following systems of inequalities must be satisfied

$$(A) \qquad M_{11} > 0 \quad M_{12} > 0 \;\ldots\ldots\; M_{1n} > 0$$

$$(B) \qquad M_{11} < 0 \quad M_{12} < 0 \;\ldots\ldots\; M_{1n} < 0.$$

We have just now made use of the last $(n-1)$ equations of system (V) to calculate the x's. As we might have chosen $(n-1)$ other equations it is evident that for the existence of a stationary point M_{pq} must always be either > 0 or < 0. The set of inequalities given above is however sufficient to judge the possibility of the mixture.

At most *one* of these n mixtures can be realized. Suppose that two different possible mixtures were to be found

$$[(x_1)_1,\ (x_2)_1,\ \ldots\ (x_n)_1] \quad \text{and} \quad [(x_1)_2,\ (x_2)_2,\ \ldots\ (x_n)_2]$$

for which $\frac{a}{b}$ were stationary. Now as in consequence of the set of equations (V) equal roots λ lead to equal constitutions, different values λ belong to different mixtures. If we call the roots λ belonging to the above mentioned mixtures λ_1 and λ_2 we arrive at the following sets of equations

$$V_1 \begin{cases} \left(\dfrac{\partial a}{\partial x_1}\right)_1 - \lambda_1 \left(\dfrac{\partial b}{\partial x_1}\right)_1 = 0 \\ \left(\dfrac{\partial a}{\partial x_2}\right)_1 - \lambda_1 \left(\dfrac{\partial b}{\partial x_2}\right)_1 = 0 \\ \vdots \\ \left(\dfrac{\partial a}{\partial x_n}\right)_1 - \lambda_1 \left(\dfrac{\partial b}{\partial x_n}\right)_1 = 0 \end{cases} \text{and} \quad V_2 \begin{cases} \left(\dfrac{\partial a}{\partial x_1}\right)_2 - \lambda_2 \left(\dfrac{\partial b}{\partial x_1}\right)_2 = 0 \\ \left(\dfrac{\partial a}{\partial x_2}\right)_2 - \lambda_2 \left(\dfrac{\partial b}{\partial x_2}\right)_2 = 0\,. \\ \vdots \\ \left(\dfrac{\partial a}{\partial x_n}\right)_2 - \lambda_2 \left(\dfrac{\partial b}{\partial x_n}\right)_2 = 0 \end{cases}$$

Multiplying the equations V_1 resp. by $(x_1)_2, (x_2)_2, \ldots (x_n)_2$ and those of the system V_2 resp. by $(-x_1)_1,\ (-x_2)_1, \ldots (-x_n)_1$ and summing these up we find in connection with the identity holding good for homogeneous quadratic functions

$$\sum_{p=1}^{p=n} (x_p)_1 \left(\frac{\partial \Phi}{\partial x_p}\right)_2 \equiv \sum_{p=1}^{p=n} (x_p)_2 \left(\frac{\partial \Phi}{\partial x_p}\right)_1,$$

$$(\lambda_2 - \lambda_1)\left[(x_1)_2\left(\frac{\partial b}{\partial x_1}\right)_1 + (x_2)_2\left(\frac{\partial b}{\partial x_2}\right)_1 + \ldots (x_n)_2\left(\frac{\partial b}{\partial x_n}\right)_1\right] = 0$$

or, as we supposed $\lambda_1 = = \lambda_2$

$$\sum_{s=1}^{s=n} (x_s)_2\, [b_{s1}\ (x_1)_1 + b_{s2}\ (x_2)_1 + \ldots\ b_{sn}\ (x_n)_1] = 0.$$

All b_{pq}'s however being positive and all x's also for possible mixtures, the above mentioned equation cannot be satisfied.

So there is at most but one mixture possible for which $\frac{a}{b}$ becomes stationary; the λ of that mixture satisfies either the inequalities (A) or the inequalities (B).

Before passing to the investigation of the nature of the stationary point we shall first prove the theorem

$$\frac{\partial \Delta_n}{\partial \lambda} = \sum_{p=1}^{p=n} \sum_{q=1}^{q=n} (-b_{pq} M_{pq})$$

This theorem can be easily verified for $n=2$; it holds still good when $b_{pq} == b_{qp}$, i.e. for asymmetric determinants.

The general proof is supplied by showing that if the theorem is correct for determinants of $(n-1)$ rows and columns (also asymmetric ones), it also holds good for determinants of n rows and columns.

Now we have

$$\Delta_n = (a_1 - \lambda b_1) M_{11} + (a_{12} - \lambda b_{12}) M_{12} + \ldots + (a_{1n} - \lambda b_{1n}) M_{1n}.$$

Let us now make use of the following notation:

Δ_{pq} is the determinant derived from Δ_n by omitting the p^{th} row and the q^{th} column.

$\Delta_{\substack{pq\\rs}}$ is the determinant derived from Δ_n by omitting the rows with numbers p and r and the columns with numbers q and s.

We now find

$$\frac{\partial \Delta_n}{\partial \lambda} = -b_1 M_{11} - b_{12} M_{12} \ldots - b_{1n} M_{1n} + \sum_{s=1}^{s=n} (a_{1s} - \lambda b_{1s}) \frac{\partial M_{1s}}{\partial \lambda}.$$

Further we find

$$M_{1s} = (-1)^{s-1} \Delta_{1s}.$$

Δ_{1s} is an (asymmetric) determinant with $(n-1)$ rows and columns, for which we have supposed the theorem to hold good, so that

$$\frac{\partial \Delta_n}{\partial \lambda} = \sum_{r=1}^{r=n} - b_{1r} M_{1r} \pm \sum_{s=1}^{s=n} (-1)^{s-1} (a_{1s} - \lambda b_{1s}) \times$$

$$\times \sum_{p=2}^{p=n} \sum^{q=1,2,..(s)..n} (-b_{pq}) (-1)^{p-2} (-1)^{q-2} \Delta_{\substack{1s\\pq}}\,, ^{1)}$$

where the positive sign must be used for $q > s$ and the negative one for $q < s$.

Performing the summation according to s first, we find

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¹) By placing s between brackets we indicate that for the summation all values from 1 to n except s must be assigned to q.

$$\frac{\partial \Delta_n}{\partial \lambda} = \sum_{r=1}^{r=n} - b_{1r}\, M_{1r} + \sum_{p=2}^{p=n} \sum_{q=1}^{q=n} (-b_{pq})\, \Delta_{pq}\, (-1)^{p-1}\, (-1)^{q-1}$$

or

$$\frac{\partial \Delta_n}{\partial \lambda} = \sum_{p=1}^{p=n} \sum_{q=1}^{q=n} (-b_{pq})\, M_{pq}\ .$$

For a possible mixture for which $\frac{a}{b}$ becomes stationary all quantities M_{pq} have the same sign as is proved. It is now evident that for such points, whatever the sign of M_{pq} may be, $\frac{\partial \Delta_n}{\partial \lambda} M_{nn}$ is always negative. With the help of this theorem we can investigate the conditions to distinguish an absolute maximum or minimum.

Let us now write $F = a - \lambda b$.

This expression F regarded as function of $x_1, x_2 \ldots x_n$ and λ is zero for every given set of values $x_1, x_2, \ldots x_n$, if we assign to λ the value of $\frac{a}{b}$ belonging to that constitution. If inversely we start from a given $\lambda\ (= \lambda_0)$ then the solutions of the equation $F = a - \lambda_0\, b = 0$, regarded as an equation in $x_1, x_2, \ldots x_n$ furnish all the mixtures for which $\frac{a}{b}$ possesses the given value λ_0. If moreover that value λ_0 is an absolute maximum or minimum, then only a single set of possible values $x_1, x_2, \ldots x_n$ may satisfy that equation.

As F is a homogeneous quadratic expression in the n x's we can write it down as the sum of n squares.

Let us again call Δ_n the determinant forming the first member of the equation in λ of order n, Δ_{n-1} the determinant derived from the former by the omission of the n^{th} row and the n^{th} column, Δ_{n-2} the determinant obtained by the omission of the last two rows and columns, so that finally $\Delta_1 = a_1 - \lambda b_1$.

The transformation into a sum of squares is brought about in such a manner that the first square contains all the terms with x_1, the second all the remaining terms with x_2, etc., until finally x^2_n is our last square. In order to evade surds we must every time multiply our function by definite coefficients. It is now evident that by executing the development, if we represent the successive linear homogeneous expressions to be squared by $L_1, L_2 \ldots L_n$, we have :

$$\Delta^2_1\,\Delta^2_2 \ldots \Delta^2_{n-2}\,\Delta_{n-1}\,\Delta_n\,F = \Delta_1\,\Delta^2_2\,\Delta^2_3 \ldots \Delta^2_{n-2}\,\Delta_{n-1}\,\Delta_n\,L^2_1 +$$
$$+ \Delta_1\Delta_2\Delta^2_3 \ldots \Delta^2_{n-2}\Delta_{n-1}\Delta_n L^2_2 + \Delta^2_1\Delta_2\Delta_3\Delta^2_4 \ldots \Delta^2_{n-2}\Delta_{n-1}\Delta_n L^2_3 +$$
$$+ \ldots + \Delta^2_1\,\Delta^2_2 \ldots \Delta^2_{p-2}\,\Delta_{p-1}\,\Delta_p\,\Delta^2_{p+1} \ldots \Delta^2_{n-2}\,\Delta_{n-1}\,\Delta_n\,L^2_p + \ldots$$
$$\ldots \Delta^2_1\,\Delta^2_2 \ldots \Delta^2_{n-2}\,L^2_n \quad ^{1)}.$$

Here is

$$L_1 = \sum_{p=1}^{p=n} (a_{1p} - \lambda b_{1p})\,x_p \quad ^{2)}$$

$$L_2 = \sum_{p=2}^{p=n} \begin{vmatrix} a_1 - \lambda b_1 & a_{1p} - \lambda b_{1p} \\ a_{21} - \lambda b_{21} & a_{2p} - \lambda b_{2p} \end{vmatrix} x_p$$

$$L_s = \sum_{p=s}^{p=n} \begin{vmatrix} a_1 - \lambda b_1 & a_{12} - \lambda b_{12} & \ldots & a_{1,s-1} - \lambda b_{1,s-1} & a_{1p} - \lambda b_{1p} \\ a_{21} - \lambda b_{21} & a_2 - \lambda b_2 & \ldots & a_{2,s-1} - \lambda b_{2,s-1} & a_{2p} - \lambda b_{2p} \\ \vdots & & & & \\ a_{s-1,1} - \lambda b_{s-1,1} & \ldots & \ldots & a_{s-1,s-1} - \lambda b_{s-1,s-1} & a_{s-1,p} - \lambda b_{s-1,p} \\ a_{s,1} - \lambda b_{s1} & \ldots & \ldots & a_{s,s-1} - \lambda b_{s,s-1} & a_{sp} - \lambda b_{sp} \end{vmatrix} x_p.$$

$$L_n = \Delta_n\,x_n.$$

So we find

$$F = \frac{L^2_1}{\Delta_1} + \frac{L^2_2}{\Delta_1\Delta_2} + \ldots \frac{L^2_p}{\Delta_{p-1}\Delta_p} + \ldots \frac{L^2_n}{\Delta_{n-1}\Delta_n} \quad ^{3)}.$$

For a stationary point Δ_n becomes equal to 0, and so the last term disappears as it is $\dfrac{\Delta_n}{\Delta_{n-1}}\,x^2_n$ [4]).

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[1]) For the deduction a continual use has been made of the theorem:

$$\Delta\,\Delta_{\substack{pq\\rs}} = \Delta_{pq}\,\Delta_{rs} - \Delta_{ps}\,\Delta_{qr}$$

WEBER: Lehrbuch der Algebra I, 2nd edition, p. 115.

[2]) In connection with the following it is easy to find back out of this the system (V). Comp. for a ternary system: VAN DER WAALS, Proceedings Royal Acad. of Sc. 1902, Vol. 5. p. 235.

[3]) Without looking more closely at the breaking up into squares, as is performed above, ROUTH shows in his Rigid Dynamics, Advanced Part, 5th ed., p. 426 with the help of invariants that the coefficient of L_p has the sign of $\dfrac{\Delta_p}{\Delta_{p-1}}$, which agrees to the above.

[4]) There is a difficulty however when for $\lambda = \lambda_0$ also Δ_{n-1} becomes 0, so when a stationary point in the mixture $(1, 2, \ldots n-1)$ becomes at the same time a stationary point for the total mixture. When breaking up into squares we then shall change the order of succession in order to avoid x_n^2 presenting itself as last term. If all first minors belonging to elements out of the principal diagonal Δ_n are 0 then all minors must be 0, if there are to be stationary points. The equations (V) have then a higher degree of dependence and there are an infinite number of mixtures for which $\dfrac{a}{b}$ becomes stationary.

Suppose the stationary point to be an absolute maximum or minimum. Let λ_0 be the corresponding value of $\frac{a}{b}$. Then for $\lambda = \lambda_0$ there is only one constitution; thus for $x_1, x_2, \ldots x_n$ only one set of values may be found. Now this is only possible when all the coefficients of $L_1, L_2, \ldots L_{n-1}$ have the same sign for $\lambda = \lambda_0$. For, if this were not the case then it would be possible for $\lambda = \lambda_0$ (for which the last coefficient has already disappeared) to satisfy the equation $r = 0$ without the necessity of $L_1, L_2, \ldots L_{n-1}$ being individually zero and then many sets of adjacent values $x_1, x_2, \ldots x_n$ might be found for which $\frac{a}{b}$ had that absolutely maximal or minimal supposed value; which is absurd.

For a stationary point to be an absolute minimum or maximum it is therefore required

$$\left.\begin{array}{l}\Delta_1 > 0\\ \Delta_1\Delta_2 > 0 \quad (T_1)\\ \vdots\\ \Delta_{p-1}\Delta_p > 0\\ \vdots\\ \Delta_{n-2}\Delta_{n-1} > 0\end{array}\right\} \text{, so } \left\{\begin{array}{l}\Delta_1 > 0\\ \Delta_2 > 0\\ \vdots\\ \Delta_p > 0\\ \vdots\\ \Delta_{n-1} > 0\end{array}\right. \quad \text{or} \quad \left.\begin{array}{l}\Delta_1 < 0\\ \Delta_1\Delta_2 < 0\\ \vdots\\ \Delta_{p-1}\Delta_p < 0\\ \vdots\\ \Delta_{n-2}\Delta_{n-1} < 0\end{array}\right\} \text{, so} (T_2) \left\{\begin{array}{l}\Delta_1 < 0\\ (-1)\Delta_2 < 0\\ \vdots\\ (-1)^{p-1}\Delta_p < 0\\ \vdots\\ (-1)^{n-2}\Delta_{n-1} < 0\end{array}\right.$$

Let λ_0 be a root of $\Delta_n = 0$ indicating an attainable absolute maximum or minimum, then for $\lambda = \lambda_0$ the coefficient of the last square (x_n^2) in the development of r becomes zero. For $\lambda = \lambda_0 + \varepsilon$ the sign of $\Delta_{n-1} \frac{\partial \Delta_n}{\partial \lambda}$ determines the sign of that coefficient, whilst for $\lambda = \lambda_0 - \varepsilon$ the sign is determined by $- \Delta_{n-1} \frac{\partial \Delta_n}{\partial \lambda}$.

Now however, as we just before indicated, we find, for a possible stationary point

$$\Delta_{n-1} \frac{\partial \Delta_n}{\partial \lambda} = M_{nn} \frac{\partial \Delta_n}{\partial \lambda} < 0.$$

So it is evident that for $\lambda = \lambda_0 + \varepsilon$ the last term is always negative and for $\lambda = \lambda_0 - \varepsilon$ always positive.

From this ensues that in the case of an absolute minimum the inequalities (T_1) must be satisfied, whilst for an absolute maximum the inequalities (T_2) must be fulfilled. In the first case the conditions of possibility (A) are still to be added, in the second case the conditions (B).

It is clear that by a different numbering of the components other inequalities would have been obtained — evidently however the system (T_1) or (T_2) is sufficient to indicate an absolute minimum or maximum.

Suppose an attainable minimum presents itself in the mixture of some components say $1, 2, \ldots p$.

Within the limits of possibility for that mixture a second set of values of the x's for which $\Delta_p = 0$ cannot be found. As farther $\frac{\partial \Delta_p}{\partial \lambda}$ is negative for that minimum we can draw the following conclusions from the system of inequalities (T_1):

An attainable absolute minimum lies lower than $\frac{a}{b}$ for the components and lower than eventually appearing minima in any mixture to be compounded of the given components.

If the original mixture has a maximum and if there is also a maximum in the p-fold mixture $(1, 2, \ldots p)$, then for the maximum in the p-fold mixture Δ_p is equal to 0 and $\frac{\partial \Delta_p}{\partial \lambda} \Delta_{p-1}$ negative, so $\frac{\partial \Delta_p}{\partial \lambda}$ has there the sign of $-\Delta_{p-1}$. Now $(-1)^{p-2} \Delta_{p-1}$ is < 0, so Δ_{p-1} has the sign of $(-1)^{p-1}$. So $\frac{\partial \Delta_p}{\partial \lambda}$ has the sign of $(-1)^p$. Let λ_p represent that maximum, then as Δ_p becomes but once 0 for possible mixtures Δ_p is furnished for every value of $\lambda > \lambda_p$, with the sign $(-1)^p$, but for every value of $\lambda < \lambda_p$ with the sign $(-1)^{p-1}$. For the maximum in the n-fold mixture $(-1)^{p-1} \Delta_p$ is < 0, and so for Δ_p the sign is indicated by $(-1)^p$. From this ensues that the set of inequalities (T_2) can be expressed as follows:

An attainable absolute maximum lies higher than the $\frac{a}{b}$ for the components and also higher than eventual maxima in mixtures to be formed of the given components.

The question now arises whether a maximum or minimum in the n-fold mixture implies anything about maxima or minima of the binary mixtures to be formed of the n-fold mixture.

Suppose the n-fold mixture to show a minimum for $\lambda = \lambda_m$ and the constitution of that mixture to be indicated by $[(x_1)_m, (x_2)_m \ldots (x_n)_m]$, then we find

$$\begin{cases} (a_1 - \lambda_m b_1)(x_1)_m + (a_{12} - \lambda_m b_{12})(x_2)_m + \ldots + (a_{1n} - \lambda_m b_{1n})(x_n)_m = 0 \\ (a_{21} - \lambda_m b_{21})(x_1)_m + (a_2 - \lambda_m b_2)(x_2)_m + \qquad + (a_{2n} - \lambda_m b_{2n})(x_n)_m = 0 \\ \vdots \\ (a_{n1} - \lambda_m b_{n1})(x_1)_m + (a_{n2} - \lambda_m b_{n2})(x_2)_m + \qquad + (a_n - \lambda_m b_n)(x_n)_m = 0. \end{cases}$$

Now we know that for a possible absolute minimum $a_s - \lambda_m b_s > 0$ whilst of course also $(x_s)_m > 0$.

If the above equations are to be satisfied then in every equation at least *one* of the coefficients must become negative.

This is most profitably attained for $n = 2t$ if

$$a_{12} - \lambda_m b_{12} < 0, \qquad a_{34} - \lambda_m b_{34} < 0, \text{ and } a_{2t-1,2t} - \lambda_m b_{2t-1,2t} < 0.$$

So then we have e.g.

$$a_s - \lambda_m b_s > 0 \qquad a_{s,s+1} - \lambda_m b_{s,s+1} < 0 \qquad a_{s+1} - \lambda_m b_{s+1} > 0$$

so

$$\frac{a_{s,s+1}}{b_{s,s+1}} < \lambda_m \text{ and } \lambda_m < \frac{a_s}{b_s} \text{ and } \lambda_m < \frac{a_{s+1}}{b_{s+1}}$$

so that a fortiori

$$\frac{a_{s,s+1}}{b_{s,s+1}} < \frac{a_s}{b_s} \text{ and } \frac{a_{s,s+1}}{b_{s,s+1}} < \frac{a_{s+1}}{b_{s+1}}.$$

The mixture $[s, s+1]$ then possesses a minimum.

So at least minima are wanted in t binary mixtures if the whole mixture of $2t$ components is to show a minimum.

If $n = 2t + 1$ then there are at least $t + 1$ or $\frac{1}{2}(n+1)$ minima wanted in the binary mixtures if the total mixture is to show a minimum. Let us take e.g.

$$a_{12} - \lambda_m b_{12} < 0 \qquad a_{34} - \lambda_m b_{34} < 0 \; \ldots \; a_{n-2,n-1} - \lambda_m b_{n-2,n-1} < 0$$

and

$$a_{n1} - \lambda_m b_{n1} < 0.$$

For n even the case is taken that each component shows with but one other one a minimum, whilst for n odd *one* of the components gives a minimum with two other ones.

If a component forms with more other ones minima then more conditions are absolutely necessary; if a.o. we assume that $n - 1$ of the components give mutually no minima, then certainly the last component must give a minimum with each of the $(n - 1)$ remaining ones, if the total mixture is to show an absolute minimum.

Of course the above theorems may not be reversed; so at least $\frac{1}{2}n$ (resp. $\frac{1}{2}(n+1)$) minima are wanted, but these do not in the least guaranty the existence of an absolute minimum in the n-fold mixture.

In case of an attainable absolute maximum $a_s - \lambda_M b_s$ is < 0 and so in our set of equations at least *one* positive term is required to present itself in each member. From

$$a_s - \lambda_M b_s < 0, \qquad a_{rs} - \lambda_M b_{rs} > 0 \text{ and } a_r - \lambda_M b_r < 0$$

follows

$$\frac{a_{rs}}{b_{rs}} > \lambda_M, \text{ whilst } \lambda_M > \frac{a_s}{b_s} \text{ and } \lambda_M > \frac{a_r}{b_r}.$$

so a fortiori

$$\frac{a_{rs}}{b_{rs}} > \frac{a_s}{b_s} \quad \text{and} \quad \frac{a_{rs}}{b_{rs}} > \frac{a_r}{b_r},$$

so that the binary mixture (r, s) then gives a maximum.

In the same way as for a minimum we reason here, that to have an absolute maximum in a mixture of $2t$ (resp. $2t+1$) components we must require at least maxima in t (resp. $t+1$) binary mixtures.

For a further investigation we shall have to look more closely into the quantities b_{pq} and a_{pq}.

For b_{pq} we shall use the formula given by LORENTZ

$$b_{pq} = 2.\,{}^4/_3\,\pi\,(r_p + r_q)^3\ ^{1)},$$

where r_p represents the radius of the molecule of the p^{th} component.

This formula holds good for $p = q$ too.

The coefficient of λ^n in the equation $\Delta_n = 0$ is

$$(-1)^n \begin{vmatrix} b_{11} & b_{12} \ldots b_{1n} \\ b_{21} & b_{2} \ \ldots b_{2n} \\ \vdots & \\ b_{n1} & b_{n2} \ldots b_{n} \end{vmatrix} = (-1)^n \Delta_b.$$

Now we have

$$\Delta_{b=2} = -\,{}^{64}/_9\,\pi^2\,(r_1-r_2)^2\,[r_1^4+r_2^4+30\,r_1^2\,r_2^2+8\,r_1^3\,r_2+8\,r_2^3\,r_1|$$

$$\Delta_{b=3} = -({}^8/_3)^3\,\pi^3\,6\,(r_1-r_2)^2\,(r_2-r_3)^2\,(r_3-r_1)^2\,|r_1\,(r_2+r_3)^2 +$$
$$+\,r_2\,(r_3+r_1)^2+r_3\,(r_1+r_2)^2|\ ^{2)}$$

$$\Delta_{b=4} = ({}^8/_3\,\pi)^4\,9\,(r_1-r_2)^2\,(r_1-r_3)^2\,(r_1-r_4)^2\,(r_2-r_3)^2\,(r_2-r_4)^2\,(r_3-r_4)^2.$$

For five components the determinant on the b's vanishes identically; for we find

$$\Delta_{(5)}\,\underset{\substack{44\\55}}{\Delta_{(5)}} = \underset{44}{\Delta_{(5)}}\,\underset{55}{\Delta_{(5)}} - \underset{45}{\Delta^2_{(5)}} -$$
$$= ({}^8/_3\pi)^4\,9\,(r_1-r_2)^2\,(r_1-r_3)^2\,(r_1-r_5)^2\,(r_2-r_3)^2\,(r_2-r_5)^2\,(r_3-r_5)^2 \times$$
$$\times\,({}^8/_3\pi)^4\,9\,(r_1-r_2)^2\,(r_1-r_3)^2\,(r_1-r_4)^2\,(r_2-r_3)^2\,(r_2-r_4)^2\,(r_3-r_4)^2 +$$
$$-\,({}^8/_3\pi)^8\,\{9(r_1-r_2)^2\,(r_1-r_3)^2\,(r_2-r_3)^2\,(r_1-r_4)\,(r_1-r_5)\,(r_2-r_4)$$
$$(r_2-r_5)\,(r_3-r_4)\,(r_3-r_5)\}^2 = 0.$$

So $\Delta_{(5)} \equiv 0$ as $\underset{\substack{44\\55}}{\Delta_{(5)}}$ is not identical equal to 0.

For the determinant of the order 6 not only all minors belonging

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[1] Wied. Ann. 12 p. 134. In reality still another constant factor N presents itself here.

[2] These results have been obtained by remarking that Δ_b is always divisible by $(r_p - r_q)^2$; the coefficients of the remaining factor have been found by means of the method of indeterminate coefficients.

to elements of the principal diagonal become 0 but also all other minors of degree 5 [1]).

Then however it is clear that for mixtures with 6 and more components the determinants on the b's disappear identically.

Berthelot and before him Galitzine have made about the quantity a_{pq} the simple supposition $a^2_{pq} = a_p\, a_q$. Although this formula may not be strictly true, as has already been clearly proved by experiments on binary mixtures, it is worth while to consider to what conclusions the afore mentioned rule leads us for multiple mixtures.

For $a_{pq} = \sqrt{a_p\, a_q}$ all minors of degree 2 and higher of the determinant on the a's become 0, from which ensues that the equation $\Delta_n = 0$ can be reduced to

$$\lambda^{n-1} \sum_{p=1}^{p=n} \sum_{q=1}^{q=n} B_{pq}\, a_{pq} - \lambda^n\, \Delta_b = 0,$$

where when developing the determinant Δ_b the coefficient of b_{pq} is B_{pq}. So there is an $(n-1)$ fold root $\lambda = 0$, which cannot of course indicate an attainable maximum or minimum, not even another stationary point.

Let us now consider the different mixtures assuming the rule of Galitzine-Berthelot.

$n = 2$.

Beside the root $\lambda = 0$ a second root appears which can certainly not point to a maximum, for from $\frac{a_{12}}{b_{12}} > \frac{a_1}{b_1}$ and $\frac{a_{12}}{b_{12}} > \frac{a_2}{b_2}$ would ensue $\frac{a^2_{12}}{b^2_{12}} > \frac{a_1\, a_2}{b_2\, b_2}$ and in connection with $b^2_{12} > b_1\, b_2$, certainly

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[1]) So we find for the asymmetric determinant

$$D \begin{vmatrix} b_1 & b_{12} & b_{13} & b_{14} & b_{15} \\ b_{21} & b_2 & b_{23} & b_{24} & b_{25} \\ b_{31} & b_{32} & b_3 & b_{34} & b_{35} \\ b_{41} & b_{42} & b_{43} & b_4 & b_{45} \\ b_{61} & b_{62} & b_{63} & b_{64} & b_{65} \end{vmatrix}$$

$$DD_{\substack{44\\55}} = (^4/_3\pi)^4 9 (r_1-r_2)^2(r_1-r_3)^2(r_2-r_3)^2(r_1-r_4)^2(r_2-r_4)^2(r_3-r_4)^2 \times$$
$$\times (^4/_3\pi)^4 9 (r_1-r_2)^2(r_1-r_3)^2(r_2-r_3)^2(r_1-r_5)(r_1-r_6)(r_2-r_5)(r_2-r_6)(r_3-r_5)(r_3-r_6) +$$
$$- (^4/_3\pi)^4 9 (r_1-r_2)^2(r_1-r_3)^2(r_2-r_3)^2(r_1-r_4)(r_1-r_5)(r_2-r_4)(r_2-r_5)(r_3-r_4)(r_3-r_5) \times$$
$$\times (^4/_3\pi)^4 9 (r_1-r_2)^2(r_1-r_3)^2(r_2-r_3)^2(r_1-r_4)(r_1-r_6)(r_2-r_4)(r_2-r_6)(r_3-r_4)(r_3-r_6) =$$
$$= 0.$$

$$a^2_{12} > a_1 a_2.$$

The appearance of a minimum is not a priori excluded; the general conditions now pass into:

$$b_{12} > \frac{\sqrt{a_2}}{\sqrt{a_1}} b_1 \text{ and } b_{12} > \frac{\sqrt{a_1}}{\sqrt{a_2}} b_2.$$

So it is not evident, why the appearance of a minimum should coincide with $a^2_{12} < a_1 a_2$ [1]).

Even for $a^2_{12} > a_1 a_2$ a minimum can very well present itself.

In fact there are objections to assuming that $a^2_{12} < a_1 a_2$, for this supposition leads when the temperature becomes lower to partial mixability [2]) and this phenomenon probably does not appear for normal substances [3]).

The following however holds good for a possible minimum:

$$a_1 > {}_1 b\frac{a_{12}}{b_{12}} \text{ and } a_2 > b_2 \frac{a_{12}}{b_{12}}, \text{ so}$$

$$a_1 + a_2 - 2a_{12} > (b_1 + b_2 - 2b_{12}) \frac{a_{12}}{b_{12}}, \text{ so}$$

$$a_1 + a_2 - 2a_{12} > 0.$$

For all temperatures excluding partial mixability, we find thus when a minimum appears

$$\sqrt{a_1 a_2} \leqq a_{12} < {}^1/_2 (a_1 + a_2).$$

$n = 3$.

The equation $\Delta_3 = 0$ has a double root $\lambda = 0$, so we obtain the following series of signs:

I

λ	Δ_3
$+\infty$	$+$
$+$	0
$+$	$-$
0	0
$-\infty$	$-$

or

λ	Δ_3
$+\infty$	$+$
0	0
$-$	$+$
$-$	0
$-\infty$	$-$

II

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[1]) VAN DER WAALS. Proceedings, Amsterdam, Oct. 1902, p. 244.

[2]) VAN DER WAALS. Continuïtät II, p. 43. However in the deduction it has been supposed there that $b_{pq} = {}^1/_2 (b_p + b_q)$.

[3]) VAN DER WAALS. Statique des Fluides, p. 32.

Case I.

There is a positive root λ making $\Delta_3 = 0$, which can however never indicate a possible absolute maximum or minimum, for $\frac{d\Delta_3}{d\lambda}$ is positive there, denoting a negative value of the minors of degree 2 and these must be (see inequalities (T_1) and (T_2)) positive for a maximum as well as for a minimum.

Case II.

One root making $\Delta_3 = 0$ is negative, the other 0, so neither of the two can indicate a possible mixture.

So for a ternary mixture the rule of GALITZINE-BERTHELOT cannot be united with the appearance of a maximum or a minimum. A stationary point, however, being neither maximum nor minimum, is not excluded in case I.

$\Delta_n = 0$ has for $n = 4$ a threefold root $\lambda = 0$.

So the series of signs becomes:

I

λ	Δ_4
$+\infty$	$+$
0	0
$-$	$-$
$-$	0
$-\infty$	$+$

or

λ	Δ_4
$+\infty$	$+$
$+$	0
$+$	$-$
0	0
$-\infty$	$+$

II

In case I the simple root λ belongs to a negative value of $\frac{a}{b}$, so it cannot represent a possible mixture.

In table II $\frac{\partial\Delta_4}{\partial\lambda}$ is positive for the simple root; thus the minors of degree 3 must be negative in case the mixture is to be possible. So it is evident, that as soon as we put a_{pq}^2 equal to $a_p\, a_q$ quaternary mixtures cannot show a minimum in $\frac{a}{b}$. A maximum is excluded, as this would lead to maxima in at least 2 binary mixtures to be formed out of the components and these are not possible if a_{pq}^2 is put equal to $a_p\, a_q$.

For mixtures where $n > 4$ a mixture for which $\frac{a}{b}$ is stationary is certainly excluded as soon as we put $a_{pq}^2 = a_p a_q$, for there is then an $(n-1)$ fold root $\lambda = 0$ and a root $\lambda = \infty$.

Resuming:

By assuming the rule of GALITZINE-BERTHELOT, we find:

$n = 2$. No maximum; a minimum is possible.
$n = 3$. No maximum or minimum — a stationary point, but no maximum or minimum, is possible.
$n = 4$. No maximum or minimum; other stationary points are possible.
$n = 5$ and higher. All stationary points are excluded.

If we assume for b a linear function of x, thus $b_{pq} = {}^1/_2 (b_p + b_q)$, then already for $n = 3$ the determinant on the b's becomes identical to 0, so that then for ternary and higher mixtures no stationary points are any more possible as soon as we put a_{pq}^2 equal to $a_p a_q$.

Mathematics. — "*On an expression for the genus of an algebraic plane curve with higher singularities.*" By Mr. FRED. SCHUH. (Communicated by Prof. D. J. KORTEWEG.)

Lately I gave the following theorem in these Proceedings [1]:

Let P be a point of order t' of an algebraic plane curve (where t' can also be zero, namely when P does not lie on the curve) and S an arbitrary point of order t of that curve. Suppose the straight line PS intersects the curve in w points coinciding with S, then $t' + \Sigma (w_1 - t_1)$ (summed up over all points S for which w is $> t$) is independent of the situation of point P and equal to the class of the curve. If S lies in P we have to regard all straight lines through P as the line connecting P and S or if one likes only those which furnish a contribution to $\Sigma (w_1 - t_1)$ i.e. the tangents in P.

From this a corresponding and as far as I can see a more important theorem for the *genus* of an algebraic curve can be deduced, where moreover the *straight line connecting P and S* can be replaced by an *algebraic curve*. Lateron I hope to connect this with problems of contact (numbers of algebraic curves determined by conditions of contact) in particular with respect to the number of normals on a curve with higher singularities (also in connection with the circle points and the line at infinity) let down from a point (which can also have a particular situation with respect to the

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[1] On an expression for the class of an algebraic plane curve with higher singularities. These Proc. VII, p. 42.

curve) and the question annex to it after the singularities of the evolute. It seems to me that in no other way known to me these and suchlike questions can be so simply answered.

The genus has been introduced in the theory of functions by RIEMANN and is defined out of the connection of the n'-leaved RIEMANN-surface on which an n'-valued algebraic function is univalent. If s is the number of branchpoints of the function, g the genus, then we have the following relation given by RIEMANN[1] (l.c. p. 129)

$$s - 2\,n' = 2\,(g-1),$$

for which a branchpoint where t leaves of the RIEMANN-surface are connected is to be regarded as $t-1$ branchpoints.

For the theory of the algebraic curves the notion and also the name of genus ("Geschlecht") has been introduced by CLEBSCH[2], whilst HALPHEN[3] has given for the genus of a curve of order n and class k with higher singularities the equation

$$2\,(g-1) = k - 2\,n + \Sigma\,(t_1 - 1),$$

in which $\Sigma\,(t_1-1)$ represents a summation over the origins of the separate *branches* of the curve (which can be represented by *one* PUISEUX-development) whose order t differs from 1 and over as many other origins of branches as one likes. If a branch of the curve is represented by the development

$$y - \eta = a_0\,(x-\xi) + a_1\,(x-\xi)^{\frac{t+r}{t}} + \dots,$$

according to integral ascending powers of $(x-\xi)^{\frac{1}{t}}$, I call the point (ξ, η) the *origin*, the line $y - \eta = a_0\,(x-\xi)$ the *tangent* and the numbers t and r the *order* and the *class* of the branch, where thus any point of a curve can be regarded as the origin of at least one branch, for which however if the point is a common point of the curve t will be equal to 1. If one and the same point of the curve is the origin of more branches we shall regard this point successively as if belonging to the different branches.

The HALPHEN-relation is an immediate result of the RIEMANN-relation if only one decomposes the branchpoints into those which

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[1] B. RIEMANN. Theorie der ABEL'schen Functionen. *Crelle's Journal, vol. 54,* (1857), p. 115—155.

[2] A. CLEBSCH. Ueber die Singularitäten algebraischer Curven. *Crelle's Journal, vol. 64,* (1865), p. 98—100.

[3] G. H. HALPHEN. Sur la conservation du genre des courbes algébriques dans les transformations uniformes. *Bulletin de la Soc. Math. de France, vol. 4,* (1875), p. 29—41.

do and into those which do not depend upon the choice of the system of coordinates.

If $t'_1, t'_2, \ldots$ are the orders, $v'_1, v'_2, \ldots$ the classes of the separate branches having their origin in P (so that $\Sigma\, t'_1 = t'$) then

$$2\,(g-1) = k - 2n + \Sigma\,(t'_1 - 1) + \Sigma\,(t_1 - 1),$$

whilst according to the quoted theorem

$$k = \Sigma\,(t'_1 + v'_1) + \Sigma\,(w_1 - t_1). \text{ (equation (2) l. c. p. 44)}$$

In the two last equations the first Σ-sign refers to the origins in P, the second Σ-sign to the origins outside P.

From these equations follows

$$2\,(g-1) = -\,2\,(n-t') + \Sigma\,(v'_1 - 1) + \Sigma\,(w_1 - 1). \quad \ldots \ldots \quad (1)$$

Here $n - t' = n'$ represents the number of movable points of intersection of the curve with straight lines through P. If one draws through P an arbitrary straight line l which is not a tangent in P, then the points of intersection of that straight line with the curve furnish to $\Sigma\,(w_1 - 1)$ a contribution equal to $n' - N_i$, where N_i represents the number of origins of branches lying outside P on the straight line l_i [1]), thus the number of branches over which the n' movable points of intersection with the straight line l_i distribute themselves. If then we draw through P a straight line l_j touching N'_j branches through P and if we let N_j be the number of branches over which the n' movable points of intersection with the straight line l_j distribute themselves, then $N_j - N'_j$ of these N_j branches have their origin outside P. The points of intersection outside P with these straight lines give a contribution to $\Sigma\,(w_1 - 1)$ equal to

$$(n' - \Sigma\, v'_j) - (N_j - N'_j) = (n' - N_j) - \Sigma\,(v_j' - 1),$$

in which $\Sigma\, v'_j$ and $\Sigma\,(v'_j - 1)$ are taken only over the branches touching the straight line l_j in P. From this ensues:

$$\Sigma\,(w_1 - 1) = \Sigma\,(n' - N_i) + \Sigma\,(n' - N_j) - \Sigma\,(v'_1 - 1),$$

or

$$\Sigma\,(w_1 - 1) = \Sigma\,(n' - N_1) - \Sigma\,(v'_1 - 1),$$

in which now $\Sigma\,(v'_1 - 1)$ denotes a summation over all the branches with P as origin, $\Sigma\,(n' - N_1)$ a summation over *all* straight lines through P for which n' is $> N_1$ and over as many other straight lines as one likes.

If we substitute in equation (1) for $\Sigma\,(w_1 - 1)$ the obtained value and replace $n - t'$ by n' we find

$$g = 1 - n' + \tfrac{1}{2}\,\Sigma\,(n' - N_1). \quad \ldots \ldots \quad (2)$$

We can sum up what has been found in the following theorem:

THEOREM I. *If an algebraic plane curve is intersected by the straight*

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[1]) Counting here also each of the points of intersection as origin of a branch.

lines of a pencil with P as vertex in n' movable points, which distribute themselves for the various straight lines of the pencil over $N_1, N_2 \ldots$ branches of the curve, then $1 - n' + \frac{1}{2}\Sigma(n' - N_1)$, *(where* $\Sigma(n' - N_1)$ *is taken over all the straight lines through P), has for every point P the same value equal to the genus of the curve.*

This theorem however can be considerably extended by making use of the property that the genus of the curve does not change by a one-to-one transformation. If namely we apply to the whole figure a CREMONA-transformation, then g remains the same, but n' too. The straight lines of the pencil are turned by the transformation into *rational curves* having multiple points in the fundamental points of the transformation. Through every point lying outside those fundamental points only *one* of the rational curves passes, so that we treat *a pencil of rational curves;* the manifold points here making the curves to rational curves are not present as movable points but as fixed points, which gives rise to linear relations between the coefficients of the curves. The movable points of intersection with a straight line are now transformed into movable points of intersection with a rational curve, and they remain the same in number on account of the one-to-one character of the transformation.

By a CREMONA-transformation a branch is furthermore always transformed into *one single branch* (where we always understand by a *branch* the whole of the curvepoints whose coordinates satisfy the same PUISEUX-development). If thus the n' movable points of intersection with a straight line distribute themselves over N branches then in the transformed figure the n' movable points of intersection with the rational curve originated by transformation of the straight line distribute themselves also over N branches.

From this it is evident that all quantities of equation (2) are *invariant* with respect to rational transformation, so that *the equation* (2) *holds good unchanged if the pencil of straight lines is replaced by a pencil of rational curves.*

This gives rise to the following theorem:

THEOREM II. *If an algebraic plane curve is intersected by a pencil of rational curves in n' movable points distributing themselves for the different curves of the pencil over N_1, $N_2, \ldots$ branches of the fixed curve, then* $1 - n' + \frac{1}{2}\Sigma(n' - N_1)$, *(where* $\Sigma(n' - N_1)$ *is taken over all curves of the pencil), has for every pencil of rational curves the same value equal to the genus of the fixed curve.*

This theorem can then be extended from a pencil of rational curves to an arbitrary algebraic pencil of curves by means of the following considerations which are however less rigorous than the preceding ones.

If we investigate which rational curves of the theorem II contribute to $\Sigma(n' - N_1)$ then we find 1st those rational curves which pass through an origin (lying outside the basepoints of the pencil) of a *superlinear* branch (denomination of CAYLEY for a branch with order more than *one*) of the fixed curve, 2nd those rational curves touching the fixed curve outside the basepoints, 3rd those rational curves where two or more of the movable points of intersection have approached one of the basepoints along the same branch of the fixed curve. In the main theorem II comes to the determination of the number of rational curves of a pencil touching a given curve and the change which this number undergoes on account of higher singularities of the given curve and the particular situation of the basepoints with respect to that curve. Here however it is difficult to imagine how it would cause a difference whether we are working with a pencil of rational curves or with an arbitrary pencil of curves; for in both cases the coefficients of the equation of the movable curve satisfy some linear conditions amounting to *one* less than is necessary for the definition of the movable curve [1]).

Let us explain the preceding by an example. Suppose the number of cubic curves through eight points touching a given curve were required, suppose further that the given curve has a singular point S with a singular tangent l and that the C'_3 of the pencil through S also touches l. Point S will then absorb a certain number of points of contact proper with curves of the pencil, and this number will depend on the nature of the singular point S and on the order of contact of C'_3 with the given curve, but in no wise on the fact whether of the basepoints three have coincided somewhere outside S, either in such a way that in one of the basepoints tangent and curvature are given, or in such a way that the coinciding basepoints form a triangle with finite angles, in which case the condition of the passage through the three basepoints includes the curve having a double point in a given point and being thus rational.

Led by the above considerations I think I may state the following theorem:

THEOREM III. *If an algebraic plane curve is intersected by a pencil of curves in n' movable points distributing themselves for the different curves of the pencil over $N_1, N_2, \ldots$ branches of the fixed curve, then* $1 - n' + \frac{1}{2}\Sigma(n' - N_1)$, ($\Sigma(n' - N_1)$ *taken over all the curves*

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[1]) Of course it would be different if the movable curve had to be rational without the singular points reducing the genus to zero being given; if thus e.g. the question were of cubic curves through seven given points, and furnished with a double point not given in position.

of the pencil), has for every pencil of curves the same value equal to the genus of the fixed curve.

The remarkable thing here of the obtained expression for the genus is that the genus which is invariant with respect to rational transformations is really exclusively expressed in quantities each invariant in itself over against rational transformations.

I feel the more justified in stating the above theorem having found the theorem confirmed in various simpler cases, e.g. for the case that the given curve admits of double points and cusps only whilst the basepoints can assume any particular position with respect to the given curve, also for the case that the given curve is provided with higher singularities where however only the simplest particular cases with reference to the position of the basepoints have been considered, e.g. the case that one or two basepoints fall in a higher singular point.

But all the same a *rigorous* and *simple* proof which renders a subtle distinction of the great number of particular cases which can present themselves superfluous, is very desirable.

Sneek, July 1904.

Mathematics. — "*On the curves of a pencil touching an algebraic plane curve with higher singularities*". By Mr. FRED. SCHUH. (Communicated by Prof. KORTEWEG.)

In the previous paper I have stated the following theorem:

If an algebraic plane curve is cut by a pencil of curves in n movable points distributing themselves for the various curves of the pencil over N_1, N_2, ... branches of the fixed curve, then

$$1 - n' + \tfrac{1}{2}\,\Sigma\,(n' - N_1)$$

($\Sigma\,(n' - N_1)$ *taken for all curves of the pencil) has for every pencil of curves the same value which is equal to the genus g of the fixed curve.*

Expressed in a formula this runs:

$$2\,(g + n' - 1) = \Sigma\,(n' - N_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

With the aid of this theorem the following problem of contact can be solved:

To determine the number of curves of a pencil touching a plane curve C_n of order n, class k and genus g.

To this end we first substitute in equation (1) for $\Sigma\,(n' - N_1)$ a summation over the points of C_n or better (as we always count a point of C_n through which more branches pass as more than one point) over the origins of branches of C_n. Let S be an origin of a branch of C_n whilst the curve of the pencil through S intersects the branch under consideration in w points S, then $\Sigma(n' - N_1) = \Sigma(w_1 - 1)$, so that equation (1) becomes

$$2(g + n' - 1) = \Sigma(w_1 - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here $\Sigma(w_1 - 1)$ represents a summation over *all* origins S of branches of C_n, i. e. only over those origins for which $w > 1$. If one or more basepoints of the pencil lie on C_n the summation must also be extended to those origins coinciding with a basepoint B. We must then regard as movable curve through that origin the limiting position of the movable curve through P if we allow P to approach to B along the corresponding branch of C_n, in other words that curve of the pencil intersecting the branch at least in *one* point B more than any curve of the pencil. For such an origin in B the number of *movable* points of intersection, approaching B along the branch under consideration when P approaches B along the same branch, is represented by w.

The following well known relation

$$2(g + n - 1) = \Sigma(t_1 - 1) + k \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

exists between order, class and genus of C_n.

Here $\Sigma(t_1 - 1)$ is a summation over all the origins of branches of C_n whilst t represents the *order* of the branch, i. e. the number of points of intersection with an arbitrary straight line through that origin coinciding with that origin.

From (2) and (3) then follows:

$$\Sigma(w_1 - t_1) = k + 2(n' - n). \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

THEOREM I. *If a pencil of curves cuts an algebraic plane curve C_n of order n and class k in n' movable points of which w fall in the origin S of a branch of order t of C_n, we have the relation $\Sigma(w_1 - t_1) = k + 2(n' - n)$, where $\Sigma(w_1 - t_1)$ must be taken over all the origins of branches of C_n, also over those coinciding with basepoints of the pencil.*

With the equation (4) the given problem of contact for *every* C_n and *every* particular situation of the basepoints with respect to C_n can, as will be shown, be regarded as solved.

We have but to discuss the found equation.

If m is the order of the curves of the pencil, then $n' = mn$ for *arbitrary situation* of the basepoints with respect to the given curve C_n, so:

$$\Sigma(w_1 - t_1) = k + 2n(m - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Here we understand by an *arbitrary situation with respect to C_n* in the first place that the basepoints do not lie on C_n. Let us

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suppose moreover that the basepoints are situated in such a way that not a single curve C'_m of the pencil passing through a singular point S of C_n touches one of the branches through S and that not a single C'_m has with the fixed curve a contact of higher order then the first; then only the curves C'_m showing a common contact with C_n ($w=2$, $t=1$), furnish to $\Sigma(w_1-t_1)$ a contribution equal to the number of those touching curves C'_m. Here however a restriction ought to be made. It may appear namely that a C'_m of the pencil has a double or multiple point lying on C_n which then furnishes a contribution to $\Sigma(w_1-t_1)$. We can avoid this case by requiring that for an arbitrary situation of the basepoints with respect to C_n no singular point of C'_m may lie on C_n. This is however no longer possible when by mutual coincidence of basepoints the pencil admits of curves showing an infinite number of double or multiple points, in other words when the pencil contains curves, which consist of or contain two or more coinciding parts. Though the equation (3) can still be applied to these cases we shall exclude them for simplicity's sake from our discussion. With these suppositions we find that $\Sigma(w_1-t_1)$ is equal to the number of curves of the pencil touching C_n. So we find the following theorem:

THEOREM II. *For a pencil of curves of order m, none of which contains two or more coinciding parts, the number of curves touching an algebraic plane curve C_n of class k with respect to which the basepoints of the pencil have no particular situation is represented by $k+2n(m-1)$.*

If C_n is a general curve in point-coordinates then $k=n(n-1)$, and the required number is $n(n+2m-3)$. If we compare this to the number given in the above theorem we find:

THEOREM III. *Every singular point S of C_n diminishes the number of curves which belong to the pencil mentioned in theorem II and which properly touch C_n, by the same number as that with which S diminishes the class of C_n.*

We now investigate which particularities can present themselves in consequence of a particular situation of the basepoints with respect to C_n. To this end we consider in the first place an origin S of branch T of order t of C_n supposing S not to be situated in one of the basepoints; further we suppose that the curve C'_m through S touches the branch T and intersects it in $w=t+\gamma$ coinciding points (so in γ points more than when the curve through S of the pencil were not to touch the branch). Then this point S counts (as far as the branch T is concerned) according to (5) for $w-t=\gamma$ points of contact proper. If we restore by a small displacement of the basepoints their arbitrary position with respect to C_n; the curve through S of the pencil intersects the branch T in t points S and in γ points lying near S. The preceding holds good invariably when the pencil does contain curves containing two or more coinciding parts if only those do not pass through the considered point S.

This gives rise to the following theorem:

THEOREM IV. *Let S be the origin of a branch T of an algebraic plane curve C_n. If now the basepoints of a pencil of curves pass from an arbitrary position to a particular one so that no basepoint approaches S whilst γ points of intersection of C_n with the curve through S of that pencil approach S along the branch T, then as many (so γ) points of contact of C_n with curves of the pencil approach S along the same branch. Here has been supposed that if the pencil contains curves containing two or more coinciding parts these parts do not pass through S.*

If the basepoints have the particular position described in this theorem, then S counts for γ points of contact proper. So we can formulate the theorem as follows:

If S is a point of C_n not coinciding with one of the basepoints of the pencil, whilst the curve through S of the pencil cuts a branch of order t of C_n with S as origin in $t + \gamma$ points S, then S absorbs as far as that branch is concerned γ points of contact proper.

Theorem IV is an extension of a theorem of HALPHEN and STEPHEN SMITH, which I discussed in a paper in a previous number of these Proceedings [1]).

The indicated theorem can be expressed as follows:

Let S be the origin of a branch T of a curve, l the tangent of that branch in S. If a point P approaches l but not S, then as many points of intersection with PS as points of contact of tangents through P approach the point S along the branch T.

This is no other than our theorem IV where the pencil of curves is replaced by a pencil of straight lines.

Let us further consider the case of a singular point S of C_n, with which coincide one or more of the basepoints. As our only business is to determine the number of points of contact proper coinciding with S we can assume for simplicity's sake that no basepoints coincide with other points of C_n.

Further we exclude the case that the pencil contains curves admitting of coinciding parts.

Let $t'_1, t'_2, \ldots$ be the orders of the different branches $T'_1, T'_2, \ldots$ of C_n having S for origin, whilst an arbitrary curve of the pencil

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[1]) On an expression for the class of an algebraic plane curve with higher singularities. These Proceedings VI, p. 42.

cuts those branches successively in $z'_1, z'_2, \ldots$ points S. Then we have

$$n' = mn - \Sigma\, z_1'.$$

Further we can break up $\Sigma\,(w_1 - t_1)$ into the share $\Sigma\,(w_1' - t_1')$ of the point S and the share of the other points of C_n. The meaning of w'_1 is here, that the curve of the pencil cutting the branch T'_1 in more then z'_1 points S does this in $z'_1 + w'_1$ points.

For equation (4) we can then write

$$\Sigma\,(w_1 - t_1) = k + 2n\,(m-1) - \Sigma\,(w'_1 + 2\,z'_1 - t'_1), \quad . \quad . \qquad (6)$$

where $\Sigma\,(w_1 - t_1)$ must now be taken only for the curvepoints outside S. If we represent by u'_1 the number $w'_1 + z'_1$ of the points S in which the branch T'_1 is cut by the osculating curve of the pencil, equation (6) becomes:

$$\Sigma\,(w_1 - t_1) = k + 2n\,(n-1) - \Sigma\,(u'_1 + z'_1 - t'_1).$$

It is evident from this equation that the point S, as far as branch T'_1 is concerned, absorbs $u'_1 + z'_1 - t'_1$ points of contact proper. This can be formulated in the following theorem:

THEOREM V. *If a single or multiple basepoint of a pencil of curves coincides with the origin S of a branch of order t of an algebraic curve C_n, whilst that branch cuts an arbitrary curve of the pencil in z, the osculating curve of the pencil on the contrary in u points S, then the point S absorbs $u + z - t$ points of contact of curves of the pencil with C_n, in other words for an arbitrary displacement of the basepoints coinciding with S the point S furnishes $u + z - t$ points of contact, which are then situated on the considered branch.*

By allowing the basepoints to undergo not an arbitrary displacement but a particular one, another theorem in connection with theorem IV can still be deduced from this. We can namely make the basepoints change their places slightly along the osculating curve of the pencil in such a way, that no more basepoints coincide with S. In that case the point S continues to absorb after the displacement of the basepoints a certain number of points of contact proper, and according to theorem IV to the amount of $u - t$; in fact after that displacement the curve of the pencil through S intersects the branch in u points S, so that for the point S now w is equal to u. If we compare the number $u - t$ of the absorbed points of contact to the amount given in the theorem V we find:

THEOREM VI. *If the curves of a pencil cut the branch T of an algebraic plane curve in z fixed points coinciding with its origin S, then point S gives to that branch z points of contact with curves of the* *pencil, when the basepoints falling in S move away from S along the osculating curve of the pencil.*

It is clear that the theorems V and VI invariably hold good when the pencil contains curves degenerated in coinciding parts if only they do not pass through point *S*.

Theorem VI is like theorem IV an extension of the above mentioned theorem of HALPHEN and SMITH. If namely we substitute for the pencil of curves the pencil of straight lines with *S* as vertex, theorem VI passes into:

Let S be the origin of a branch T of a curve whilst that branch is intersected in t points S by an arbitrary straight line through S. If now a point P moves away from S along the tangent in S, that point S gives to that branch t points of contact with tangents through P.

It is not difficult to see that this is correlative to the formulation given above of the SMITH-HALPHEN-theorem. However when the pencil of curves is not a pencil of straight lines the theorems IV and VI are *not* correlative and so we have to regard them as entirely different theorems.

Sneek, June 1904.

Astronomy. — "*On the apparent distribution of the nebulae.*" By C. EASTON. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

It being admitted that the results of the visual observations must be kept separated from those obtained by photography, the systematic investigation of the distribution of the nebulae by means of photography begun by MAX WOLF should not prevent us from carefully examining the very extensive material regarding nebulae which has been formerly obtained by direct observation and laid down in catalogues; and the less so because it is highly improbable that even in future a visual "Durchmusterung" of this kind, which for the rest is very desirable, will be carried out on account of the different method which now is being followed at Heidelberg.

It is noways unimaginable that the distribution of the nebulae as shown by photography will differ greatly from that of the visually observed nebulae; yet it is certain that the latter distribution shows remarkable features which call for an explanation. WILLIAM HERSCHEL has found that in the main the nebulae are numerous where the stars are sparse. In a certain sense we have here the reverse phenomenon from that of the stars; NEWCOMB (The Stars, p. 187) expresses it thus:

"The latter (the stars) are vastly more numerous in the regions near the Milky Way, and fewer in number near the poles of that belt. But the reverse is the case with the nebulae proper. They are least numerous in the Milky Way and increase in number as we go from it in either direction."

Cleveland Abbe who after the publication of **John Herschel**'s catalogue in 1864 statistically investigated this peculiarity (Month. Not. R. A. S. XXVII, p. 257) rightly put the question whether the paucity of nebulae in the Galaxy did not rest upon a mere optical delusion due to the luminous background of the Milky Way. He thought himself justified, however, in answering this question in the negative, because the regions on either side of the Galaxy proper did not show a considerable increase in the number of nebulae; nor was this the case with increasing optical power.

With a much more extensive material — 9264 objects — **Stratonoff** (Publ. Tachkent N°. 2) arrived at chiefly the same result. With some reservation, however. For in fact if we develop **Stratonoff**'s data in a somewhat different way we find that, as we go from the galactic plane, the faint nebulae increase more rapidly than the bright ones. This fact, also because it contradicts a preliminary result of **Max Wolf**: that the (photographed) small nebulae are in general distributed more equally over the sky, raises the surmise that in visual observation the light of the smallest and faintest nebulae in the galactic region is to a certain amount extinguished (table I).

TABLE I.

Increase of the mean density of bright and faint nebulae in the direction from the Galaxy.

Mean gal. latitude	Bright nebulae (N. brillantes)	Faint nebulae (N. faibles)
+ 35°	7.5	10.2
+ 25°	3.8	7.0
+ 15°	2.3	3.4
+ 5°	1.9	1.5
— 5°	2.3	1.8
— 15°	3.7	5.1
— 25°	6.2	11.0
— 35°	6.5	12.5

In order to investigate this problem more fully I have compared the density of nebulae in the different parts of the northern Galaxy with the intensity of the galactic light in those same portions. For if really the luminous background of the Milky Way had a highly disturbing influence, a certain parallelism between the distribution of the galactic light over that girdle (which distribution is very irregular) and the distribution of the nebulae in the same region would manifest itself in this sense that the nebulae, especially the faint ones, are least numerous in those patches where the galactic light is strongest. Table II gives the galactic zone proper between — 10° and + 10° gal. latitude (northern hemisphere) divided into areas of 30 degs. in galactic longitude; the two upper lines show for each area the mean density of nebulae derived from STRATONOFF's data; the lower line shows the mean intensity of the galactic light derived from the table on p. 18 of my "Distribution de la lumière galactique" (Verhand. Kon. Akad. v. Wet. VIII, 3).

TABLE II.

The density of the nebulae and the galactic light in the Milky Way compared.

	180°			90°		0°
Bright nebulae	1.2	0.7	1.3	0.9	1.0	0.9
Faint nebulae	0.8	0.7	1.8	0.7	1.0	1.0
Galactic light	1.03	0.72	0.78	1.09	1.31	1.08

No parallelism is to be detected.

Other causes which might influence in the same way as the "extinction" due to the luminous background of the Milky Way, must be disregarded. Up to now the investigation has yielded nothing in contradiction to the view that the peculiar distribution of the nebulae in the sky results, at least in the main, from their particular *real* distribution in space.

CLEVELAND ABBE tried to explain the paucity of nebulae in the galactic region and the (supposed) increase of their number towards the two Poles of the Milky Way by the supposition that the visible universe consists of systems of which our Milky Way, the two Nubeculae and the nebulae are the individuals, which in their turn are composed of stars and (or) nebulae; that moreover the galactic plane is nearly at right angles to the major axis of "a prolate ellipsoid" in which all visible nebulae are equally scattered.

This theory is founded on the supposed symmetrical distribution of the nebulae with regard to the Galaxy. Also **Bauschinger** (V. J. S. 24, p. 43) and **Stratonoff** adopted this symmetry. **Stratonoff** supposes first that the sky from the North Pole to $\delta - 20°$ has been surveyed uniformly with a view to nebulae (l. c. p. 43); secondly — like his predecessors — that the actually observed *decrease* in the number of nebulae between about $-50°$ and the South Pole of the Galaxy must be ascribed to the incompleteness of the observations made in the southern hemisphere.

I shall now proceed to demonstrate that **Stratonoff**'s first surmise is certainly erroneous and that the second, considering the present state of our knowledge, is not justifiable and moreover improbable.

That the nebulae-material from the North Pole to $\delta - 20°$ would be collected with equal completeness throughout, as would follow from **Stratonoff**'s first supposition, cannot, apart from the lack of a systematic "Durchmusterung", be the case on account of the great difficulty to detect faint objects like the nebulae, which arises from the atmospheric absorption in regions far from the zenith. In Lord **Rosse**'s telescope, for instance, it has never been possible to observe properly the Omega nebula, though it lies only at $-16°$. (**Dreyer**, Trans. Dublin Soc., N. S. II p. 151).

Besides, the circumstance that the summer nights are never totally dark in the relatively high latitudes of the observatories of the northern hemisphere where the nebulae observations have for the greater part been made, must render the number of catalogued nebulae in the southern regions which then rise above our horizon much too small in proportion to the opposite equatorial region.

With regard to this I have investigated the tables of **Bauschinger**. I have compared two equally large areas, occupying the same position with respect to the celestial equator and the Milky Way, A: α 5^h to 9^h, $\delta + 15° - 30°$. B: α 17^h to 21^h, $\delta + 15° - 30°$.

The number of bright and faint nebulae in those areas A and B may be seen on table III:

TABLE III.

Numbers of bright and faint nebulae in opposite equatorial regions.

	A	*B*
bright nebulae	26	20
faint nebulae	157	101

There appears indeed to exist a difference at the expense of area

B and this difference, as might be expected, is much greater for the faint than for the bright nebulae.

It may be remarked that such a difference is not found — rather the contrary — in areas which in the northern galactic zone border upon those mentioned, where therefore the influence meant cannot manifest itself so strongly. It remains possible of course that the number of nebulae in the direction *B* is indeed smaller than in the direction *A*; but we cannot consider such a large difference as established where the disturbing influence is undoubtedly at hand.

If we consider only the northern galactic hemisphere, then the nebulae seem indeed to increase fairly gradually though not regularly towards the Pole of the Milky Way. For the southern hemisphere such an increase is also visible in the table of STRATONOFF as far as about —60° galactic latitude. STRATONOFF, however, constructed his table omitting the two Nubeculae. Now it seems to me that for such a statistics this omission is not justifiable. The MAGELLANIC CLOUDS must not at all be considered as patches torn off from the Milky Way, which also appears from the fact that the nebulae proper [1]), which are scarce in the Milky Way are four times more numerous than the star clusters in the MAGELLANIC CLOUDS (JOHN HERSCHEL, Results Obs. Cape). As to their composition the Nubeculae keep the middle between the Milky Way and the accumulations of nebulae (sometimes intermingled with star clusters and stars) in Coma, Pisces, etc. — and though the latter agglomerations are less dense than the CLOUDS it is not allowed, in my opinion, to include these agglomerations in our table and to exclude the CLOUDS. Especially also because, as may be seen clearly on STRATONOFF's own maps (Publ. Tachkent, N°. 2, Atlas, pl. 16 et 18; comp. SIDNEY WATERS, M. N. XXXIII, p. 558) the Nubeculae are connected with streams of nebulae and not with the Milky Way.

If, however, we include the Nubeculae into the statistics then we must substitute my table *B* (table IV) for STRATONOFF's own table *A* for the southern gal. hemisphere:

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[1]) Where in this paper we speak of nebulae proper or nebulae without more, we mean the relatively regular and well-defined nebulae ("white nebulae"), while with diffused nebulae are meant the extensive, formless and according to their spectra gaseous masses ("green nebulae").

TABLE IV.

Mean density of nebulae in the southern gal. hemisphere, according to STRATONOFF.
(A including, B omitting the Nubeculae).

	A	*B*
β gal. — 85°	19	19
— 75	24	24
— 65	29	29
— 55	36	36
— 45	25	26
— 35	22	31
— 25	19	19
— 15	10	10
— 5	4	4

If we consider what has been said above on the incompleteness of the observations also in the zone between 0° and — 20° gal. latitude, little remains of the systematic increase as far as about — 60° which, according to STRATONOFF's table *A*, seems to exist.

One more remark. An eminent observer as JOHN HERSCHEL, for the very reason that he naturally avoided the South Pole in his "sweeps", is sure to have accounted for the incompleteness arising from that circumstance and yet he says emphatically (Outlines, Ed. 1851, pg. 596): "In the southern hemisphere a much greater uniformity of distribution prevails, and with exception of two very remarkable centers of accumulation, called the MAGELLANIC CLOUDS, there is no very decided tendency to their assemblage in any particular region."

We have, however, a means to find indirectly whether the real distribution of the nebulae with regard to the galactic plane is in the main symmetrical, and consequently that the greater incompleteness of the observations in the southern hemisphere is the cause that the tables do not show a similar progression towards the galactic South Pole as they do towards the galactic North Pole.

The galactic equator and the celestial equator form a large angle: 60°. A considerable segment of the northern galactic region occurs south of the celestial equator — hence within the less thoroughly investigated portion of the sky —; on the other hand an equally large segment of the southern galactic hemisphere lies within the well-investigated region north of the equator. The strong influence of the incompleteness of the observations (the real distribution of the nebulae being about the same in the two galactic hemispheres) would then reveal itself in those two segments, so that the southern galactic segment *B* (lying on the northern hemisphere) is found to be richer in nebulae than the northern galactic segment *A* (lying on the southern hemisphere), and the difference would be most marked in the small and faint nebulae.

TABLE V.

Nebulae in the segments between the celestial equator and the galactic equator.

	A, segm. north. gal. hemisphere (southern hemisphere)	*B*, segm. south. gal. hemisphere (northern hemisphere)
bright nebulae . . .	152	71
faint nebulae . . .	754	1043

In table V the difference meant is indeed very great for the faint nebulae; it is remarkable, however, that for the bright ones there is a large difference in the opposite sense. This raises the surmise that the possible influence mentioned above does not play a preponderating part.

If we compare the structure of segment *A* with that of the remaining part of the northern gal. hemisphere it appears that the density of nebulae in the segment is only 0.6 — which is by no means surprising as it borders upon the galactic plane — but it is very remarkable that the proportion $\frac{\text{faint}}{\text{bright}}$ in the segment, 4.96, is exactly the same in the remaining part of the northern gal. hemisphere, viz. $\frac{2670}{539} = 4.95$.

The relation in the segment *B*, the southern galactic segment, is on the other hand quite different: $\frac{\text{faint}}{\text{bright}} = 14.7$. This points very markedly to a surplus of faint nebulae in the southern galactic segment situated on the northern hemisphere, and this circumstance together with the presence of the Nubeculae and their relation with the accumulations of nebulae in the southern gal. hemisphere makes it very probable that the structure of the southern galactic sky with regard to the nebulae differs entirely from that of the northern galactic sky.

In the very improbable case that by a more accurate survey the northern galactic segment would be enriched so considerably by faint nebulae that the proportion of the numbers of bright and faint nebulae agrees more or less with that in segments *B*, i. e. **1:15**, we should count there 2500 nebulae against 3200 in the remaining $^2/_3$ of the northern galactic hemisphere, and the increase towards the Pole, at least for the faint nebulae, would then almost disappear in the northern galactic hemisphere.

But whether the number of faint nebulae remains **754** or increases to 2500, in either case a symmetrical increase is out of the question and hence there is no reason why we should adopt **Cleveland Abbe**'s prolate ellipsoid which moreover was not very probable.

Several considerations plead against the view that the nebulae must be considered as distant galactic systems; the most important, which has been expressed half a century ago, is the occurring together, in most cases even in streams, of nebulae and stars, and also the existence of stars and nebulae in the Nubeculae; (it is obvious that in such cases we have to do with objects of the same order of magnitude). Moreover we have the well-established fact that a star may pass into a nebula. (Comp. Valentiner, Handwörterbuch d. Astron. III, 2, p. 524; also Moulton, Astrophys. Journal XI, 2, Schaeberle, Nature, Vol 69, No 1785, Seeliger, Abh. bayer. Akad. XIX, p. 572). Should on the other hand a "distant galactic system" be visible to us it can only appear to us as a nebula. But the scarcity of nebulae in the galactic region, if that phenomenon is real, points to an unmistakable organic connection between the great mass of the nebulae and our system of stars.

If then we may accept that the basis on which **Cleveland Abbe** built his theory of the ellipsoidal figure does not hold and if moreover we need not consider the nebulae as being situated at enormously vast distances on either side of the Milky Way, but if, on the contrary, it is far more likely that these distances are comparable with those of the stars, it becomes probable that the greater part of the nebulae are contained in a space similar to the oblate spheroid in which Seeliger places our whole stellar system, in other words: we may begin by adopting that the great mass of the nebulae belongs to our stellar system and that they are asymmetrically scattered on either side of the chief plane.

Moreover, if we supposed that the great mass of the nebulae were systems outside our own, the problem would not be capable of further development. We must therefore not start from such an hypothesis.

Astronomy. — "*The nebulae considered in relation to the galactic system.*" By C. Easton. (Communicated by Prof. H. G. van de Sande Bakhuyzen.

If we consider the nebulae as forming part of our galactic system (comp. my previous paper "On the apparent distribution of nebulae") their distribution must be considered in connection with that of the other classes of objects in this system. And then, speaking generally, we not only find a contrast between the apparent distribution of the stars (and clusters) and the nebulae, but also between the distribution of the large diffused nebulae (which, as far as we know, occur almost exclusively in the region of the Milky Way) and that of the nebulae proper; on the other hand it is probable that the galactic agglomerations for the greater part consist of stars of the first spectral type.

Starting from the consideration that the nebular and the star-like conditions are phases in the development of matter and no invariable final phases, it is obvious that as the distribution of the star-like matter in some parts of the system differs from that in the others — which is accompanied by a different constitution of most of the centers themselves, as appears from the spectral differences — so the distribution and the constitution of the matter which exists in the nebular condition will not be the same throughout the system.

In the galactic region of the system we find a great number of star-like objects probably placed for the greater part at (relatively) small distances from each other, mostly of the first spectral type. In the "extra-galactic" portions of the system we observe a smaller number of suns, separated by vast distances and belonging for a great part to the second spectral type.

In the same way we find in and outside the galactic region proper two forms of nebulae. In it are found the "green" nebulae with a spectrum formed of lines, sometimes round and fairly well-defined (planetary nebulae), but mostly extending over immense regions which they cover as with a veil (large diffused nebulae). In the extra-galactic regions we find the "white" nebulae with a continuous or — more probably — a mixed spectrum; isolated and generally widely separated objects, probably as a rule of a spiral form, and certainly more condensed than those of the other kind.

As little as we can sharply distinguish between star-like and nebular objects, is the above mentioned distinction intended as a precise classification. But thus taken in connection with the "galactophily" of the "green" nebulae, the "galactophoby" of the nebulae proper does not appear as something exceptional; this principal peculiarity of the distribution of the different kinds of nebulae may then be considered as a natural sequence of the same cause as in the agglomerations of the Galaxy has given rise to a type of stars differing in constitution and distribution from those outside the Milky Way.

For the investigation of the problem mentioned at the head of this paper we must take into consideration:

a. The place of the sun in the solar system.

b. The great difficulty to detect a nebula as compared with a star at the same distance from us which has the same quantity of matter.

Further I adopt as established:

1. That besides a gradual increase in the number of stars towards the galactic plane there exist real agglomerations in the galactic region.

2. That the sun is situated in a region of the Milky Way which is relatively poor in stars, hence as to the type of distribution in a region that must be considered as "extra-galactic", or perhaps in a transition layer. (Comp. Kapteyn, *Versl. K. A. v. W.* 1892/93, *Publ. Groningen* n° 11, p. 32; Easton, *Astr. Nachr.* 3270, Seeliger, *Betracht.* p. 627; Newcomb, *The Stars,* Chap. XX).

As probable:

3. That the system of stars is contained within a spheroid with the galactic plane as its principal plane (Seeliger).

And from my own investigations (*Versl. K. A. v. W.* 1897/98; *Astrophys. Journal* XII, 2; *Verhand. K. A. v. W.* VIII, 3) it seems to follow:

4. That in the Cygnus-Aquila region of the Milky Way the preceding branch is much nearer to us than the following.

5. That the brightest galactic portion in Cygnus occupies almost a central position in the system of the stars.

Now, while discussing the distribution of the nebulae catalogued after visual observation, I shall try to give an explanation founded on the supposition that, the dim light of the nebulae in general taken into consideration, the very distant nebulae escape visual observation (though they for the greater part perhaps may be registered photographically), and hence that, according to what has been said above especially sub 4, the very distant part of the system in which the Aquila branch of the Galaxy is situated, must be disregarded.

If the sun lies about in the central plane of the system in a poor region amidst galactic agglomerations, and if that poor region is comparable with the "extra-galactic" regions on either side of the galactic plane, the thus connected "extra-galactic" regions acquire more

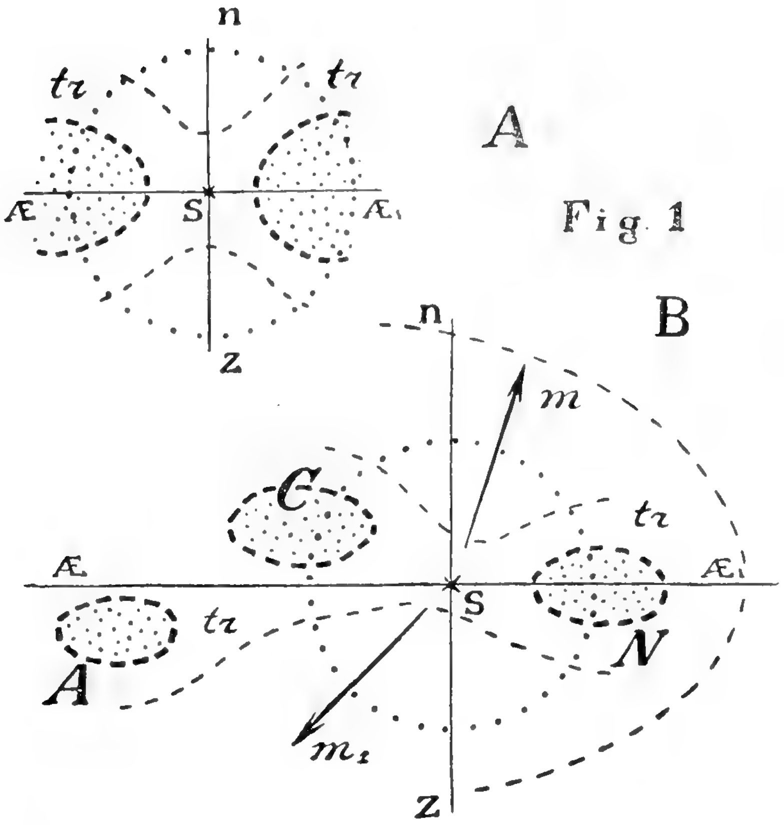

Fig 1

or less the shape of dumb-bells (comp. fig. 1, *A*), the sun lying in its bar *n*—*z*. If the *nebulae* proper are in the main confined to that extra-galactic region, the galactophoby of these nebulae and their accumulation towards the two Poles would be explained by it.

If, however, we leave the Aquila branch of the Galaxy [1]) out of consideration, we must bear in mind that in the remaining and nearer region of the Milky Way the galactic agglomerations on the Cygnus side have a northern galactic latitude; i. e. that the sun now lies south of the plane passing through those agglomerations (C) and the opposite ones in Argo, N; hence it is no longer in the middle but at the bottom of the bar of the dumb-bells, and consequently the apparent crowding of the nebulae towards the North galactic

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[1]) Comp. Fig. 1, B. The section of the Aquila branch is A, that of the Cygnus agglomeration is C, that of the Galaxy in Argo is N. The circle round the sun is the area within which are situated all nebulae of which the luminosity exceeds a certain minimum. The region *tr* is considered as a transition region between the (dotted) agglomerations of stars in the galactic plane Æ and the extra-galactic region contained within the spheroid. The bar of the dumb-bells is represented much thicker.

Pole will increase and that towards the South galactic Pole will diminish or disappear. From the circumstance that the nearest galactic region in the direction of XIX h. (towards C) has a northern galactic latitude it moreover follows that the maximum of nebulae of the northern gal. hemisphere lies within more than 90 degs. of the galactic equator in a great circle passing through C and M, whereas in the southern galactic hemisphere the maximum of nebulae is situated on the Cygnus side of the Pole (towards m_1).

This theoretical consideration has been tested by observation in the following way. On the maps for the distribution of the nebulae by STRATONOFF (*Publ. Tachkent* 2, pl. 18 and 19) we have estimated in a zone 15° wide in the direction of the galactic meridian of 45°, which crosses the Cygnus region the densities in areas from 10 to 10 degrees galactic latitude. The result is given in table VI. (For tables I—V see the paper *"On the apparent distribution of nebulae"*).

The much smaller densities of the southern galactic hemisphere could be expected owing to the greater incompleteness of the observations; for the rest the displacements of the maxima from the Poles are in the same sense as they should be according to theory. In how far the hypotheses made are thus supported cannot be decided because of the incompleteness of the data, at any rate they are not at variance with the results of the observations.

If, with the now available data, particulars are to be detected concerning the true distribution of the nebulae, we shall have to look for traces of them in those regions where the galactic and the extra-galactic regions meet. In a mean galactic latitude we shall have to search for the great irregularities in the apparent distribution of the nebulae and compare the places where they occur with the places where the irregularities in the distribution of the stars are found, especially the irregularities in brightness and in width of the diffused light of the Milky Way.

To this end the following tables have been constructed (VII, VIII, IX).

Over STRATONOFF's maps of the distribution of the bright (n. brillantes) and faint (n. faibles) nebulae, a galactic system of coordinates was laid. For each area of 15° in gal. longitude and 10° in gal. latitude we have then estimated as carefully as possible the density of bright and faint nebulae. These values were combined with due regard to the unequal surfaces of the areas in order to obtain the mean densities for zones of 15° gal. longitude between 0° and 50° gal. latitude on either side of the galactic equator (table VII). For the galactic zone proper, between + 10° and — 10° gal. latitude,

TABLE VI.

Density of the nebulae in the direction of the galactic meridian of 45°.

Northern galactic hemisphere.			Southern galactic hemisphere.		
α gal.	β	△ Neb.	α gal.	β	△ Neb.
45	+ 5	2.5	225	− 5	0.4
	15	3.5		15	0.2
	25	8.0		25	3.7
	35	13.8		35	5.7
	45	12.5		45	9.3
	55	11.8		55	9.2
	65	18.2		65	4.2
	75	21.0		75	9.5
45	85	41.0	225	85	8.1
225	85	43.0	45	85	10.3
	75	40.3		75	12.0
	65	22.2		65	11.3
	55	17.8		55	16.5
	45	13.0		45	15.0
	35	11.4		35	11.3
	25	12.0		25	5.8
	15	6.0		15	3.3
225	+ 5	0.8	45	− 5	1.9

we have combined in table VIII the regions north and south of the gal. equator, as it was of no use to consider these regions separately. On the construction of the two tables the compensation method used by STRATONOFF has probably influence, but in my opinion it is of no consequence that the details of the distribution are more or less obliterated and hence the contrasts are less distinct. For an investigation of the main features this is rather an advantage; the method is only inconvenient with the Nubeculae. In these two tables the data relating to the southern hemisphere have been added,

TABLE VII.

Density of nebulae in the zones 0° to 50° galactic latitude.

A. Bright nebulae.

(Values of the upper line north, values of the lower line south of the gal. equator).

360		330		300		270		240		210		180		150		120		90		60		30		0° α γuλ
2.2	4.2	2.3	2.8	3.5	12.1	9.2	7.2	8.6	6.3	4.1	3.1	3.7	6.0	4.7	4.5	8.9	11.8	4.7	5.1	4.4	1.9	1.7	2.3	
2.7	2.9	6.1	6.8	3.8	2.8	5.0	28.4	9.9	2.5	5.2	3.8	9.0	2.7	2.4	2.5	7.5	8.8	4.1	4.7	4.2	3.1	4.5	3.7	

B. Faint nebulae.

(Values of the upper line north, values of the lower line south of the gal. equator).

4.5	4.0	2.8	3.0	2.9	6.0	4.9	4.5	8.2	6.6	6.5	7.2	6.8	7.2	4.9	4.5	4.5	5.2	4.0	8.6	8.7	6.4	6.9	7.1
3.7	2.5	3.0	2.5	2.4	1.6	1.8	10.0	4.1	1.9	2.4	4.6	9.4	7.6	4.5	5.8	15.5	11.7	9.0	9.5	8.2	5.8	7.0	5.2

TABLE VIII.

Density of nebulae of the galactic-equatorial areas (— 10 to + 10° gal. latitude).

A. Bright nebulae.

1.9	4.1	2.0	1.7	1.9	4.4	3.1	4.1	4.4	2.7	3.4	1.6	4.3	2.0	2.4	1.1	3.1	3.4	2.1	2.5	2.2	2.8	2.4	2.2

B. Faint nebulae.

1.1	3.0	2.8	1.2	0.9	0.9	1.3	1.4	0.4	1.0	1.5	1.8	3.2	2.6	1.9	2.4	8.5	2.4	1.2	2.9	3.0	2.8	3.7	2.2	
360		330		300		270		240		210		180		150		120		90		60		30		0°

TABLE IX.

Intensity of the light of the Galaxy in gal. equat. areas, — 14° to + 14° gal. latitude.

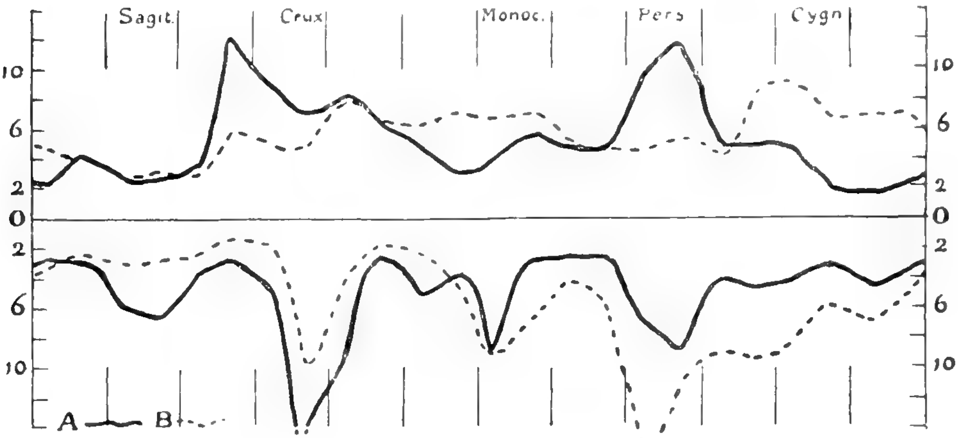
(Values of the upper line north, values of the lower line south of the gal. equator).

1.14	1.29	1.19	0.63	0.57	0.64	0.80	1.14	1.34	1.74	0.97	1.10	
0.82	1.00	0.37	0.67	0.81	1.14	1.20	1.39	1.36	1.07	1.37	1.19	
180	165	150	135	120	105	90	75	60	45	30	15	0°

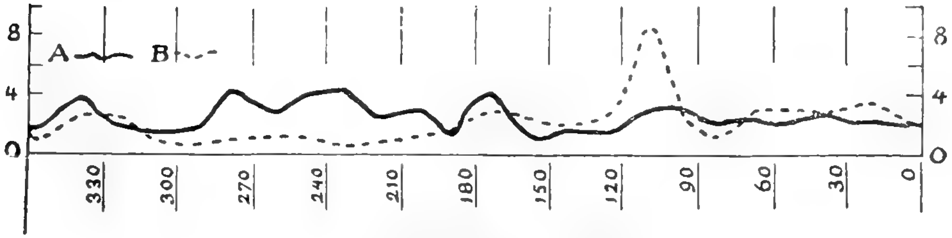
but only for completeness, for especially for the faint nebulae these data have but little value and especially from the curves of table VIII it may be easily seen that the material relating to the southern hemisphere cannot be compared with that for the northern hemisphere.

Table IX gives for areas of 15° gal. longitude and 28° gal. latitude, 14 degrees on either side of the gal. equator, the brightness of the light of the Milky Way expressed in terms of the mean brightness of the northern hemisphere derived from the table of p. 18—19 of

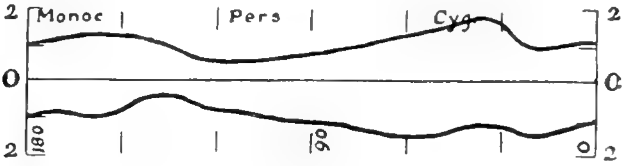
Fig. 2.



Graphical representation of table VII.



Graphical representation of table VIII.



Graphical representation of table IX.

La distribution de la lumière galactique by the author, (1903); therefor we had only to accept that the diffused light of the Milky Way in the middle areas (—2° to + 2° gal. β) is equally distributed.

A detailed discussion of these tables and of the curves which are constructed by means of them (fig. 2) would lead us too far. We shall only draw the attention to the following points:

The general smoothness and the small values of the ordinates of the curve belonging to table VIII B, southern hemisphere, can certainly *not* lead to the conclusion that the nebulae in the southern galaxy proper are indeed much sparser and more uniformly scattered. It is remarkable that about 110° gal. longitude, even within the galaxy proper the density of faint nebulae nearly equals their average number in the entire northern hemisphere (8.5 and 10.0).

If we consider the general shape of the curves for the density of the nebulae we perceive a certain contrast with the curves of table IX for the galactic light — as compared with the minimum of IX the maximum of VII seems somewhat displaced towards 90° — but in the details no complementary shape can be detected.

The most remarkable feature of the nebulaecurves is a strong maximum about 100° to 110° in the northern and in the southern hemisphere, which seems to find its counterpart, at least in the northern gal. hemisphere, 180 degrees further on at about 280°.

If in the neighbourhood of the galactic zone the space occupied by nebulae extended equally far in all directions from the sun (which, with the suppositions we have made, would mean that the nearest agglomerations of stars in that plane do not lie at greatly varying distances) and if within that space the distribution of those nebulae were almost uniform, there would be no reason why the curves of VII and VIII show considerable maxima and minima.

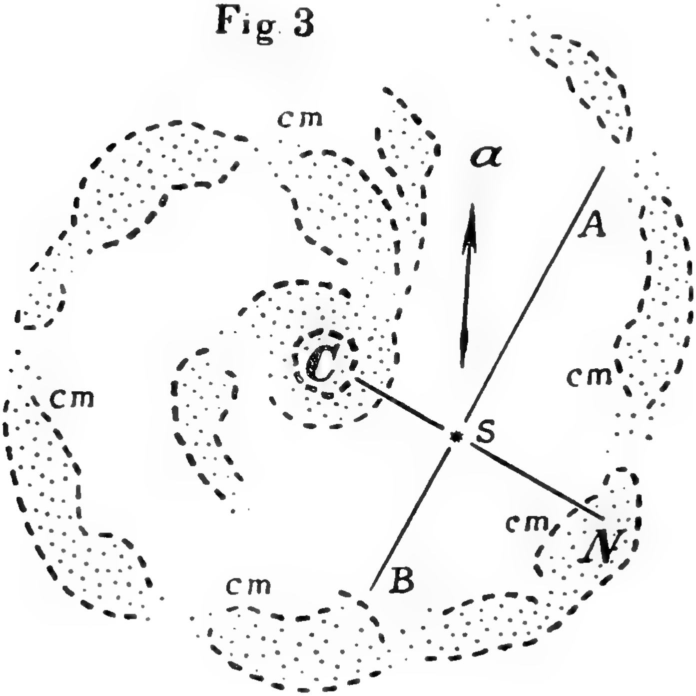
We know, however, that the nebulae show a strong tendency to occur in "streams" and "nests", hence in the details their distribution must be very irregular. Consequently the peculiar positions of the principal maxima of the curves might be explained by accepting one or more nebular streams, running from 100° to 280° gal. longitude somewhat obliquely towards the galactic plane. Obviously this supposition is arbitrary.

Another acceptable explanation is that the region of the nebulae, viz. the extra-galactic region, extends in and near the galactic plane farther in the direction 100° towards 280° than in other directions; in other words: that in the direction mentioned the galactic aggregations of stars are lying at greater distances.

It deserves attention that the line which in space connects the points represented by the greatest maxima of the nebulaecurve (table VII), (excluding the maximum at 280° in the southern hemisphere, due to the Nubeculae) is almost at right angles to the direction of the great agglomeration of stars in Cygnus (comp. table IX, 30° to 45° north). If, as it has been argued in *Ap. J.* XII, 2 — comp. Versl. K. A. v. W. 1897/98 — the agglomeration of stars in the direction of Cygnus forms the center of the mainly spirally arranged galactic system, of which the unequally dense windings surround the sun, this result (if we also accept the other suppositions mentioned in this paper) was to be expected.

For then (comp. fig. 3) the poorer region between the principal star-windings in the galactic plane — which, as regards the type of condensation of the matter, has been identified with the "extra-galatic" regions (rich in nebulae proper) extending on either side of the galactic plane — will extend farthest out in the direction *AB*, at right angles to a line passing through the sun and the central condensation of the system. This will especially be the case at 90 degs. from the central condensation or rather a little nearer to it in the direction *a* where the great gap between the windings (Perseus

Fig 3



region) is to be found. And indeed we find in table VII fig. 2 the best marked maxima of the nebulaecurves at about 105° gal. longitude at less than 90 degs. from the Cygnus region and a less strongly pronounced one in the northern hemisphere at 280°.

The available material is certainly not sufficient for us to decide with any probability whether the secondary maxima (at 165° etc.) of the curves of the tables VII and VIII result indeed from the arrangement of the galactic agglomerations or whether they are produced by a merely local accumulation of nebulae. Among such "local deviations" from the uniform distribution we ought then also to reckon the Nubeculae, which apparently have such a great influence on the distribution of the nebulae in the southern galactic hemisphere. It should be borne in mind that the Nubeculae are *not* connected by streams of nebulae with the southern Milky Way and neither probably by streams of stars. Nor is the influence of the vast nest of nebulae, which constitutes the Nubecula Maior perceptible in table VIII.

Finally, if the nebulae in the very distant regions of the system remain in general invisible and hence are not included in the statistical data given here, while they can be more easily photographed, this would in connection with our preceding remarks explain the fact observed by MAX WOLF (*Sitzungsber. München* XXXI, II, p. 126) that the mass of the very faint nebulae photographed by him are scattered more uniformly over the sky than those observed visually.

Physics. — "*Dispersion bands in absorption spectra.*" By Prof. W. H. JULIUS.

(Communicated in the meeting of May 28, 1904).

The appearance of absorption lines depends on various circumstances. As to the absorption phenomena in gases and vapours, such conditions as temperature, density, pressure, velocity in the line of sight, intensity and direction of magnetic field, have been fully studied and discussed. In the present paper we purpose to show that anomalous dispersion in the absorbing gas is also, to a great extent, accountable for certain typical features of the dark lines.

An originally parallel beam of light, when passing through a mass of matter, the density of which is unequally distributed, will not remain parallel and, generally speaking, the greatest incurvations will be noticed in those rays, for which the medium has refractive indices differing most from unity, i. e. in those which, in the spectrum, lie closest to the absorption lines on either side. These particular kinds of light, while diverging into space, will spread in many more different directions than the average waves, and, as a rule, a smaller portion of them will fall into the spectroscope, than of waves with refractive indices nearer to unity.

Accordingly, there must always be certain places in the absorption spectrum, from which light is absent owing to dispersion in the absorbing vapour, for it may be taken for granted that the latter is never absolutely homogeneous. These darker parts in the spectrum we shall call *dispersion bands*. It stands to reason that these bands will overlap the regions of real absorption; so they might easily be mistaken for strengthened absorption lines, which no doubt has often been done.

We will now look somewhat closer into the characteristics by which dispersion bands may be distinguished from absorption bands.

The curvature of a ray of light of a definite wave-length, at any point of a non-homogeneous medium, not only depends on the gradient of optical density at that particular spot, but also on the angle which the beam makes with the levels of equal density. Its divergence will be greatest when this angle is zero.

Strong ray-curving through anomalous dispersion in vapours may, therefore, be artificially produced in two ways: first, by using masses of absorbing vapour, presenting in a small space considerable differences in density, such as e.g. occur in the electric arc[1]); secondly in larger spaces where the density varies but moderately, by making the light travel over a considerable distance under small angles with the levels of equal density.

I have chosen the latter method of investigation, especially on account of the extensive use, which may be made of the phenomena presenting themselves, by applying them to the interpretation of numerous peculiarities of the spectra of celestial bodies [1]).

The absorbing medium was a Bunsen flame, of a peculiar shape, containing sodium vapour and so arranged, that the introduction of the salt could be easily regulated.

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[1]) H. EBERT, Wirkung der anomalen Dispersion von Metalldämpfen, BOLTZMANN Festschrift, S. 448.

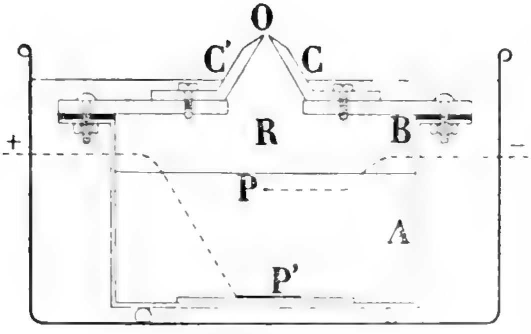

Fig. 1.

Fig. I represents a section of the burner. A is a copper trough, 80 cM. long, 8 cM. wide and 5 cM. deep, thickly coated with varnish and having a broad flange. The planed brass plate B is firmly screwed upon the flange and a leather packing makes the joint air-tight. On this cover, which has a rectangular opening 75 c.M. long and 2 cM. wide, are fixed two brass rulers, C and C'', 75 cM. long. They are so adjusted that at O they form a slit, having an exactly uniform width of about 0,1 cM. over the whole length. The prismatic space between C and C'' is closed at each end by a small triangular brass plate. The trough is filled to a certain height with a saturated solution of soda, and into the remaining space a mixture of illuminating gas and air is conveyed by means of tubes, entering at both ends. These tubes are fed from a mixing bottle in which the gas and the air are being driven through two separate regulating taps.

If now the flame were left to burn without any further precautions, the slit O would soon be closed in consequence of the onesided heating of the rulers. It was therefore found necessary to place the trough in a vessel with running water, reaching up to the burner. In this way a uniform and steady flame was obtained.

A few millimeters below the level of the salt solution a platinum wire P is stretched over the whole length of the lamp. Its ends are soldered to insulated copper wires, which pass through the walls of the trough, and are connected to the negative pole of a storage battery of 20 volts. From the positive pole two insulated wires lead to the ends of a long strip of platinum P', which rests on a glass plate at the bottom of the trough. As soon as the circuit is closed, innumerable minute particles of the fluid rise into the space

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1) The abnormal solar spectrum of Hale; the peculiar distribution of light in several of the Fraunhofer lines, even in normal conditions; the variations in the average appearance of the spot spectrum accompanying the eleven year period, all these phenomena have been easily explained from the considerations here alluded to (See W. H. Julius, Proc. Roy. Acad. Amst. IV, p. 589—602; 662—666; V, p. 270—302).

The present investigation is a continuation of the experiments with the long sodium flame, a short account of which has already been given on those former occasions in support of our theory.

R, and cause the flame to emit a beautiful, clear and constant sodium light, the intensity of which can be controlled and regulated by means of an ampèremeter and a variable resistance.

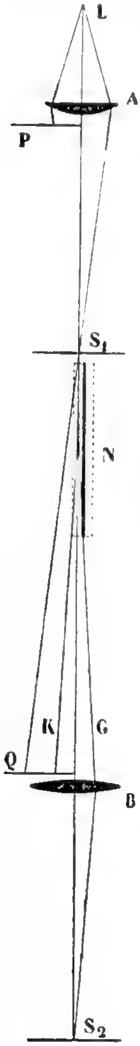

Fig. 2 *a*.

Fig. 2 *b*.

In Fig. 2, *a* and *b* are shown two different ways in which the light travels through this long sodium flame. *L* represents the crater of an electric arc of 20 ampères. The lens *A* throws an image of the crater on the slit S_1, which, in its turn, is depicted by the lens *B* on the slit S_2 of a grating spectroscope. About half of the conical beam of light which leaves *A* is intercepted by the screen *P*, and the part, which the slit S_1 allows to pass, falls almost entirely on the screen *Q*, which has been shifted so close to the optical axis of both lenses, that only a narrow streak of light can reach the slit S_2, through the middle of *B*. The large gas burner stands on a horizontal slide, which is movable up and down and round a vertical axis; thus, by means of screws, it can easily be put in any position required.

When the axis of the flame (which we assume to be in its most luminous part, i.e. a little above the blue-green core) coincides with the optical axis of the system of lenses, both the *D*-lines will be seen symmetrically widened in the spectroscope. If not perfect, the symmetry will easily be corrected by slightly shifting the screens *P* and *Q*.

Picture 1 Fig. 3 (see Plate) refers to the case when the flame *N* is not burning; the narrow absorption lines are due to traces of sodium surrounding the carbon points. When the flame is burning, a very weak current passing through the sodium solution will produce the effect shown in 2. The photographs 3, 4 and 5 were obtained with currents of about 1, 3 and 6 ampères, the flame always being in the symmetrical position.

We will now examine the case represented by Fig. 2, *a*. Here the axis of the flame has been shifted 3 m.M. towards the right. The narrow beam of light which reaches S_2, only penetrates that part of the flame, where the density of the sodium vapour *increases* from left to right. In a structure of this kind, waves, for which the vapour has a great index of refraction, deviate towards the right, e.g. S_1G. They are not intercepted by Q and consequently reach the slit S_2. In fact, the presence of the sodium vapour allows similar waves to enter that slit even in larger quantity than they would do without it, for rays of this kind, issuing from the uncovered half of A, which if travelling in a straight line would be intercepted by Q can, when refracted, penetrate the lens B.

The case is entirely different for those kinds of rays for which sodium vapour has refractive indices that are smaller than unity. Such rays deviating towards the left (as shown in S_1K), are intercepted by Q and consequently will be absent from the spectrum.

Nos 6, 8 and 10 are reproductions of photographs taken under these conditions. On the left are seen the smaller, on the right the greater wave-lengths (in fact, in the whole series of photographs the stronger D-line appears on the left side); so it is obvious that really the waves lying on the red-facing side of the D-lines, i.e. those for which the vapour has high refractive indices, are *strengthened* by anomalous dispersion; and that, on the other hand, the waves on the violet side have been considerably *weakened*.

Alternately with 6, 8 and 10 the photographs 7, 9 and 11 were taken. The position of the flame was now as indicated in Fig. 2, *b*, i. e. its axis had been shifted 3 mM. to the left, so that the central beam had to traverse that part of the flame where the density of the sodium vapour *decreases* from left to right. Here we notice that the rays with low refractive indices deviate towards the right and that a larger number of them reach the slit S_2, e.g. S_1K, whilst the rays with high refractive indices, such as S_1G, are intercepted by Q.

Nos 6 to 11 show the effect of a gradual increase in the density of the sodium vapour. In No. 12 we again notice the sharply defined sodium lines after the flame has been extinguished at the end of the series of experiments; they are somewhat stronger than those at the beginning of the series, because much sodium vapour had spread through the room during the operations.

When carefully examining the original negatives it is possible in most of them to distinguish the rather sharp central absorption lines from the overlaying dispersion bands (especially in the photographs, obtained when the position of the flame was symmetrical; the reproductions fail to bring out this peculiarity). Advantage has been taken of this fact in so arranging the twelve photographs here reproduced, that equal wave-lengths occupy corresponding places. Then it is seen

W. H. JULIUS: "Dispersion bands in absorption spectra."

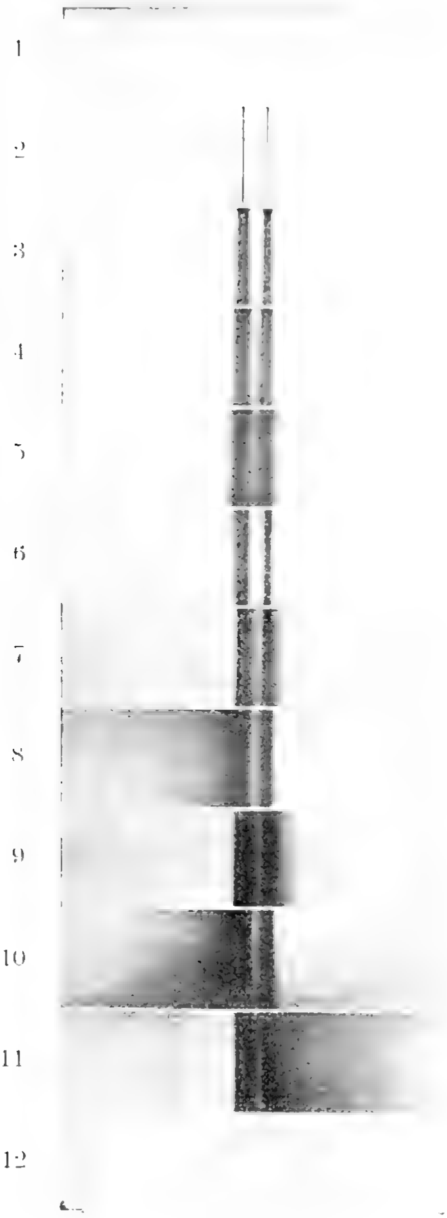

Fig. 3.

Fig. 4.

that the "centres of gravity" of the two dark bands, as well as the brighter space between them, have been alternately shifted to the left and to the right — a phenomenon which needs no further explanation.

As a matter of course the interposed flame causes the illumination in the plane of the slit S_2 to be very irregular, especially with regard to those radiations undergoing anomalous dispersion in the vapour. It is evident that some kinds of rays which are absent from one part of that plane, will be found in excess at another. The distribution of light in this irregular field of radiation might be explored by moving S_2, together with the spectroscope, within it. The same object can be obtained with less trouble by means of a thick piece of plate glass, mounted vertically between B and S_2 in such a manner, that it may be moved round a vertical axis. When turning it a little we make the whole radiation-field beyond the plate glass shift parallel to itself, thus causing other parts to cover the slit. This influences the aspect of the dispersion bands very materially. In certain positions apparent emission lines of sodium vapour may happen to be seen, which disappear as soon as the arc-light at S_1 is intercepted [1]).

In conclusion we wish to draw attention to a peculiarity we repeatedly observed in the dispersion bands. The dark shading in a dispersion band does *not* become deeper in proportion as we approach nearer to the central absorption line, but seems to reach its maximum obscurity at certain (though not always equal) distances on both sides of the centre; whilst in the space between, the light appears somewhat intensified just as if a wide absorption band had been partly covered by a narrower emission band, the centre of which is again occupied by the fine absorption line. This phenomenon cannot, however, be attributed to radiation emitted by the absorbing sodium flame; for in our arrangement the intensity of the emission from the flame could bear no comparison with that of the arc for corresponding waves. In order to make sure we tried to photograph the emission spectrum of the flame, exposing the plate during the same length of time and under the same conditions as had been done for obtaining the absorption spectrum; but not a trace of any impression could be detected on the photographic plate.

The light on both sides of the central line therefore originates in the carbon points and this we explain on the principle of ray-curving. The kinds of rays which are most strongly refracted in the flame may, under certain conditions, be curved twice or even more

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[1]) These bright lines originate in the same manner as the light of the chromosphere. The chromospheric lines are not emission lines, but "bright dispersion bands".

times, when passing nearly parallel to the system of the levels of equal density (in the manner described on a former occasion[1])) and will therefore have a greater chance of reaching the slit S_1, than rays which are less strongly curved. The relative intensity with which the waves, belonging to those central parts of the dispersion bands, appear in the spectrum increases with the distance over which the light has travelled along such a lamellar or tubular structure. Should the true absorption line happen to be exceedingly narrow, the dispersion band may give the impression of a double absorption band, which need not be symmetrical[2]).

We hold that the dispersion bands play an important part in many of the well known spectral phenomena, such as the widening, shifting, reversal and doubling of lines. In a subsequent communication I purpose to examine from this premise various phenomena observed in the spectra of variable stars and other celestial bodies.

Physics. — "*Spectroheliographic results explained by anomalous dispersion.*" By Prof. W. H. Julius.

It is not surprising that the scientific world should be highly interested in the beautiful results, obtained by Hale and Ellerman with the spectroheliograph[3]). The brilliant method elaborated and applied by these investigators enables us to see at a glance as well as to study in minute details how the light of any selected wavelength was distributed on the total solar disk at any given moment. W. S. Lockyer, in giving an abstract from the paper here alluded to in Nature N°. 1800, rightly entitles it: "A new epoch in solar physics." Indeed, the spectroheliograph proves capable of providing us with an abundance of new information, which other existing methods could never give and the value of which will remain, whatever may be the ideas on the Sun's constitution derived from it.

But, nevertheless, even the most splendid collection of new facts is useless so long as we have no theoretical ideas connecting them with achieved knowledge. Hale and Ellerman, accordingly, in

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[1]) Proc. Roy. Acad. Amst. IV, p. 596.

[2]) In Fig. 4 on the plate is given an enlargement of one of the photographs obtained by an almost symmetrical position of the flame. It has been somewhat spoiled in the reproduction. The original is less blotchy and the transition of the dispersion bands to the bright background of the spectrum is there much more gradual.

[3]) G. E. Hale and F. Ellerman, "The Rumford Spectroheliograph of the Yerkes Observatory," Publications of the Yerkes Observatory, Vol. III. Part. I, (1903).

describing the observed phenomena, lay down quite definite conceptions regarding certain conditions and configurations of matter in the solar atmosphere, by which the observed distribution of the light in the image of the Sun is assumed to be produced. In the cited publication they put forth the working hypothesis that the "calcium-flocculi" or bright regions showing themselves all over the image of the Sun when it is photographed in so-called calcium light, are columns of calcium vapour rising above the columns of condensed vapours of which the photospheric "grains" are the summits (l.c., p. 15). This hypothesis, though at first proposed mainly as a guide to further research (l.c., p. 13), has been subsequently[1] employed by the same authors with much less restriction as the basis on which the photographs ought to be interpreted.

The great authority of HALE and of such critics as W. S. LOCKYER, J. EVERSHED and others who, in abstracts from the work of HALE and ELLERMAN, concur in most of the interpretations there given, might cause the value of those ideas to become overestimated and extended beyond the original intention of the authors.

It is not superfluous, therefore, to show how we may quite as well account for all the new phenomena thus far revealed by the spectroheliograph, if we start from the entirely different conceptions of the Sun's constitution, which the consequences of ray-curving in non homogeneous media and of anomalous dispersion of light in absorbing vapours have suggested to us.

Both these circumstances are left absolutely out of consideration by HALE and ELLERMAN. Their conclusions are all founded on the erroneous supposition that the monochromatic light by which their images of the Sun are photographed, has travelled from the source in straight lines, and that they are right, accordingly, in supposing light-emitting masses of calcium vapour to exist in the exact directions, along which calcium-radiations seem to reach us. In making this supposition they fall into the same error as one who would assume the refracting facets of the crystal globe of a burning lamp to be independent sources of light.

Our new explanation of the spectroheliographic results will be founded on the hypothesis that the Sun is an unlimited mass of gas in which convection currents, surfaces of discontinuity and vortices are continually forming under the influence of radiation and rotation, so that the various composing elements are mingled as completely as nitrogen

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[1] G. E. HALE and F. ELLERMAN, "Calcium and Hydrogen Flocculi," Astrophysical Journal XIX, p. 41—52.

and oxygen in the Earth's atmosphere [1]). This hypothesis too will, of course, want modification in the light of future results; but for the present it seems, so far as the visible phenomena are considered, not to clash with any observation or physical law.

The irregular motion of electrons in the deeper layers of the Sun, where the density is very great, gives rise to the radiation with a continuous spectrum. We shall only take *this* radiation into account. Peculiar radiations, emitted by the more rarefied outer parts of the gaseous body and giving a bright-line spectrum, may perhaps add a perceptible quantity of light to the bulk, but this selective emission, if present, does not play any part in our explanations. So we behold the brilliant core of the Sun through an extensive envelope, consisting of a transparent but selectively absorbing mixture of gases, into which the core gradually spreads. It stands to reason that the average density of this envelope slowly decreases in the direction from Sun to Earth; but at right angles to that direction the density must be in some places much more variable. For it is a minimum in the axes of vortices; and the average direction of the whirl-cores, lying between the Earth and the central parts of the Sun in the surfaces of discontinuity, differs but little from our line of sight. The rays of the Sun thus reach us after having travelled a great distance along lines, making small angles with the levels of slowest density-variation in a lamellar, partly tubular, structure [2]).

Under these circumstances the solar rays will be sensibly incurvated on their way through the envelope, especially those suffering anomalous dispersion. As a rule, beams consisting of the latter kinds of rays will show an increased divergence; they will reach the Earth with less intensity than the normally refracted light and so will give rise to dark *dispersion bands* [3]) in the solar spectrum. And the degree of divergence will not only be different with waves, which in the spectrum are found at different distances from the absorption lines, but it is also clear that the divergence with which various beams of *any definite* kind of light arrive at the Earth must differ largely according to the dioptrical properties, exhibited along the

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[1]) A sketch of a solar theory, based on this hypothesis, is to be found in the Revue générale des Sciences, 15, p. 480—495, 30 May 1904.

[2]) For considerations which have induced us to hold that a similar structure of the Sun is very probable, I refer to former publications: Proc. Roy. Acad Amst. IV, p. 162—171; 589—602; V, p. 270—302.

[3]) W. H. Julius, Dispersion bands in absorption spectra, Proc. Roy. Acad. at Amst. Vol. VII, p. 134.

paths of those beams by the system of surfaces of discontinuity.

The foregoing inferences really imply the whole of our interpretation of the results, thus far obtained with the spectroheliograph. This we shall show by amply discussing some of their main features.

The broad dark bands, designated by HALE and ELLERMAN as H_1 and K_1, are not absorption bands, but dispersion bands. Real absorption by the solar calcium vapour we hold to be restricted to the central dark lines H_3 and K_3. The bright bands H_2 and K_2, predominating in the spectrum of the "flocculi" and attributed by HALE and ELLERMAN to strongly radiating calcium vapour, result in our theory from the fact, that with beams of light the wavelength of which is very near to that of the central absorption lines, the divergence may be diminished or even changed to convergence by the tubular structure. Indeed, such rays deviate more strongly than those standing farther from the absorption lines; and as soon as they undergo more than one incurvation, they have a chance of reaching the Earth with increased intensity. This chance improves in proportion as the index of refraction departs from unity, be it in a positive or in a negative sense[3]). We conclude from it, that the brightness of the calcium flocculi must, as a rule, increase as the monochromatic light in which the Sun is photographed approaches the true absorption line.

This consequence of our theory exactly corresponds to one of the chief peculiarities, which immediately struck HALE and ELLERMAN on inspecting sets of photographs taken at short intervals of time with the second slit in different positions within the H and K bands. In order to account for the same fact, those investigators are obliged, by their working hypothesis, to suppose that in higher regions of the Sun's atmosphere the calcium vapour radiates more strongly than in lower levels. This cannot be called a very satisfactory inference; and less so, as the supposition is added that the incandescent vapour is rising from much deeper layers and, therefore, considerably expanding — a process during which, according to our physical notions, the temperature must fall. Here we meet with a serious difficulty; HALE and ELLEMAN try to get rid of it by means of the rather vague assumption, that some electrical or chemical effect may be responsible for the bright radiation emitted by this calcium layer, which is intermediate between two absorbing layers[2]).

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[3]) In the experimental investigation on dispersion bands, before mentioned, this brightening in the middle of the dark bands has been distinctly observed. Cf. also: Proc. Roy. Acad. Amst. Vol. IV, p. 596.

[2]) HALE and ELLERMAN, Astrophysical Journal XIX, p. 44.

Our theory can dispense with such additional hypotheses.

Another characteristic peculiarity, observed in every series of photographs taken at short intervals with the slit set at various points on the broad H and K bands, is the following. When the slit is set, e.g., at a remote point of K_1, the structure of the solar image appears relatively fine, sharp and detailed; approaching the central line, we see some of the brilliant spots vanish, others grow more extensive, especially those lying in the vicinity of sun-spots; at the same time their outlines become less sharp, so that finally the whole image gives us the impression of a coarser and at the same time a more woolly structure[1]).

Hale and Ellerman hold that the successive photographs refer to gradually higher levels and conclude that the masses of calcium vapour must have a tree-like shape. W. S. Lockyer, in Natur No. 1800, draws a scheme showing this conception.

Against this interpretation we propose the following one.

The amount by which the divergence of a beam of light is altered in consequence of the presence of calcium vapour in the streaming and whirling mass depends, of course, on the proportion of calcium in the mixture, and besides on two other circumstances, viz. 1st on the position occupied in the spectrum by the selected kind of light with regard to the absorption lines, and 2nd on the steepness of the density gradients in the mixture along directions perpendicular to the path of the beam.

Let us suppose the selected light to correspond to the extreme edge of H_1 or K_1, then its index of refraction differs but little from unity. Accordingly, very considerable inequalities of density are required to cause a perceptible change in the divergence of such beams. Similar great inequalities may indeed occur at many separate places, but at each of them they cannot, of course, extend very widely. This accounts for the fine and rather sharply defined reticulation shown by the so called "low-level" photographs.

If the second slit were set a little nearer to the centre of the line, the distribution of the light in the solar image would at all events differ considerably from that of the former case; for the indices of refraction being very different for neighbouring waves within a dispersion band, the divergence of beams, starting from the same point of the Sun, must vary largely with the wave-length. So it is clear

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[1]) Such series of photographs are reproduced in: Publications of the Yerkes Obervatory, Vol. III, Part I, Pl. V, VI, X, XI, XII, XIII.

that bright or dark spots, visible on one photograph, may be wanting in the other.

Moreover, the general character of the image must change as we approach the central line. For in proportion as the indices of refraction depart from unity, slower variations of density suffice for producing sensible differences of divergence. And, as a matter of course, in any whirling region slightly inclined density-gradients will take up larger spaces than very steep ones. Besides, when the second slit of the spectroheliograph, having a given width, is set near to the central absorption line, the wave-complex which it allows to pass, covers a greater variety of refractive indices, than when it is set farther from the central line. In the former case the distribution of the light in the solar image must, therefore, be less differentiated. Both circumstances cooperate in causing the bright-and-dark structure generally to appear coarser and more woolly in proportion as the spectroheliograph is adjusted for kinds of rays that are more liable to anomalous dispersion.

From the same point of view it is not surprising that on photographs, taken in H_2 or K_2 light, the calcium flocculi are particularly bright and extensive in spot regions, for in such regions the "tubular" structure of the gaseous mass, by which the strongly curved rays are kept together and conducted, is most developed.

HALE and ELLERMANN also mention "dark calcium flocculi" [1]), which they describe as special objects, visible in so-called "high-level photographs" and not to be confounded with the general dark background, produced by the absorbing calcium vapour of deeper layers. Dark flocculi often surround the large bright flocculi of spot regions, as is shown e. g. in Fig. 4, Plate V of the cited publication. The explanation given by them is, that we might have here some indications of the cooler K_3 calcium vapour, which rises to a considerably greater height than the K_2 vapour of the bright flocculi.

In our theory the presence of these darker regions is a direct consequence of the fact, that the particular distribution of the light in the solar image is not produced by local absorption and emission, but by irregular ray-curving. The rays are only caused to change their places; so an excess of light in the bright flocculi must necessarily be counterbalanced by a deficit in the surroundings.

H and K are by far the broadest bands of the visible solar spectrum; even with moderate dispersion the second slit of the spectro-

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[1]) Publications Yerkes Observatory, l. c. p. 19.

heliograph could easily be set at different points within these bands. When the dispersion of the instrument was increased by means of a grating, photographs of the Sun could be obtained with light falling entirely within a widened line of hydrogen or of iron.

Photographs made with H_δ or H_γ light showed also a flocky structure, differing, however, materially from that obtained with H and K. Hale and Ellermann therefore assume dark and bright clouds of hydrogen to exist in the solar atmosphere. Upon the whole, but not in the details, the hydrogen flocculi correspond in form and position to the calcium flocculi photographed with H_2 or K_2 light; the general aspect of the photographs is fainter, they show less contrast, and the detailed structure observed in H_1 or K_1 light is wanting. The most striking fact, however, is that the bright calcium flocculi of the H_2 or K_2 photographs are replaced on the H_δ photograph by dark structures of similar form. Only in a few places in the vicinity of sunspots small *bright* hydrogen flocculi occur which coincide with parts of bright calcium flocculi.

Hale and Ellerman hardly make an attempt to explain these facts which, in the light of their working hypothesis, are really puzzling.

We get a much clearer view of the matter as soon as we suppose the widening of the hydrogen lines also to be produced by anomalous dispersion, instead of by absorption only.

Indeed, the ray-curving in the solar gases must generally be less with waves belonging to those narrower dispersion bands than with waves lying near the centres of the broad H and K bands. Even in the powerful whirls of spot regions there will only sporadically be found places where the tubular structure is sufficiently marked to keep together rays belonging to the dispersion bands of hydrogen in the same way, as it does gather the strongly curved H_2 and K_2 light in the large, bright calcium flocculi. Accordingly, we shall meet with very few places in bright calcium flocculi, where the photographs in H_δ or H_γ light also exhibit brilliant points. All the rest of the bright H_2 and K_2 regions correspond to those parts of the gaseous mass where the differences of density — though not so excessive — are nevertheless very considerable; but whereas in that structure the H_2 rays are repeatedly curved and may be made to converge, the less strongly incurvated H_δ rays will in the same regions diverge and be dissipated in a considerable degree, thus giving rise to dark places in the photographs. Outside the bright calcium flocculi, finally, where the H_2 and K_2 photographs are dark in consequence of increased divergence of the beams, no strong incurvation is given to the H_δ or H_γ light; at those places the image of the Sun, photographed in hydrogen lines, must therefore be less dark.

The rather faint character of the hydrogen flocculi, the absence of sharp outlines and of strong contrasts in the structural elements, we ascribe to the dispersion bands of hydrogen being relatively narrow and so allowing rays with a great variety of refractive indices to pass simultaneously through the second slit of the spectroheliograph. The hydrogen photographs too would show finer details, like those in K_1 light, if the dispersion of the apparatus were still greater and the second slit still narrower.

We believe that we have shown that every peculiarity, thus far noticed in the photographs obtained with the spectroheliograph, may easily be deduced from the same fundamental hypothesis regarding the constitution of the Sun, which has already proved capable of giving a coherent interpretation of the solar phenomena known before. Not a single new hypothesis was required.

Physiology. — *"On artificial and natural nerve-stimulation and the quantity of energy involved."* By Prof. H. Zwaardemaker.

A living nerve, laid bare, can be stimulated artificially in a number of ways; there are but two kinds of stimuli, however, the effect of which is instantaneous and whose strength can be accurately regulated, namely mechanical and electrical stimuli. Mechanical stimulation has been considerably improved by an artifice of Schäfer[1]), who used falling drops of mercury instead of electrically driven little hammers. When using droplets the size of which is about equal to the breadth of the nerve, even with a very small height of fall distinct effects we obtain, manifesting themselves by contraction of the muscle which has remained connected with the nerve. Schäfer himself obtained this result with a drop weighing 100 mgr. falling through 10 mm. In our laboratory his method gave still better results; an effect was noticed already with a drop of 50 mgr. and a height of fall of 5 mm. Such a drop possesses at the end of its fall an energy of 24.5 ergs. Not the energy as such is a measure of the stimulus, however. Apparently the energy has also in this respect to be considered as consisting of an intensity-factor and a capacity-factor[2]), and this

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[1]) Proc. Physiol. Soc. 26 Jan. 1901.

[2]) W. Ostwald. Ber. d. k. Sächs. Ges. d. Wissenschaften 1892, math. physik. Cl. S. 215.

G. Helm. Die Energetik in ihrer geschichtl. Entwicklung 1898 S. 277.

after its being transferred to the nerve. That it is not the intensity-factor before the transfer which must be regarded here as the physiologically "auslösende" (liberating) force, appears from some curious results obtained on varying the height of fall. A fall of 5 mm. gives an excellent lifting distance when the muscle is loaded with 50 grams, which is reduced to $^2/_3$ with a fall of 15 mm. and to $^1/_2$ with a fall of 30 mm. Consequently a smaller effect is found when the velocity with which the drop comes down is increased, instead of a larger effect. This would be impossible if the intensity-factor of the kinetic energy of the falling drops had been decisive. On diminishing the height of fall again the original lifting distance returns [1]).

The second kind of artificial stimuli can be measured in a very simple manner if at the instance of CYBULSKY, MARES, HOORWEG and others, condensers are used. A preliminary trial in the laboratory showed that the best results are obtained with a condenser of a capacity of 0.004 microfarad. This has only to be charged to a potential of 0.012 volts to show already a contraction of the nerve-muscle preparation. The available energy in this case amounts to 0.00029 ergs, which is much less than what was found for mechanical stimulation [2])

But it is clear that the one as well as the other is a most unsatisfactory way of stimulating. The mechanical stimulus only reaches part of the axial cylinders constituting the nerve-bundle and it is questionable whether the softness of the mass does not to a great extent obviate the suddenness of the pressure. The electrical discharge, although more instantaneous, spreads in no small measure, besides over the axial cylinders, also over the sheaths and the septa between the separate fibres. A means of diminishing the resistance and so making the time of discharge shorter is hitherto lacking. It is always the full resistance of the nerve, measured across, which one is obliged to put in.

These difficulties will never be completely overcome with artificial stimuli; in order to find the real minimum one must have recourse to natural stimuli. It is only with sensory nerves that we have these at our command for the present.

There are two organs of sense in which the nerve-cells themselves (or their immediate prolongations) receive the stimulus, viz. the organs of sight and of smell. In the former case it is the rods and

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[1]) An analogous phenomenon has been observed by WEDENSKY for faradic stimuli (of a frequence of 100 per second).

[2]) J. CLUZET. Journal de Physiologie et de Pathologie générale 1904 p. 210 gives as smallest values 8, 5 and 7, 2 milli-ergs.

cones, in the latter the fine smelling-hairs which both form part of the terminal neuron. We will consider the stimulation of these senses a little more closely.

A. Organ of sight.

If one looks through an artificial orifice of 2 mm. at a small Hefner lamp at a distance of 6 metres, a definite amount of the light emitted by the lamp will enter the eye. This energy is concentrated on a small circumscript field of the retina, where cones and rods lie ready to receive the light-stimulus. When the room is made dark and the light is made feebler by a system of more or less crossed Nichols, the much less sensitive cones will at last cease to be active and the feeble glimmer that remains, will be perceived by means of the rods only. For this the visual axis will have to deviate a little, as in the fovea centralis itself no rods occur, so that the point-shaped feeble little star seems to be displaced a little upward, at any rate for my eye.

It is clear that with such an arrangement of the experiment those rays only will be effective that are absorbed by the purple of the rods. According to A. König [1]) these are the rays the wave-length of which ranges from 600 to 420 micra. From K. Ångström's recent determinations [2]) we know the energy of this part of the spectrum for the Hefner lamp. It is 2.61×10^{-8} gram-calories per second and per square centim. at a distance of one metre. At a distance of 6 metres this becomes 0.03 ergs per second and per square centim.

In this experiment we supposed the Hefner lamp to be looked at through a system of more or less crossed Nichols, leaving only a feeble glimmer. Besides this we will also insert an instantaneous shutter the time of exposition of which has been adjusted so as to give the most favourable results for feeble visual impressions. From a series of experiments by Messrs. Grijns and Noyons, the results of which will be communicated later by these gentlemen themselves, I knew that a time of exposition of the order of a milli-second is most suitable. An instrument formerly used by Dr. Laan and described in his doctor-dissertation [3]), with slits moving in opposite directions, gave expositions of about 0.6 milli-second, repeated every 0.06 second.

By these two means in addition to the narrowness of orifice, hence in all by three circumstances:

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[1]) A. König. Stzber. d. Berliner Akademie 1894 p. 585.

[2]) K. Ångström, the Physical Review, Vol. XVIII. p. 302, 1903.

[3]) H. A. Laan. Onderz. Physiol. Lab. Utrechtsche Hoogeschool. (5) III p. 182.

1. crossing of the Nichols
2. shorter time of exposition
3. narrow orifice

the stimulus which otherwise would have amounted to 0.03 ergs per second and per square centim. was still considerably enfeebled.

The Nichols were completely crossed at 28° 12′ of the scale. Hence full light was obtained at 118° 12′. In this position, which is most favourable for the transmission of light, something is lost on and in the Nichols as well as on and in the media of the eye, but we shall neglect this amount, since it is small compared with the uncertainty of the coefficient of absorption of the retinal purple, which we will take into account presently, and of the disturbing influence of adaptation, which cannot be entirely eliminated.

When the instantaneous shutter is moving and gives a flash every 0.06 sec. one of the Nichols is slowly turned. The sharp image of the flame disappears and instead of it we see a dot-shaped glimmer, which at last seems to move a little upward. A minimum glimmer I found *without previous adaptation to the dark*

coming from the right at 36°. 6′ of the scale
coming from the left at 20° ,, ,, ,,

which means a rotation of the Nichols of 82°.6′ and 81°.48′ or a mean rotation of 81°.57′ reckoned from the position for full light.

On account of the crossing of the Nichols we may assume that the intensity in the ratio of $\cos^2. 81°.57'$ to $\cos^2.0°$ or as 0.0196 to 1.

Besides the time of exposition was only 0.6 milli-seconds every time.

Finally the artificial pupil had a surface of no more than 0.0314 cm^2.

By all these circumstances the original quantity of energy of 0.03 ergs, contained in the rays that can be absorbed by the rods, has been reduced to

$$0.0196 \times 0,0006 \times 0.0314 \times 0.03 \text{ ergs} = 1.1 \; 10^{-8} \text{ ergs.}$$

From the measurements of absorption by A. König it follows that $^1/_{50}$ of the light of these rays is retained in the retinal purple and since only the really absorbed light must be taken into account for the stimulation, this amount is still further reduced to

$$0.02 \times 1.1.10^{-8} \text{ ergs} = \underline{2.2 \times 10^{-10} \text{ ergs.}}$$

In a second series of experiments with a time of exposition of 0,00062 sec. repeated every 0.64 sec., and an angle of the Nichols of 84°42′ from the position of full light, I found

$$0,00854 \times 0.00062 \times 0.314 \times 0.03 \text{ ergs} = 4.9 \times 10^{-9} \text{ ergs.}$$

And $^1/_{50}$ part of this is again

$$0.02 \times 4.9 \times 10^{-9} = \underline{1 \times 10^{-10} \text{ Ergs.}}$$

So the energy capable of causing the impression of an extremely feeble glimmer is, in the case of eccentric vision, of the order of 1.10^{-10} ergs. This quantity would have been found still 100 times less if I had completely adapted myself to darkness. By a corresponding method Messrs. GRIJNS and NOYONS made such experiments, which will be published later.

The transformation of the retinal purple into retinal yellow under the influence of light is a reversible process. Hence it must depend on a displacement of the equilibrium, which towards the end of the adaptation is complete, in a direction opposed to the chemical forces which are the cause of it. The small variation of thermodynamic potential, brought about in the appendix of the retinal nerve-cell by a quantity of energy of the order mentioned, is sufficient to cause a state of stimulation in this nerve-cell. Hence the natural nerve-stimulus can be taken ever so much smaller than the artificial stimulus, even in its most favourable form.

B. Organ of smell.

If one wishes to make an attempt at calculating the value of the energy of the natural stimulus in the case of the organ of smell, this can be done in the following manner.

In the so-called smelling-box [1]) (a closed space of 64 litres, having glass walls on all sides), let a smelling substance be diluted to the utmost degree at which it is still perceptible. Let this be done by completely evaporating a few drops of the substance itself or of an aqueous solution of it. Let then a little air from this space be sniffed in. The quantity of air inhaled in a single sniff is estimated by VALENTIN at 50 cc. which I believe to be correct, since in sniffing at my olfacto-meter (which is done unilaterally) 30 cc. are inhaled on the average. If we now suppose that part of this air is directly conveyed to the olfactory fissure, in the most favourable case the air there present will be replaced by fresh air perfumed in the manner indicated. In this case ± 0.2 cc. of this air is in contact with the olfactory mucous membrane on both sides of the narrow fissure.

We shall now indicate for a few substances the quantity that must be present in 0.2 cc. in order to be exactly perceived by the smell. This quantity is for

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[1]) Physiologie des Geruchs. Leipzig 1895 p. 34.

methyl alcohol	0.000.06 mgr.
formic acid	0.000.12 mgr.
acetone	0.000.008 mgr.
camphor	0.000.000.009.6 mgr.
ionon	0.000.000.000.019 mgr.

Let us restrict ourselves to these substances for the present. When fully oxidised they are converted into H_2O and CO_2. Hence their products of combustion may be considered as entirely indifferent additions to the cell-substance if they are produced gradually and in small quantities. If we regard smell as an intra-molecular property, which is probable for these substances (leaving it an open question whether for substances containing atoms like *S*, *As*, etc. smell may perhaps depend on intra-atomic conditions), the quantity of energy involved in an olfactory stimulus will never exceed the heat of combustion.

For the four first-mentioned substances the heat of combustion is known and amounts to 5.7, 1.5, 7.5 and 9.3 gram-calories per milligram respectively; that of ionon is unknown, but may be estimated at 9.6 gram-calory. Then the quantities of energy involved here (for the amount of smelling substance contained in 0.2 cc.) are for:

methyl-alcohol	14443	ergs
formic acid	7460	,,
acetone	2520	,,
camphor	3.9	,,
ionon	0.008	,,

Attempts made in order to find out how much of these smelling substances is absorbed in the olfactory mucous membrane were hitherto unsuccessful. Neither in oil, nor in nerve-substance we were able to detect an appreciable quantity of ionon, after they had been left in contact for some time with an atmosphere of ionon. Presumably very little is absorbed. Moreover it follows from the remarkably different degree in which chemically related substances show smelling power[1]) that only an extremely small part of the intra-molecular energy displays any olfacto-chemical effect. So we are justified in assuming that here also the minimum stimulus in the nerve-terminal will later appear to be of the order of the light-stimulus or even smaller.

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[1]) Onderzoekingen Physiol. Lab. d. Utrechtsche Hoogeschool (5) IV. p. 232. Chloroform, bromoform, iodoform have a specific smelling-power of which the mutual ratio is as 1 : 69 : 153 24.

So of the direct natural nerve-stimuli moments only the light-stimulus has for the present been quantitatively calculated. Bearing in mind that the stimulus we found in what precedes to be of the order 10^{-10} ergs, is a minimum stimulus on a small field of the retina scarcely measuring 0.002 square millimetres, whereas the total surface containing retinal purple is put by König at 700 sq. mm.; moreover bearing in mind that the light of the sun at Marseilles is estimated by Fabry [1]) at 100.000 candles and that this enters the eye not under an angle of 23′, under which the Hefner lamp was seen, but from all parts of the field of view, it will be clear that the light-stimuli of ordinary life can by no means be called immeasurably small. Nor do they act for a single milli-second but all day long. The energy entering the nervous system in this way will not be a fraction of an erg but a number of ergs. It is difficult to make an estimate in this respect as with strong light not the rods but the cones serve as terminal apparatus and in these teleneurons only by analogy a photochemical process is assumed, which for the rest is unknown to us. Therefore we must refrain from such an estimate, but at the same time it seems to us to be undoubtable that the nervous system receives relatively large quantities of energy in a different way from that by metabolism.

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[1]) Compt. Rend. 7 Dec. 1903.

(August 26, 1904).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday September 24, 1904.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 24 September 1904, Dl. XIII).

CONTENTS.

The following papers were read:

Physics. — *"The derivation of the formula which gives the relation between the concentration of coexisting phases for binary mixtures."* By Prof. J. D. van der Waals.

(Communicated in the meeting of June 25, 1904).

Already in my molecular theory (Cont. II, p. 10) I derived a formula for the concentration in coexisting phases of binary mixtures. This formula has the following form:

$$\left\{MRT\,l\frac{x}{1-x}+MRT\frac{\frac{db}{dx}}{v-b}-\frac{\frac{da}{dx}}{v}\right\}_1=\left\{MRT\,l\frac{x}{1-x}+MRT\frac{\frac{db}{dx}}{v-b}-\frac{\frac{da}{dx}}{v}\right\}_2$$

In the case that the second phase is a rarefied gasphase, the second member is simplified to $MRT\,l\frac{x}{1-x}$ and we find:

$$MRT\,l\frac{x_1}{1-x_1}\frac{1-x_2}{x_2}=\left\{\frac{\frac{da}{dx}}{v}-MRT\frac{\frac{db}{dx}}{v-b}\right\}_1 \quad . \quad . \quad . \quad . \quad (1)$$

From this I have drawn the conclusion that the circumstance that two coexisting phases have the same concentration can only occur for mixtures, for which a minimum value of the quantity $\frac{a_x}{b_x}$ occurs, and so a minimum value for the critical temperature. For the limiting case, with exceedingly low values of T, the mixture for which $\frac{a_x}{b_x}$ has a minimum value, would be exactly the mixture, for which the value of x is the same in the two phases; but for increasing values of T this concentration shifts to the side of the substance with the lowest value of the size of the molecules. (Cont. II, p. 19 and p. 120).

Afterwards I have derived in "Ternary Systems" for equation (1) the following equation:

$$l\frac{x_1}{1-x_1}\frac{1-x_2}{x_2}=-\frac{f}{T}\frac{dT_k}{dx}+\frac{1}{p_k}\frac{dp_k}{dx}\,, \quad . \quad . \quad . \quad . \quad (2)$$

which also holds only approximately for the case that the second phase is a rarefied gas-phase. For the derivation of (2) I have not directly used the equation of state, but I have considered the well-known formula for the vapour-pressure $-l\frac{p}{p_k}=f\frac{T_k-T}{T}$ as sufficiently accurate for liquid volumes which are not much smaller than that of the pressure of coincidence (pressure of the saturated vapour for the unsplit mixture).

Equation (2) however, can also be found directly from the equation of state. It was to be expected that this was possible, because as I have shown in "The liquid state and equation of condition"[1]) the formula for the vapour may be derived from this equation. If we want to find also for the factor f the real value of about 7, it is necessary to consider b as function of the volume. This not only renders the derivation very complicate, but it places us before the unsolved question: in how far is the decrease of b with the volume to be ascribed to real or quasi diminution?

I have therefore confined myself for the moment to examining what follows for the form of (2) from the equation of state, when b is put independent of the volume.

We have then to reduce:

$$\frac{MRT\frac{db}{dx}}{v-b}-\frac{\frac{da}{dx}}{v}.$$

We write for this successively:

$$\frac{MRT\frac{db}{dx}}{v-b}-\frac{\frac{da}{dx}}{v}=\left(p+\frac{a}{v^2}\right)\frac{db}{dx}-\frac{1}{v}\frac{da}{dx}=$$

$$=p\frac{db}{dx}-\frac{d\frac{a}{b}}{dx}+\left(\frac{a}{v^2}-\frac{a}{b^2}\right)\frac{db}{dx}-\left(\frac{1}{v}-\frac{1}{b}\right)\frac{da}{dx}.$$

Now for $a\frac{db}{dx}\left(\frac{1}{v^2}-\frac{1}{b^2}\right)-\left(\frac{1}{v}-\frac{1}{b}\right)\frac{da}{dx}$ we may write:

$$\frac{a(v-b)}{bv}\left\{\frac{1}{a}\frac{da}{dx}-\frac{v+b}{v}\frac{1}{b}\frac{db}{dx}\right\}=\frac{a(v-b)}{bv}\left\{\frac{1}{a}\frac{da}{dx}-\frac{2}{b}\frac{db}{dx}-\left(1-\frac{b}{v}\right)\frac{1}{b}\frac{db}{dx}\right\}$$

and as according to the equation of state $\frac{a(v-b)}{bv}$ is equal to

$$\frac{a(v-b)}{bv}=MRT+(MRT-vp)\frac{v-b}{b}$$

we find after some reductions:

$$\frac{MRT\frac{db}{dx}}{v-b}-\frac{\frac{da}{dx}}{v}=p\frac{db}{dx}-\frac{d\frac{a}{b}}{dx}+MRT\frac{dl\frac{a}{b^2}}{dx}+\frac{v-b}{b}(MRT-vp)\frac{dl\frac{a}{b^2}}{dx}+$$

$$+\frac{v-b}{b}\frac{1}{b}\frac{db}{dx}[MRT-p(v-b)]\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(3)$$

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[1]) These Proc. VI. p. 123.

We may also write the second member of (3) as follows:

$$p\left\{\frac{db}{dx}-\frac{v}{b}(v-b)\frac{d\,l\frac{a}{b^2}}{dx}-\frac{(v-b)^2}{b^2}\frac{db}{dx}\right\}-$$

$$-\frac{d\frac{a}{b}}{dx}+MRT\frac{d\,l\frac{a}{b^2}}{dx}+MRT\frac{v-b}{v}\frac{d\log\frac{a}{b}}{dx}\quad .\ .\ .\ .\ .\ (4)$$

In order to examine the general value of the quantity which is to be reduced, we have to distinguish two cases. The first case, that $v-b$ is small and $p(v-b)$ may be neglected compared with MRT. In this case (4) may be simplified to:

$$p\frac{db}{dx}-\frac{d\frac{a}{b}}{dx}+MRT\frac{d\,l\frac{a}{b^2}}{dx}.$$

The second would hold for high pressures; then the value of $p(v-b)$ approaches to MRT, when v approaches to b. In this case (4) is simplified to:

$$p\frac{db}{dx}-\frac{d\frac{a}{b}}{dx}.$$

As we assume coexistence with a rarefied gasphase we have only to deal with the first case. In the second there would not even be question of coexistence with a second phase. We find now for the formula, giving the relation for the concentration of the two phases:

$$l\frac{x_1}{1-x_1}\frac{1-x_2}{x_2}=\left(\frac{1}{MRT}\frac{d\frac{a}{b}}{dx}-\frac{d\,l\frac{a}{b^2}}{dx}\right)_1\quad .\ .\ .\ .\ .\ (5)$$

in which $p\frac{db}{dx}$ is neglected, or rather where it is cancelled by an almost equal value, which would occur in the second member of the equation given at the beginning of this paper.

Let us put:

$$MRT_k=\frac{8}{27}\frac{a}{b}$$

and

$$p_k=\frac{1}{27}\frac{a}{b^2},$$

then (5) assumes the form of:

$$l\frac{x_1}{1-x_1}\frac{1-x_2}{x_2}=\left(\frac{27}{8}\frac{1}{T}\frac{dT_k}{dx}-\frac{dp_k}{p_k dx}\right)_1.$$

The factor $\frac{27}{8}$ is in perfect concordance with the factor which occurs in the formula of the vapour pressure, when we put the quantity b independent of the volume. I have shown before that it must be about doubled, when we assume variability for b — or rather the factor $\frac{27}{8}$ is not increased, but the assumption of the smaller value of b comes to doubling the factor, when we substitute the value of T_k for $\frac{a}{b}$. Without carrying out the elaborate calculations, which in our case might be the consequence of assumption of the variability of b, I think to be justified in concluding to the doubling of that factor as a sufficiently approximated value. Then we find back exactly the same value as I had found in "Ternary Systems", viz.

$$l\,\frac{x_1}{1-x_1}\,\frac{1-x_2}{x_2} = \left(\frac{f}{T}\frac{dT_k}{dx} - \frac{1}{p_k}\frac{dp_k}{dx}\right)_1, \quad . \quad . \quad . \quad . \quad (6)$$

in which formula f may put about 7.

As $\frac{T_k}{8\times 273 p_k} = b$, we may put for $\frac{dlp_k}{dx}$:

$$\frac{d\,log\,T_k}{dx} - \frac{d\,log\,b}{dx}.$$

Hence (6) becomes:

$$l\,\frac{x_1}{1-x_1}\,\frac{1-x_2}{x_2} = \left(\frac{f}{T} - \frac{1}{T_k}\right)\frac{dT_k}{dx} + \frac{1}{b}\frac{db}{dx}, \quad . \quad . \quad . \quad . \quad (7)$$

From the form (7) we derive, that only when $\frac{db}{dx} = 0$, and so when the molecules of the mixed substances are of the same size, the concentration of the coexisting phases is the same for the mixture with minimum critical temperature. If the size of the molecules is not the same $x_1 = x_2$ for the mixture for which

$$\left(\frac{f}{T} - \frac{1}{T_k}\right)\frac{dT_k}{dx} = -\frac{1}{b}\frac{db}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If $\frac{db}{dx}$ is positive, as is the case for mixtures of acetone and ether (ether as second component), then $x = x_2$ for a mixture for which $\frac{dT_k}{dx}$ is negative. Then the concentration where x_1 and x_2 are equal and therefore also the maximum pressure in the p, x line has shifted to the side of the component with the smallest molecule. If we multiply both members of (8) by T, the shifting proves to increase for increasing value of T; and so we arrive at a conclusion, to which I came already before, viz. that the concentration of the maximum value of p in the p,x curve is sufficiently the same as that of the mixture with minimum critical temperature only for the very lowest values of T. It only appears that already at ordinary temperatures the shifting mentioned above may be rather considerable. A consequence of this is, that the shifting between the ordinary temperatures and $T = T_k$ may be only slight. This shifting is however the greater as the difference in the size of the molecules is the more considerable, and as the decrease in critical temperature takes place the more slowly.

Now that we have found an approximate value for μ'_x, we can immediately derive from it an approximate value for μ''_x, a quantity which must be known, if in the equation:

$$v_{21}\, dp - (x_2 - x_1)\left(\frac{\partial^2 \zeta}{\partial x_1^{\,2}}\right)_{pT} dx_1 + \frac{w_{21}}{T}\, dT$$

the factor of dx_1 is to be considered as known. We have viz.

$$\left(\frac{\partial^2 \zeta}{\partial x_1^{\,2}}\right)_{pT} = MRT \left\{ \frac{1}{x_1(1-x_1)} + \mu''_x \right\}$$

We find then:

$$\mu''_x = -\frac{1}{MRT}\frac{d^2\frac{a}{b}}{dx^2} + \frac{d^2 l\frac{a}{b^2}}{dx^2},$$

or

$$\mu''_x = -\frac{f}{T}\frac{d^2 T_k}{dx^2} + \frac{d^2 l p_k}{dx^2}.$$

So for small vapour pressure the equation:

$$\frac{1}{p}\left(\frac{dp}{dx_1}\right)_T = (x_2 - x_1)\left\{ \frac{1}{x_1(1-x_1)} - \frac{f}{T}\frac{d^2 T_k}{dx_1^{\,2}} + \frac{d^2 l p_k}{dx^2} \right\}$$

holds approximately.

In general the quantity $\frac{d^2 T_k}{dx_1^{\,2}}$ will be positive, and this is certainly so when there is a minimum value for T_k; the value of the other term may change this of course. But as a rule μ''_{x_1} will be found negative for normal substances.

In the value of the quantity $\frac{T}{p}\left(\frac{dp}{dT}\right)_{x_1}$ only one of the two parts of μ'_{x_1} occurs, viz. $\frac{f}{T}\frac{dT_k}{dx_1}$ and not the other part $\frac{dlp_k}{dx_1}$. So only the part depending on T is kept. In different ways the value of this quantity may be found. It is easily found from the equation, occurring in Cont. II p. 146, slightly reduced, viz:

$$\frac{p}{MRT} = \{(1-x_1) + x_1 e^{\mu'_{x_1}}\} e^{\mu_{x_1} - x_1 \mu'_{x_1} - 1}$$

From this form we derive, keeping x_1 constant:

$$\frac{dp}{pdT} - \frac{1}{T} = \frac{x_1 e^{\mu'_{x_1}} \dfrac{d\mu_{x_1}}{dT}}{1 - x_1 + x_1 e^{\mu'_{x_1}}} + \frac{d(\mu_{x_1} - x_1 \mu_{x_1} - 1)}{dT}$$

for which we may write:

$$\frac{dp}{pdT} - \frac{1}{T} = x_2 \frac{d\mu'_{x_1}}{dT} + \frac{d(\mu_{x_1} - x_1 \mu'_{x_1})}{dT}$$

or

$$\frac{dp}{pdT} - \frac{1}{T} = (x_2 - x_1) \frac{d\mu'_{x_1}}{dT} + \frac{d\mu_{x_1}}{dT}.$$

For $\dfrac{d\mu'_{x_1}}{dT}$ we find $\dfrac{f}{T^2} \dfrac{dT_k}{dx}$, and for $\dfrac{d\mu_{x_1}}{dT}$ we get the value $\dfrac{f}{T^2} T_k - \dfrac{1}{T}$.

Hence:

$$\left(\frac{Tdp}{pdT}\right)_{x_1} = \frac{f}{T} \left\{ T_{k_1} + (x_2 - x_1) \frac{dT_{k_1}}{dx_1} \right\}$$

Multiplying the second member by MRT, we find w_{21}. For w_{21} we find then 2 terms, the first $MRf\,T_k$ representing the heat of evaporation, when the mixture x_1 evaporated as an unsplit substance, and therefore the vapour phase would have the same concentration as the liquid phase. The second part $\dfrac{f}{T}(x_2 - x_1)\dfrac{dT_k}{dx_1}$ denotes the modification, which is the consequence of the circumstance, that the vapour phase has another concentration than the liquid phase. This modification can be very considerable in certain cases, viz. when $x_2 - x_1$ is very large. If T_k should depend linearly on x, then $T_{k_1} + (x_2 - x_1)\dfrac{dT_{k_1}}{dx_1} = T_{k_2}$ and for T_{k_2} we might write in that case, denoting the components of the mixture by a and b: $T_{k_2} = T_{k_a}(1 - x_2) + T_{k_b} x_2$. (Cont. II, p. 155) or $\dfrac{T}{p}\left(\dfrac{dp}{dT}\right)_{x_1} = (1 - x_2)\dfrac{T}{p_a}\dfrac{dp^a}{dT} + {}$ $+ x_2 \dfrac{T}{p_b}\dfrac{dp_b}{dT}$. Then $w_{21} = M_a r_a (1 - x_2) + M_b r_b x_2$, and the process of mixing in the liquid state will take place without heat of mixing.

If the graphical representation of T_k as function of x, is a curve (Cont. II, p. 45), lying everywhere above the tangent, which is the case when $\frac{a_1}{b_1^2}+\frac{a_2}{b_2^2}-\frac{2a_{12}}{b_1 b_2}$ is positive, then $T_{k_1}+(x_2-x_1)\frac{dT_{k_1}}{dx_1}$ is smaller than T_{k_2}.

If we draw a tangent to the curve in the point x_1, this tangent cuts the ordinate of x_2 in a point which lies lower than the curve, and the distance from that point of intersection to the curve is a measure for the quantity of heat required for mixing the condensed vapour with the liquid phase considered. As μ''_x consists of two terms, the latter of which is only negative, when the mixing in the liquid state is attended by absorption of heat, we are not justified in expecting that this latent heat of mixing alone determines the sign of μ''_x.

Physics. — "*On P_x-curves of mixtures of acetone and ethyl-ether and of carbon tetrachloride and acetone at 0° C.*" By G. C. Gerrits. (Communicated by Prof. J. D. van der Waals).

(Communicated in the meeting of June 25, 1904).

The imperfect concordance found by Cunaeus 1) between the relation deduced by van der Waals 2) in his theory between the vapour tension over a mixture of two liquids, the molecular concentration of the vapour and that of the liquid, induced us to take up the investigation once more according to the same method as had been used by Cunaeus and with the same substances, acetone and ethyl-ether. Afterwards also mixtures of carbon tetrachloride and acetone were examined.

It had viz. appeared, that improvements might be applied to the method of investigation.

By means of the determination of the refractivity of the vapour, both of the simple substances and of the mixtures, the molecular concentration of the vapour was determined by means of the law of Biot and Arago.

This determination of the refractivity was made according to the method of Lord Rayleigh 3) also followed by Cunaeus 4).

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1) Cunaeus, Proefschrift, Amsterdam, 1900, blz. 47—51.

2) van der Waals, Arch. Néerl. 24, blz. 44; Continuität des gasf. und flüss. Zustandes II, blz. 137.

3) Rayleigh, Proc. Roy. Institution, Vol. XV, Part. 1, pag. 1; Proc. Roy. Soc. Vol. 59, blz. 201.

4) Cunaeus, Proefschrift, blz. 4—6. Proc.

RAYLEIGH always compares the gas, the refractivity of which he wishes to determine, with dry air free from carbonic acid. He takes care that the gas and the air are both in such circumstances that their refractive indices are the same in these circumstances, which may be tested by means of a Fraunhofers' diffraction phenomenon. This equality of refraction indices is obtained by regulating the pressure of the two gases. With the aid of a cathetometer and the barometer the pressure is determined, and from the two pressures the refractivity of the gas.

This is applied to mixtures of vapours coexisting with mixtures. The pressure of the air, the refractivity of which is compared with that of the vapour, is regulated in such a way that the vapour and the air are in such circumstances that their refractive indices are the same.

From the relation between the pressures the molecular refractivity of the vapour (or of the vapour mixture) may be determined, the law of BIOT and ARAGO gives then the concentration of the vapour mixture x_2.

The vapour pressure is of course, also known. The concentration of the liquid was obtained by weighing the original quantities of liquid brought into the apparatus, and diminishing each with the weight of the quantity of that substance in the vapour.

The arrangement agreed on the whole with that of CUNAEUS. It was a modification of one given by FRAUNHOFER based on the interference of light, which fell through two vertical parallel slits, after having passed through two tubes of equal length, shut off by two plates of plate-glass. Then it was converged by the object-glass of a telescope and the diffraction phenomenon brought about in this way, was observed by means of an eye-glass consisting of two cylindric lenses. In one of the tubes mentioned the vapour is found, in the other air or dry carbonic acid, the refractivity of which was known, and the pressure of which was now regulated in such a way that the diffraction phenomenon occupied the place which it would also have taken, when the two tubes had been filled with the same gas under the same circumstances.

The two tubes were connected with open manometers and an apparatus to increase or decrease the pressure of the air.

The improvements which were applied, were chiefly the following:

1st. The two substances which were used for the determination were sealed in two separate small pieces of glass tube, so that the air could be removed from the liquid as much as possible by boiling the liquid under decreased pressure.

KOHNSTAMM [1]) has proved that the way in which these little tubes are filled, may give rise to errors in the determination of the vapour pressure, even when they are filled with a simple substance, and not as with CUNAEUS with a mixture. [2])

2nd. By adjusting a glass spiral between the globe in which the liquid was brought and the experimental tube the globe could be violently shaken, which prevented insufficient mixing of the layers of the liquid.

3rd. The difference in appearance between successive fringes was very slight with CUNAEUS, which rendered the adjustment of the movable interference phenomena compared with the firm, pretty uncertain. By taking a more favourable relation of the distance between two corresponding edges of the slits to the width of each of those slits, spectra were distinctly visible on the sides of the bands, all turning their violet rim to the middle fringe. So there was a means of ascertaining the latter.

Moreover it was investigated whether possible absorption of vapour on the plates of plate glass would have influence on the course of the px-curves. This appeared not to be the case, however, so that this was no longer done in the examination of the second mixture.

The temperature at which the substances were examined, was 0°C.

The substances were obtained from KAHLBAUM at Berlin and were purified before use by distilling them a few times by means of a YOUNG and THOMAS' [3]) dephlegmator with twelve constrictions.

The mixture acetone-ethylether.

The results of the experiment are stated in Table I. (p. 165). For the refractivity that of dry air free from carbonic acid has been taken as unity, the pressure is given in mm. of mercury at 0°C. Ethylether must be considered as admixture.

The px_1x_2 diagram obtained in this way is graphically represented in fig. 1.

From the course of the curves appears: There is a maximum pressure, just on the side of the ether.

The point of inflection found by CUNAEUS is also found here, and at about $x_2 = 0,66$.

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[1]) KOHNSTAMM, Proefschrift, Amsterdam, 1901, blz. 170—180.

[2]) How difficult it is to get the substance pure and free from air has been lately observed once more by TEICHNER, Ann. de Phys. 13 p. 603.

[3]) SYDNEY YOUNG and THOMAS, A dephlegmator for fractional distillation. Chem. News, 71, blz. 177.

TABLE I.

Pressure.	Refractivity	x_2	x_1
69.08	3.7658	0.	0.
80.27	4.0410	0.173	0.024
98.03	4.3097	0.342	0.083
107.03	4.4353	0.421	0.124
127.01	4.6458	0.553	0.232
134.40	4.7036	0.590	0.295
164.72	4.9548	0.748	0.561
180.15	5.1112	0.846	0.796
185.60	5.3562	1.	1.

The $p = f(x_2)$ curve is convex from $x = 0$ to $x = 0,66$.

The curve $p = f(x_1)$ has a very simple course: it turns everywhere its concave side to the x-axis.

From the course of the curves follows finally, that the vapour is always richer in admixture than the liquid, the greatest difference between x_1 and x_2 amounting to about 0,33.

These curves were now compared with the differential equations derived by VAN DER WAALS:

$$\frac{1}{p} \cdot \frac{dp}{dx_2} = \frac{x_2 - x_1}{x_2 (1 - x_2)},$$

which the curve $p = f(x_2)$, must satisfy throughout its course, when the volume of the liquid may be neglected by the side of the volume of the vapour and when the vapour phase may be considered as being rarefied, and:

$$\frac{1}{p} \cdot \frac{dp}{dx_1} = \frac{x_2 - x_1}{x_1 (1 - x_1)}$$

which must hold chiefly for the borders of the curve $p = f(x_1)$ under the same conditions.

From the figure p and $\frac{dp}{dx_2}$ have been found for the values of x indicated in Table II, then $x_2 - x_1$ is derived from the equation and from this x_1 and these values are compared with the observed values:

TABLE II.

x_2	p	$\frac{dp}{dx_2}$	$x_2 - x_1$		x_1	
			calc.	observed.	calc.	observed.
0.1	74	71	0.086	0.084	0 014	0.016
0.2	82.5	88.5	0.172	0.170	0.028	0.030
0.3	93	109	0.246	0.238	0.054	0.062
0.4	104	133	0.307	0 292	0.093	0.108
0 5	119	158	0.332	0.315	0 168	0.185
0.6	136	188	0.332	0.314	0.268	0.286
0.7	154	190	0.258	0.250	0.442	0 450
0.8	174	140	0.129	0.122	0.671	0.678
0.9	183	73	0.004	0.004	0.896	0.896

The differences between the observed and the calculated values of x_1 are evidently slight, so that the observations may be considered as satisfying the equation in question.

When testing the observations by means of the second equation, we got the following result:

TABLE III.

x_1	p	$\frac{dp}{dx_1}$	$x_2 - x_1$		x_2	
			calc.	observed	calc.	observed
0 05	90	385	0 203	0.224	0.253	0.274
0.1	102	252	0 222	0.280	0 322	0.380
0.2	122	198	0.260	0.322	0.460	0.522
0.3	138	156	0.239	0.314	0.539	0.614
0.4	149 5	119	0.191	0.276	0.591	0 676
0.5	159	102	0.160	0.224	0.660	0.724
0.6	168	83	0.119	0 168	0.719	0.768
0.7	176	79	0 094	0.120	0.794	0.820
0.8	180.5	46	0.041	0.052	0.841	0.852
0.9	183 5	12	0.004	0.006	0.904	0.906

The closest concordance between the observed and the calculated values of x_2 seems to be found at the edges of the curves.

Van der Waals derived from the equation of $\left(\frac{\partial\psi}{\partial x}\right)_{v.T}$ for both phases:

$$\frac{x_1}{1-x_1} e^{\mu'_{x_1}} = \frac{x_2}{1-x_2}$$

in which:

$$\mu'_{x_1} = \left(\frac{d\mu_{x_1}}{dx_1}\right)_p \text{ and } \mu_{x_1} = \frac{1}{MRT}\left\{pv - MRT\, log\,(v - b_{x_1}) - \frac{a_{x_1}}{v}\right\}.$$

With the aid of the observed x_1 and x_2 we may derive μ'_{x_1} as function of x_1 from this equation. The values found in this way are given in Table IV. For x_1 smaller than 1 and larger than 0,9 the values of μ'_{x_1} are too inaccurate, so that they are not given for the borders of the curves:

TABLE IV.

x_1	x_2	$e^{\mu'_{x_1}}$	μ'_{x_1}
0.1	0.380	5.516	1.71
0.2	0.522	4.368	1.47
0.3	0.614	3.712	1.31
0.4	0.676	3.130	1.14
0.5	0.724	2.623	0.96
0.6	0.768	2.207	0.79
0.7	0.820	1.952	0.67
0.8	0.852	1.439	0.36
0.9	0.906	1.071	0.07

The function μ'_{x_1} as function of x_1 has been graphically represented in fig. 2. Evidently the points give a pretty continuous curve.

It appears from the table that μ'_{x_1} approaches to 0 for higher values of x. This is in accordance with the fact that the px-line has a maximum on the ether side, so for $x_1 = 1$.

Van der Waals has given [1]) an explicit expression for p as function

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[1]) van der Waals, Versl. K. A. v. W. Amsterdam, Januari 1891, bl. 409; Continuität II, p. 146.

of x_1, from which $\frac{dp}{dx_1}$ may be derived:

$$\frac{dp}{dx_1} = p \frac{(e^{\mu'_{x_1}} - 1)\{1 + x_1 (1 - x_1) \mu''_{x_1}\}}{1 - x_1 + x_1 e^{\mu'_{x_1}}}.$$

So for $x_1 = 1$:

$$\frac{dp}{dx_1} = p \cdot \frac{e^{\mu'_{x_1}} - 1}{e^{\mu'_{x_1}}}$$

If p is a maximum for $x_1 = 1$, then $\mu'_{x_1} = 0$.

VAN DER WAALS has also given an approximate value for μ'_{x_1} in "Ternary Systems"[1]):

$$\mu'_{x_1} = -\frac{f}{T}\frac{dT_{cr}}{dx_1} + \frac{d \log p_{cr}}{dx_1}$$

where T_{cr} and p_{cr} represent the critical temperature and pressure of the unsplit mixture and f the known constant, about 7, which inter alia also occurs in the formula, given much earlier by VAN DER WAALS for a pure substance: $Nep. \log \frac{p}{pk} = -f \frac{T_k - T}{T}$.

This formula for μ'_{x_1} has been derived by VAN DER WAALS also directly from the equation of state[2]).

If it only contained the first term, then a minimum critical temperature would be attended by a maximum pressure, the minimum would therefore lie near the pure ether. Now however this minimum will not be found there, as appears from the occurrence of the second term.

If we now assume that T_{cr} depends linearly on x and that this is also the case for p_{cr}, then $\frac{dT_{cr}}{dx_1}$ is about -43 and $\frac{dp_{cr}}{dx_1}$ about -15, in consequence of which we find for μ'_{x_1} about 0,8, a value which really lies between the values found.

Also μ''_{x_1}, the differential quotient of μ'_{x_1} with respect to x_1 may be determined. The accurate relation derived by VAN DER WAALS for the dependence of the vapour pressure on the molecular concentration of the liquid mixture, where it is only assumed that the liquid volume may be neglected by the side of that of the vapour, and that the vapour phase may be considered as a rarefied one, is

$$\frac{1}{p} \cdot \frac{dp}{dx_1} = (x_2 - x_1) \left\{ \frac{1}{x_1 (1 - x_1)} + \mu''_{x_1} \right\}.$$

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[1]) VAN DER WAALS, These Proc. V, p. 9.

[2]) VAN DER WAALS, These Proc. VII p. 156.

From this μ''_{x_1} may be found. These values, calculated, are given in Table V:

TABLE V.

x_1	p	$\frac{dp}{dx_1}$	$x_2 - x_1$	$\frac{1}{x_1(1-x_1)} + \mu''_{x_1}$	μ''_{x_1}
0.1	102	252	0.280	8.8	— 2.3
0.2	122	198	0.322	5.0	1.2
0.3	138	156	0.314	3.6	— 1.2
0.4	149.5	119	0.276	2.9	— 1.2
0.5	159	102	0.224	2.9	— 1.1
0.6	168	83	0.168	2.9	- 1.2
0.7	176	79	0.120	3.7	— 1.1
0.8	180.5	46	0 052	4.9	— 1.4
0.9	183.5	12	0.006	10.9	— 0.2

The values given for $x_1 = 0{,}7$, $0{,}8$ and $0{,}9$, however, are not very reliable, on account of the small value which $x_2 - x_1$ then has, by which the first member is to be divided. For the same reason μ''_{x_1} cannot be given for x_1, smaller than 0,1.

Evidently all the values of μ''_{x_1} are negative and as to their absolute value, they are smaller than 4. This in accordance with the fact, that for stable phases, $\left(\frac{\partial^2 \zeta}{\partial x_1^{\,2}}\right)_p$ must be larger than 0.

From the course of the curve $\mu'_{x_1} = f(x_1)$ appears that the differential quotient of about $x = 0.2$ to $x = 0.6$ must have a constant value. And this is really found for μ''_{x_1}.

With regard to μ''_{x_1} we may still remark, that its numerical value may be found also for the x_2 of the inflection point and the corresponding x_1. VAN DER WAALS has namely derived: [1])

$$\frac{d^2p}{dx^2_{\,2}} = \frac{dp}{dx_2} \cdot \frac{dx_1}{dx_2} \left[\frac{2\left(e^{\mu'_{x_1}} - 1\right)}{1 - x_1 + x_1 e^{\mu'_{x_1}}} + \mu''_{x_1} \left\{ \frac{2\, x_1 e^{\mu'_{x_1}}}{1 - x_1 + x_1 e^{\mu'_{x_1}}} - x_1 + \frac{1}{e^{\mu'_{x_1}} - 1} \right\} \right].$$

$\frac{d^2p}{dx_2^{\,2}}$ being 0 for the point of inflection, the factor of $\frac{dp}{dx_2} \cdot \frac{dx_1}{dx_2}$ must be 0.

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[1]) These Proc. III p. 172.

With the aid of the relation $e^{\mu'_{x_1}} = \frac{x_2}{1-x_2} \cdot \frac{1-x_1}{x_1}$ we find from this:

$$\mu''_{x_1} = -\frac{2\frac{(x_2-x_1)^2}{x_1(1-x_1)}}{2(x_2-x_1)^2+x_1(1-x_1)}$$

For the inflection point we have about $x_2 = 0{,}66$ and $x_1 = 0{,}40$. For μ''_{x_1} we find then about $-$ 1,5. Taking into consideration that the place of the point of inflection cannot be determined accurately, and that with change of the x_2 of this point at the same time also its x_1 is changed, the agreement may be called satisfactory.

The mixture carbontetrachlorid-acetone.

These two substances, carbontetrachloride and acetone were chosen with a view to the critical pressure, which is about the same for them.

Now VAN DER WAALS [1]) has derived, that for $\mu'_{x_1} =$ constant the relation between p and x_1 is represented by a straight line, that between p and x_2 by a hyperbola.

On the supposition that at low temperature for μ'_{x_1} may be written:

$-\frac{1}{MRT}\frac{d\frac{a_{x_1}}{b_{x_1}}}{dx_1}$; for b_{12}: $\frac{1}{2}$ $(b_1 + b_2)$ and that also the relation of GALITZINE—BERTHELOT $a_{12} = \sqrt{a_1 a_2}$ holds good, the condition $\mu'_{x_1} =$ constant involves, that the critical pressures of the components are the same.

Now the above mentioned improved approximation for μ'_{x_1} has already been given by VAN DER WAALS himself instead of the one mentioned here; moreover the relation $a_{12} = \sqrt{a_1 a_2}$ has already been discussed and rejected by KOHNSTAMM. [2]) It is therefore not surprising, that a strong deviation from the straight line and the hyperbola was found for this mixture [3]).

The px_1x_2 diagram is given in Table VI. Acetone is to be considered as admixture:

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[1]) These Proc. III p. 168–169.

[2]) KOHNSTAMM, Proefschrift, blz. 99.

[3]) From the survey of the investigated mixtures given by KOHNSTAMM, Zeitschr. f. Phys. Chem. XXXVI. 1, it appears also, that equality of critical pressure of the components does not necessarily involve the existence of a straight line for the $p = f(x_1)$ line.

TABLE VI.

Pressure.	Refractivity.	x_2	x_1
34.20	6.1407	0.	0.
44.46	5.7352	0.172	0.044
46.43	5.4772	0.281	0.122
52.27	5.1253	0.430	0.234
55.47	4.9261	0.515	0.333
60.43	4.6135	0.647	0.477
64.49	4.3219	0.771	0.696
69.32	3.7813	1.	1.

In fig. 3 it is graphically represented.

Both the curves have a very simple shape. They turn their concave side to the x-axis. The vapour is always richer in the admixture than the liquid. The greatest difference between x_1 and x_2 is about 0,190.

Both the curves are now compared with the differential equations:

$$\frac{1}{p} \cdot \frac{dp}{dx_2} = \frac{x_2 - x_1}{x_2(1-x_2)}$$

$$\frac{1}{p} \cdot \frac{dp}{dx_1} = \frac{x_2 - x_1}{x_1(1-x_1)}$$

The results are given in table VII and table VIII:

TABLE VII.

x_2	p	$\frac{dp}{dx_2}$	$x_2 - x_1$		x_1	
			calculated	observed	calculated	observed
0.1	39	39	0.090	0.090	0.010	0.010
0.2	43	37.5	0.139	0.141	0.061	0.059
0.3	47	37	0.165	0.178	0.135	0.122
0.4	51	36	0.169	0.190	0.231	0.210
0.5	55	35.5	0.161	0.184	0.339	0.316
0.6	59	35	0.142	0.165	0.458	0.435
0.7	62.5	29	0.097	0.122	0.603	0.578
0.8	65	24.5	0.060	0.080	0.740	0.720
0.9	67.5	23	0.031	0.035	0.869	0.865

TABLE VIII.

x_1	p	$\frac{dp}{dx_1}$	$x_2 - x_1$		x_2	
			calculated	observed	calculated	observed
0.05	41.5	102	0.117	0.120	0.167	0.170
0.1	45.5	72	0.143	0.160	0.243	0.260
0.2	50.5	48	0.152	0.180	0.352	0.380
0.3	54.5	39	0.150	0.182	0.450	0.482
0.4	58	33	0.137	0.172	0.537	0.572
0.5	61	24	0.098	0.154	0.598	0.654
0.6	63	20	0.076	0.120	0.676	0.720
0.7	64.5	15.5	0.050	0.078	0.750	0.778
0.8	66	15	0.036	0.040	0.836	0.840
0.9	68	14.5	0.019	0.020	0.919	0.920

Evidently the curves satisfy the first differential equation much better than the second. For the second the closest agreement is obtained, here too, on the borders of the curves.

Also for this mixture μ'_{x_1} as function of x_1 was determined by means of the relation :

$$\frac{x_1}{1-x_1} e^{\mu'_{x_1}} = \frac{x_2}{1-x_2} .$$

The values, found in this way, are given in Table IX :

TABEL IX.

x_1	x_2	$e^{\mu'_{x_1}}$	μ'_{x_1}
0.1	0.260	3.162	1.15
0.2	0.380	2.452	0.90
0.3	0.482	2.171	0.78
0.4	0.572	2.005	0.70
0.5	0.654	1.890	0.64
0.6	0.720	1.714	0.54
0.7	0.778	1.502	0.41
0.8	0.840	1.313	0.27
0.9	0.920	1.278	0.25

Here too the values of μ'_{x_1} are not accurate on the borders of the curve. In fig. 4 the results have been represented. Here too the points give a continuous curve.

The critical pressures of the components being the same for this mixture, the second term in the equation:

$$\mu'_{x_1} = -\frac{f}{T}\frac{dT_{cr}}{dx_1} + \frac{d\log p_{cr}}{dx_1}$$

will be small compared to the first. If we take for μ'_{x_1} only the term $-\frac{f}{T}\frac{dT_{cr}}{dx_1}$ and if we assume linear dependence of T_{cr} on x_1, then $\frac{dT_{cr}}{dx_1}$ is here about -40, so μ'_{x_1} about 1. In this neighbourhood also the values of μ'_{x_1} are found.

Also in this case μ''_{x_1} is determined from the equation:

$$\frac{1}{p}\cdot\frac{dp}{dx_1} = (x_2-x_1)\left\{\frac{1}{x_1(1-x_1)} + \mu''_{x_1}\right\}$$

The values found from this are given in Table X.

TABLE X.

x_1	p	$\frac{dp}{dx_1}$	x_2-x_1	$\frac{1}{x_1(1-x_1)}+\mu''_{x_1}$	μ''_{x_1}
0.1	45.5	72	0.160	9.9	—1.2
0.2	50.5	48	0.180	5.3	—1.0
0.3	54.5	39	0.182	3.9	—0.9
0.4	58	33	0.172	3.3	—0.9
0.5	61	24	0.154	2.6	—1.4
0.6	63	20	0.120	2.6	—1.5
0.7	64.5	15.5	0.078	3.1	—1.7
0.8	66	15	0.040	5.7	—0.6
0.9	68	14.5	0.020	10.7	—0.4

Here too the value of μ''_{x_1} for $x_1 = 0{,}7$, $0{,}8$ and $0{,}9$ is not very reliable on account of the small value of x_2-x_1.

The quantity μ''_{x_1} proves again to be negative and in absolute value smaller than 4.

From the course of the curve $\mu'_{x_1} = f(x_1)$ appears that it seems to have two points of inflection, one at about $x_1 = 0{,}3$, the other at about $x_1 = 0{,}7$. It is remarkable that this also follows from the change of the μ''_{x_1} in Table X; just as we had to expect from the course of the curve $\mu'_{x_1} = f(x_1)$ μ''_{x_1} gets a maximum at about $x_1 = 0{,}3$, and a minimum at $x_1 = 0{,}7$.

Chemistry. — *"On the latent heat of mixing for associating solvents."* By J. J. van Laar. (Communicated by Prof. H. W. Bakhuis Roozeboom).

(Communicated in the meeting of June 25, 1904).

1. When some substance is solved in an *associating* liquid, as e.g. *water*, and we try to find an expression for the latent heat of mixing of these two substances, we shall in the first place have to take into account, besides the change of the potential energy, the heat of *ionisation* of the solved substance, if this substance is an electrolyte. The fact, however, that the state of *association* is changed by the solving, is nearly always overlooked. We are inclined to reason, that in much diluted solutions the influence of the addition of a few molecules of the solved substance must necessarily be exceedingly slight, with regard to the degree of association of the solvent; but in doing so it is overlooked that the *number* of molecules of the solvent which each undergo a very slight change in their state of association, is *very great*. For infinitely diluted solutions therefore, a value is obtained approaching to $0 \times \infty$, and I shall demonstrate in what follows, that the absorbed *heat* in consequence of the change in the state of association, approaches to a definite value, which is *finite* and even comparatively high.

2. In *diluted* solutions — which we solely have in view in the following pages — the state of equilibrium of the associating molecules of the solvent may be expressed as follows:

$$\frac{\left(\frac{(1-x)\beta}{N}\right)^2}{\frac{{}^1/_2\,(1-x)(1-\beta)}{N}} = K,$$

i.e.:

$$\frac{\beta^2}{1-\beta}\,\frac{1-x}{N} = {}^1/_2\,K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For, given $1-x$ mol. H_2O, normally reckoned, x mol. salt (calling the solved substance *salt* for convenience' sake), then there are ${}^1/_2\,(1-x)$ mol. H_2O, if all are double. Therefore if the degree of dissociation of these double-molecules is β, then there are:

${}^1/_2\,(1-x)(1-\beta)$ double mol. ; ${}^1/_2\,(1-x)\,2\beta = (1-x)\,\beta$ single mol.

The total number of particles is N. If the degree of dissociation of the saltmolecules is α, then there are (in *binary* electrolytes):

$x(1-\alpha)$ neutral mol.; $\quad 2x\alpha$ Ions.

We have therefore:

$$N = {}^1/_2\,(1-x)(1+\beta) + x(1+\alpha),$$

or with ${}^1/_2\,(1+\beta) = \gamma$, $1+\alpha = i$, where therefore i has the usual meaning, and γ is the reverse of the so-called association-coefficient:

$$N = \gamma(1-x) + ix = \gamma(1-x)\left[1 + \frac{i}{\gamma}\,\frac{x}{1-x}\right].$$

Our equation (1) becomes therefore:

$$\frac{\beta^2}{1-\beta}\;\frac{1}{\gamma\left[1+\frac{i}{\gamma}\,\frac{x}{1-x}\right]} = {}^1/_2\,K,$$

or γ being $= {}^1/_2\,(1+\beta)$:

$$\frac{\beta^2}{1-\beta^2} = {}^1/_4\,K\left(1+\frac{i}{\gamma}\,\frac{x}{1-x}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From this follows, putting $\frac{i}{\gamma}\,\frac{x}{1-x} = \delta$:

$$\beta = \sqrt{\frac{{}^1/_4\,K(1+\delta)}{1+{}^1/_4\,K(1+\delta)}} = \sqrt{\frac{{}^1/_4\,K}{1+{}^1/_4\,K}}\sqrt{\frac{1+\delta}{1+\frac{{}^1/_4\,K}{1+{}^1/_4\,K}\,\delta}}\,.$$

Now evidently

$$\beta_0 = \sqrt{\frac{{}^1/_4\,K}{1+{}^1/_4\,K}}\,,$$

i. e. the value of β, if x or $\delta = 0$, so that we have got the *pure* solvent, for which the equation $\frac{\beta_0^{\,2}}{1-\beta_0^{\,2}} = {}^1/_4\,K$ holds. Therefore we obtain:

$$\beta = \beta_0\sqrt{\frac{1+\delta}{1+\beta_0^{\,2}\,\delta}} = \beta_0\left(1+\frac{1-\beta_0^{\,2}}{2}\,\delta\right),$$

if, δ being very small and approaching to 0, we content ourselves with a first approximation.

Substituting for δ its value, and taking into account that $\gamma = {}^1/_2\,(1+\beta)$, we obtain:

$$\beta = \beta_0\left(1+\frac{1-\beta_0^{\,2}}{2}\;\frac{i}{{}^1/_2\,(1+\beta)}\;\frac{x}{1-x}\right),$$

or with $1+\beta = 1+\beta_0$:

$$\beta = \beta_0\left(1+(1-\beta_0)\,i\,\frac{x}{1-x}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

So this is the sought-for expression for the change in β_0, caused by the addition of x gr.mol. salt.

3. Now on 1 saltmol. there are $\frac{1-x}{x}$ gr.mol. H_2O (normally reckoned), among which there are evidently $\frac{1}{2}\left(\frac{1-x}{x}\right)2\beta = \frac{1-x}{x}\beta$ single mol. In consequence of the fact, that the state of dissociation of the watermolecules is changed by the solved substance, this number according to (3) will amount to

$$\frac{1-x}{x}\beta = \frac{1-x}{x}\beta_0 + \frac{1-x}{x} \times \beta_0 (1-\beta_0)\, i\, \frac{x}{1-x},$$

that is to say an *increase* of

$$\frac{1-x}{x} \times \beta_0 (1-\beta_0)\, i\, \frac{x}{1-x}.$$

And now it is clear that, as was already observed above, the one factor of this product, viz. $\frac{1-x}{x}$, approaches to ∞, while the other factor, viz. $\beta_0 (1-\beta_0)\, i\, \frac{x}{1-x}$, approaches to 0. The product however is evidently *finite*, viz.:

$$\underline{\Delta = \beta_0 (1-\beta_0)\, i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now if Q is the heat, absorbed when 1 gr.mol. (18 Gr.) H_2O changes from the state of double molecules to that of single molecules, then the heat, absorbed in consequence of the state of association being changed by 1 mol. of the solved substance, is:

$$\underline{W = \beta_0 (1-\beta_0)\, i\, Q} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

And *this* heat it is, which we have to take into account for *associating* solvents.

For H_2O at 18° $\beta = 0{,}21$ [1]), so that the factor $\beta_0 (1-\beta_0)$ becomes $= 0{,}17$. Further Q (as I calculated some time ago [2])) $= \pm 1920$ gramcalories, so for water (at 18°) will be:

$$\underline{W = 326\, i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

If the solved substance is *no electrolyte*, then $i = 1$, so for much diluted solutions about 325 gr.cal are absorbed with *every* concentration, if 1 gr.mol. is solved in the water, only in consequence of the change in the degree of association of the water; for salts, acids

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[1]) Zeitschr. für Phys. Ch., **31,** p. 4 (1899); Lehrbuch der math. Chemie, p. 36 (1901).

[2]) Z. f. Ph. Ch., **31,** p. 5 (1899); Lehrb. der math. Chem., p. 37 (1901).

and bases, where $i =$ nearly 2, this number becomes 650 gr. cal.

So e. g. for KCl, of which the heat of ionisation of 1 gr.mol. $= -720$ gr. cal.[1]), the total heat of mixing with much H_2O, (excluded the change in potential energy) will therefore be not -720 gr. cal., but only $-720 + 650 = -70$ gr. cal.

So it is seen, that the order of magnitude of the heat to be expected, can be totally modified, and that in general a great mistake would be committed, when we neglected the above calculated $326\,i$ gr. cal. in the calculation of the heat of mixing.

Therefore, with *diluted* solutions of *non-electrolytes* in *associating* solvents, 325 gr. cal. on each gr. mol. of the solved substance must always be subtracted from the absorbed heat determined by experiment, in order to calculate the *pure* (absorbed) heat of mixing, that is to say that heat, which is caused solely by the change in potential energy.

Physics. — Prof. Bakhuis Roozeboom, in the name of Dr. A. Smits, presents a paper, entitled: *"On the phenomena appearing when in a binary system the plaitpointcurve meets the solubility curve."* (Third communication).[2])

(Communicated in the Meeting of June 25, 1904).

The previous qualitative examination of the binary system ether-anthraquinone showed that a good survey of the whole could only be obtained by continuing the examination in quantitative direction with the aid of the pump of Cailletet.

Some difficulties were to be foreseen; the investigation would have to be extended over a range of temperature from ± 170° to ± 300°, in which the pressure might be expected to reach a pretty considerable amount — and the combination of high temperature and high pressure being exactly the thing against which glass is but seldom proof, it seemed at first that we should meet with great experimental difficulties in the quantitative examination. The experiment however showed that the pressures were not exceedingly high; it appeared a maximum pressure of 100 atm. would suffice, and this pressure Jena-glass could withstand up to more than 300°[3]).

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[1]) Z. f. Ph. Ch., **24**, p. 611 (1897); Lehrb. der math. Chem., p. 53 (1901).

[2]) This paper is a continuation of the two preceding ones on the system ether-anthraquinone. The title chosen first seemed to me undesirable and was therefore modified.

[3]) With pleasure I avail myself of this opportunity to thank professor Kamerlingh Onnes for his kindness towards me in procuring the necessary information and in lending me some instruments wanted.

The object of the experiment was to determine the p-x-sections of the p-x-t-surface at different temperatures, and if possible also the v-x-sections of the v-x-t-surface. At the same time I should get to the knowledge of some projections already spoken of in the previous paper, viz. the projections of the p-x-t-surface on the p-t and the t-x-plane. I shall briefly state the result here.

In order to have the same succession as was chosen in the preceding communications, the p-t-projection will be treated first.

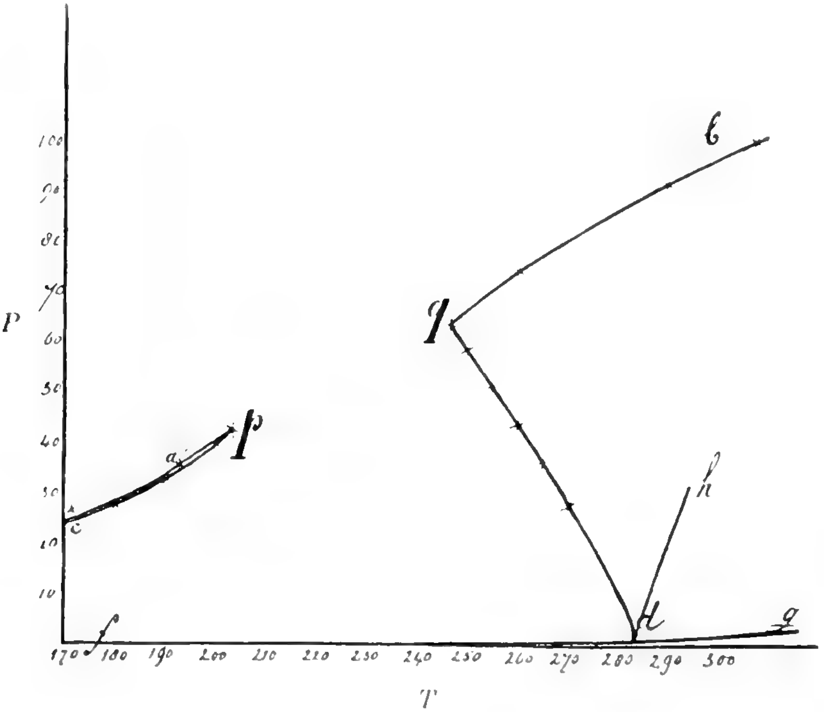

Fig. 1.

In fig. 1, ea represents the vapour pressure curve of pure ether with the critical point in a (193° and 36 atm.). ep and qd represent the portions of the three phase curve which can be realized. Up to 193° the three phase curve practically coincides with the vapour pressure curve ea of pure ether, in consequence of the very small solubility of anthraquinone in ether. On the curve ap lie the plaitpoints of the unsaturated solutions of anthraquinone in ether, and p denotes the *first* plaitpoint of a *saturated* solution (203° and 43 atm.).

The *second* plaitpoint of a *saturated* solution of another concentration lies in q (247° and 64 atm.) and on the curve qb lie the plaitpoints of the second series of unsaturated solutions. Probably this curve, which runs on to the critical point of anthraquinone, has a maximum.

The line fd, which partly coincides with the T-axis, is the vapour pressure curve of solid anthraquinone, and dg that of liquid anthraquinone. dh is the meltingpoint-curve, which (as VAN DER WAALS[1]) has proved) marks the direction of the three phase curve near the meltingpoint d. These last three curves are drawn here schematically.

The main result represented by this p-t-figure is this that by the meeting of plaitpointcurve and three phase curve a part of the latter has vanished or rather has become imaginary, and in the examined system that part that contains the maximum.

The plaitpointcurve is metastable between p and q and therefore still to be realized, but this is not the case with the three phase curve. However it appeared to me that at temperatures between p and q, with concentrations greater than those of point q, three phases could temporarily appear together, if they had originated at a temperature above 247° and if afterwards the system in equilibrium had quickly cooled down to less than 247°. The three phases however were not in equilibrium now, for at a constant temperature a slight change in volume proves to cause a great change in pressure.

The liquid therefore, though in contact with solid anthraquinone, was supersaturated; it was very viscous and passed very slowly, at times not until after an hour, to the stable condition of solid fluid, under secretion of solid anthraquinone.

Fig. 2 gives a number of p-x-sections for different temperatures, the pressure being given in atmospheres and the concentration in 1 mol. total of the mixture.

We may immediately point out here that all the lines in this figure joining points of equal value, as plaitpoints (k), liquids coexisting with vapour and solid anthraquinone (c), vapour coexisting with liquid and solid anthraquinone (e), are all projections on the p-x-plane of curves, which occur in the p-x-t-surface[2]).

The branches $c_0\,p$ and $e_0\,p$, which pass into each other continuously, represent the series of liquids and vapours which if we come from a lower temperature, coexist with solid anthraquinone. In p, the point of confluence of the two branches, we have *the first* point, where a *saturated* solution reaches its critical condition. This takes place at a concentration 0,015, temperature 203° and pressure 43 atm. If we pass on to higher temperatures a stable solution is impossible over the range of temperature 203°—247°, and instead we

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[1]) These Proc. VI p. 230.

[2]) If the plaitpointcurve has a maximum, it must possess a maximum also in fig. 2. In the t-x-projection on the contrary no maximum occurs.

get fluid phases coexisting with solid anthraquinone. Above 247° liquids can again exist and the continuous curve $d\,c_7\,c_6\,c_5\,c_4\,c_3\,q\,e_3\,e_4\,e_5\,e_6\,e_7$ consisting of two branches then represents the series of liquids and vapours which coexist with solid anthraquinone above 247°. The point of confluence here is q, in which therefore for *the second* time a *saturated* solution reaches its critical condition. This occurs with a concentration 0,13, temperature 247° and pressure 64 atm.

The liquid branch $c_0\,p$ of the first loop and the liquid branch $q\,c_5\,d$ of the second loop are what we are accustomed to call two parts of the solubility curve. As however the two liquid branches pass continuously into their vapourbranches, there is no objection to calling the two continuous loops solubility curve.

Branch $c_0\,p$ of the first solubiliy curve and branch $d\,c_5\,q$ of the second show here a particularity. The circumstance that these branches pass continuously into the branches $e_0\,p$ and $d\,e_5\,q$ and that the point of confluence coincides with the highest pressure involves the phenomenon of *retrograde solubility.*

c_0p points to retrograde solubility in the liquid branch (cf. also fig. 4) and $d\,e_5\,q$ to retrograde solubility in the vapour branch. The extent of these phenomena however surpassed all expectations. It was known that the liquid and the vapour branch of the curve $d\,c_4\,q\,e_4\,d$ from q to a higher temperature have to separate first in order to come together again afterwards, but it was not to be foreseen that the distance would be so large as to make the vapour branch extend to the concentration 0,01. From this particular situation results the very interesting phenomenon that, after we have reached point p, with a concentration 0,015 or in other words after the saturated solution has reached its critical condition, at a higher temperature there may again occur three phases. The vapour branch $q\,e_4\,d$ extends namely as already mentioned, to the concentration 0,01, and the concentration of point p is 0,015; therefore we get from point p at a higher temperature into the region on the right of the vapour branch $d\,e_4\,q$, in which three phases may occur. This phenomenon was observed at a temperature nearly 60° above the plaitpoint-temperature of the concentration 0,015 (p), that is at 260°. After the formation of the three phases, first the solid and then the liquid might be pressed away by raising the pressure, so that finally only a fluid phase was left.

Fig. 2 shows further the p-x-sections at temperatures above that of point q, beginning at 250°. The p-x-section corresponding with this temperature is separately drawn in figure 2a. The continuous curve $c_3\,k_3\,e_3$ which represents the coexisting unsaturated liquids and vapours, has a peculiar shape and shows that retograde condensation is wanting.

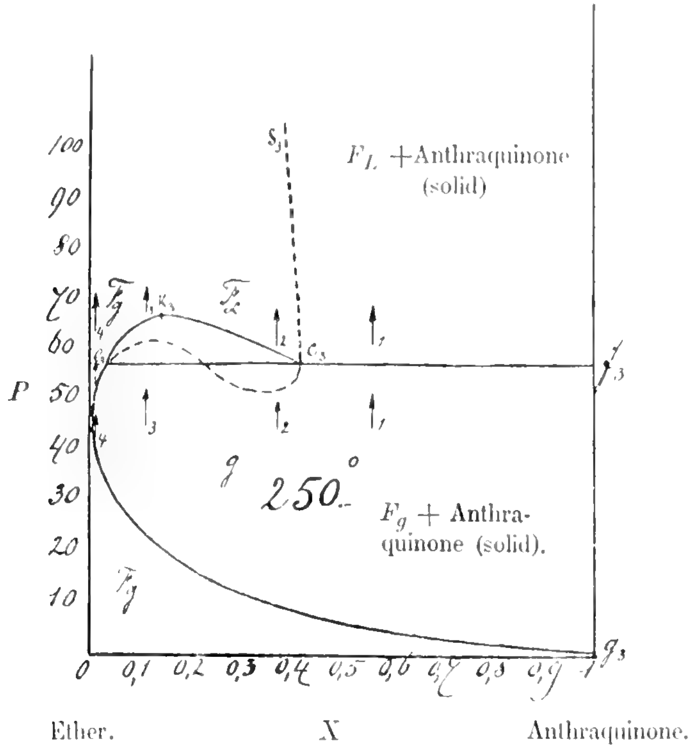

Fig. 2*a*.

The curve $g_3 e_3$ on the contrary indicates a tolerably strong retrograde solidification. The curve $e_3 s_3$ shows that here the solubility of anthraquinone in ether decreases with increased pressure. The curves $g_3 e_8$ and $e_3 s_3$ are two portions of a continuous curve, of which the partly not realizable intermediate part is schematically represented by a dotted curve. I propose to call this continuous curve henceforth *isotherm of solubility.*

Passing on to a higher temperature, we see that the *p-x*-section at 255° is still of the same type as that at 250°. At 260° (fig. 2*b*) however, the situation is already considerably changed; not only the *p-x*-loop $e_5 k_5 e_5$ has become much larger, because the points e_5 and c_5 have become more widely separated and k_5 has moved to higher pressure, but also it is clearly visible that the retrograde condensation, which is still wanting here, will have appeared at a slightly higher temperature.

In the part $g_5 e_5$, though in a smaller degree than at 250°, the

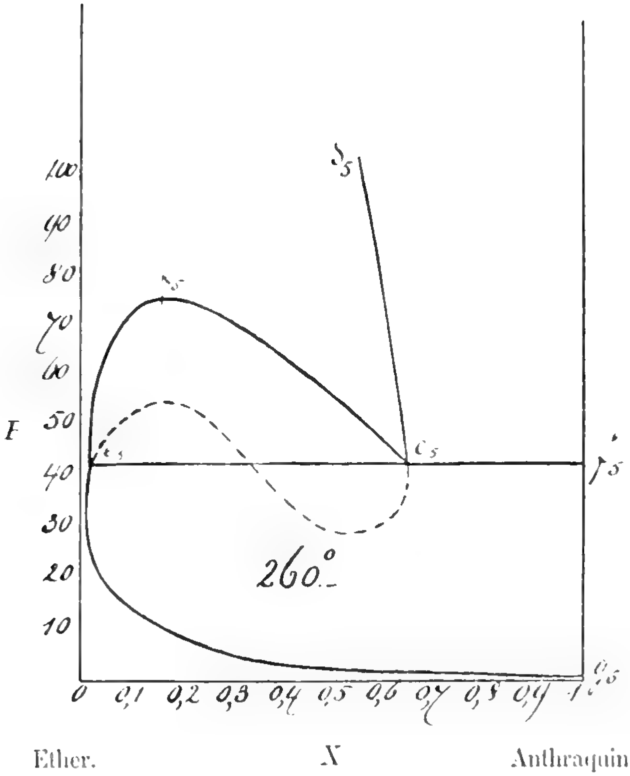

Fig. 2*b*.

isotherm of solubility shows still clearly the phenomenon of retrograde solidification.

At a still higher temperature the region of retrograde condensation becomes greater and greater, so that at 270° we get a *p-x*-section like that drawn in fig. 2*c*.

The retrograde condensation is here very strong and undoubtedly ranges over more than 40 atm. A retrograde condensation of such strength, however, could not be observed because the volume of the compression tube was too small; the strongest retrograde condensation observed by me covered a range of pressure from 55 to 39, of 16 atmospheres therefore. The small volume of the tube prevented us from observing whether any retrograde solidification still existed at 270°. As, however, it is not very probable that we still should have retrograde solidification here, it is not represented in the figure.

Above the melting-point of anthraquinone (283°) the retrograde condensation is enormous, so that I could observe it at 290° over a pressure-range of 83 to 40 atmospheres.

Further I mention that most of the *p-x*-sections are crossed in

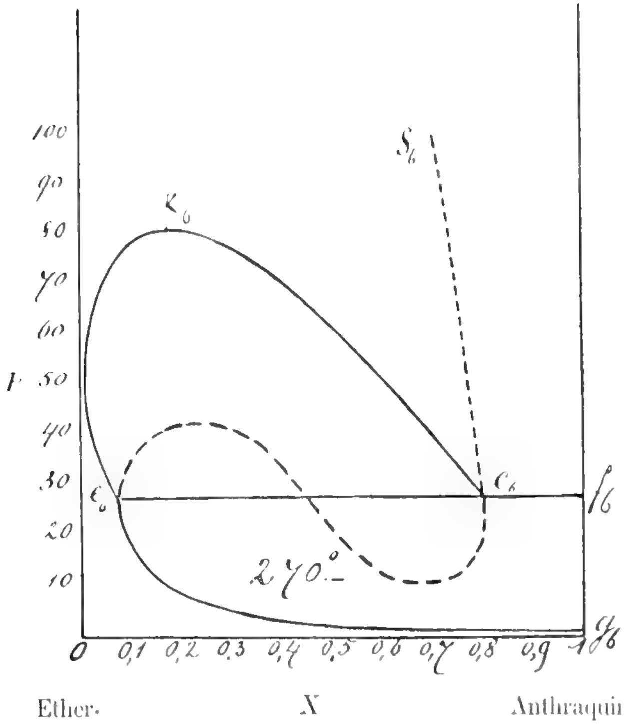

Fig. 2c.

different ways. In fig. 2a the regions passed are marked with arrows.

1 indicates the transition from the region for F_g + solid anthraquinone into the region for F_L + solid antraquinone, the three phases appearing intermedially. F_g denotes here a fluid phase which in ordinary circumstances, that is to say below the critical temperature of ether, would be called gas-phase; and F_L denotes a fluid phase which in ordinary circumstances would be styled liquid phase. It is evident that the difference between F_g and F_L exists solely in their foregoing history.

2 marks the transition from the region F_g + anthraquinone into the region F_L, the three phases appearing intermedially.

3 indicates essentially the same as 2, but yet the phenomenon is somewhat different, because now we do not in the end pass the liquid branch, as in 2, but the vapour-branch; this is marked by the sign F_g over the branch $e_3\,k_3$.

4 is a very remarkable transition, as here we pass directly from the region for F_g + solid anthraquinone into the region for F_g.

As to the lack of retrograde condensation at temperatures between 247° and ± 260° and its appearance at higher temperatures, I want to say a few words about it in connection with the appearance of retrograde solidification.

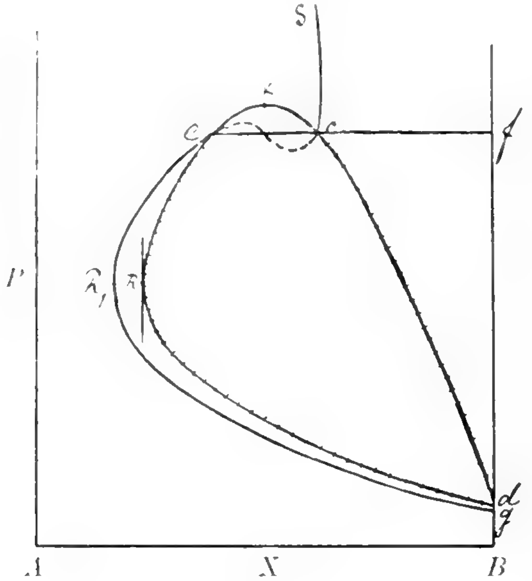

Fig. 3.

If in fig. 3 the p-x-loop $dckeR$ represents the liquids and vapours which may coexist at a given temperature, but of which a series of liquids and vapours are not to be realized in a stable state because of the appearance of the threephase pressure curve [1]), then several cases are possible. If the threephase pressure curve, as drawn in fig. 4 lies above the critical point of contact R, then no retrograde condensation will occur, notwithstanding its possibility is strongly pronounced in the character of the p-x-loop, because the part giving rise to the retrograde condensation lies in the metastable region. Now this occurs in the system ether-anthraquinone from 247° to 260°.

The dotted vapour and liquid curves below the threephase-pressure curve $e\,c\,f$ are metastable; the stable state here is solid B by the side of a fluid phase, and now the question was raised: "how is this part of the isotherm of solubility situated?" Evidently this stable curve must lie left of the metastable curve $d\,R\,e$ or in other words towards smaller B-concentrations. This conclusion is of great importance for us, for from it follows that, *if the threephase-pressure-curve lies above the critical point of contact of the vapour curve coexisting with liquid and for that reason the retrograde condensation falls in the metastable region, retrograde solidification must occur instead of retrograde condensation*, and this retrograde solidification must be *stronger* than the retrograde condensation would have been. If the threephase-pressurecurve passes exactly through the critical point of contact, retrograde solidification is no longer necessary.

Resuming, we conclude that, given the case that the plaitpoint-

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[1]) I propose to give this name to the curve that in a p-x-section denotes the pressure at which the three phases coexist. This curve refers therefore to one temperature, whilst the *threephasecurve* embraces a series of temperatures.

curve meets the solubility curve, it is possible to prove in a very simple way the necessity of the appearance of retrograde solidification in p and q.

Here however we must at once point out that, as will be discussed presently, retrograde solidification also occurs between $p\,q$. The fact that theory requires this, can only be proved mathematically [1]).

Returning to fig. 2, we must still state that the curve $q\,b$ uniting the plaitpoints of the different p-x-loops, is very steep and, as far as it has been observed, parallel to the first part of the plaitpointcurve $a\,p$. This course however will probably change towards a higher temperature, for if the plaitpointcurve possesses a maximum, which is probably the case, then the projection of the plaitpointcurve on the p-x-plane must also show a maximum.

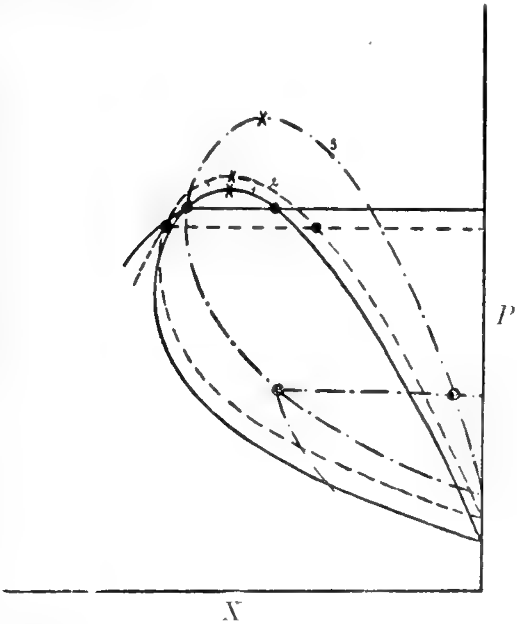

Fig. 4a.

The p-x-sections below the temperature 203° are not drawn in fig. 2, as the scale is too small to render the particulars conspicuous. Therefore this part of fig. 2 is separately reproduced on a larger scale in fig. 4.

In accordance with the preceding we see that, though at 200° no retrograde condensation occurs, instead of it there appears retrograde solidification. Soon however the situation changes here, for already at 196° retrograde condensation could be observed.

What was observed when going from point q to a higher temperature, is naturally also found in point p, but here towards a lower temperature. This is illustrated by figures 4a and 4b; fig. 4a applies to temperatures above point q and fig. 4b applies to temperatures below point p. In both figures three p-x-sections are represented schematically; the sections 1 and 2 differ but slightly in temperature, and 3 applies to a temperature considerably different from that with which 2 corresponds.

In fig. 4a section 1 applies to the lowest and 3 to the highest of

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[1]) VAN DER WAALS, l. c.

the observed temperatures; in fig. 4*b* the reverse is seen, but all the same it is seen that in the two figures the same things are to be met with in the succession of sections 1, 2 and 3. The three

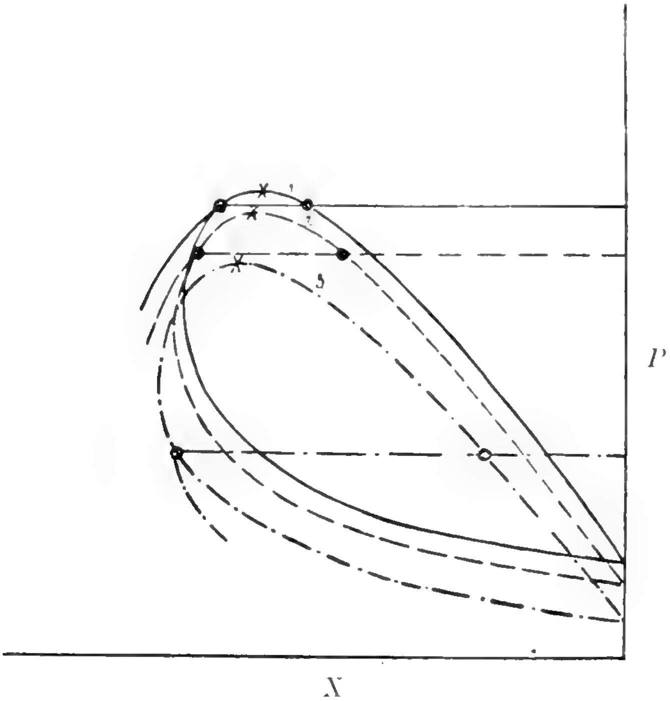

Fig. 4*b*.

pressure curve lies highest in 1 and lowest in 3. In 1 and 2 we do not find any retrograde condensation, but retrograde solidification, and in 3 we find retrograde condensation only. In fig. 4*a* however the plaitpointpressure increases in the order 1, 2, 3, and decreases in fig. 4*b*, but this is due to the fact that in the first case the order 1, 2, 3 means towards higher temperatures, and in the second towards lower.

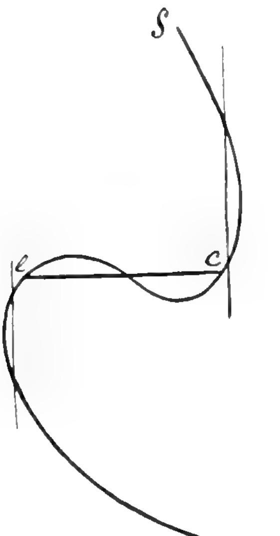

Fig. 5.

Concerning the course of the isotherms of solubility above the three phase pressure curve, VAN DER **WAALS** has shown the probability of a course as given in fig. 5, from which results that the branch *cs* also shows retrograde solidification. This case, in which the whole isotherm of solubility points to a double retrograde solidification, has not been ascertained as yet. What has been found, is that below 240° the upper part of the isotherm of solubility runs toward the right, which points to an increase of solubility of anthraquinone in the fluid phase with increase of pressure [1]), whereas above 250° a reversed course was found. Between 240° and 250° a change of direction seems to have taken place, and in this range it might be possible to ascertain the course foretold by VAN DER WAALS. As however the small range of temperature 240°—250° corresponds with a great difference in concentration, the point when the change of direction takes place is not easily ascertained.

The results obtained at temperatures between 203° and 247° are represented in fig. 6. Here the isotherms of solubility for the fluid phases at 210°, 220°, 230° and 240° are drawn. All these isotherms show, as predicted by VAN DER WAALS [2]), the phenomenon of retrograde solidification, and the nearer we get to point q, in other words the nearer to 247°, the larger the region of this retrograde solidification.

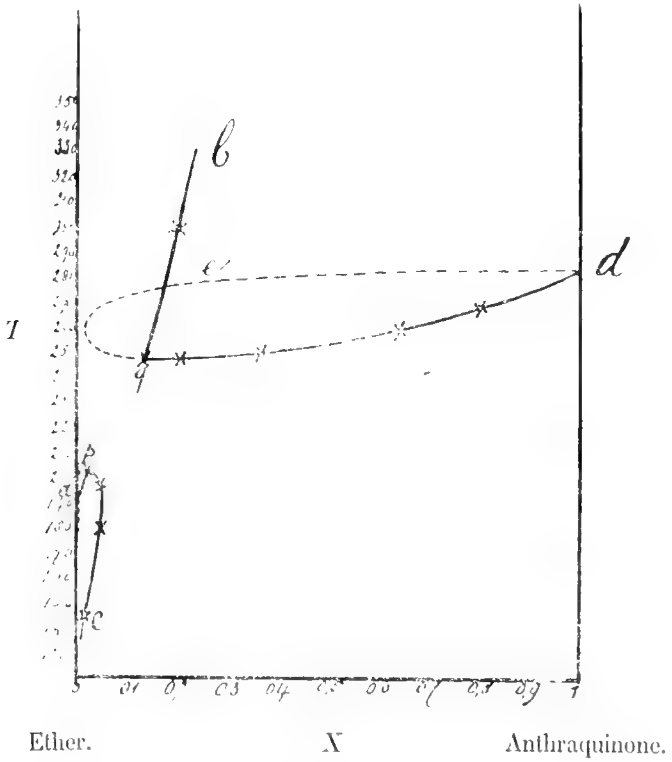

Fig. 7.

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[1]) This influence of pressure has been examined up to more than 100 atmospheres.
[2]) loc. cit.

This isotherm of 210° has the steepest course; with increase of temperature the course becomes at first less steep, but at 240° a steeper course seems to reappear, which is probably connected with the change of direction which appears above 240°.

The projection of the solubility curve and the plaitpoint curve on the t-x-plane is represented in fig. 7, where the dotted curves represent the vapourbranches. The projections of the two parts ap and qb of the plaitpointcurve are almost straight lines. If we examine the course of the line qb, in order to see at what temperature this line will meet the line for pure anthraquinone, we shall find ± 800°.

Lastly we find in fig. 8 the course of the molecular volumina of

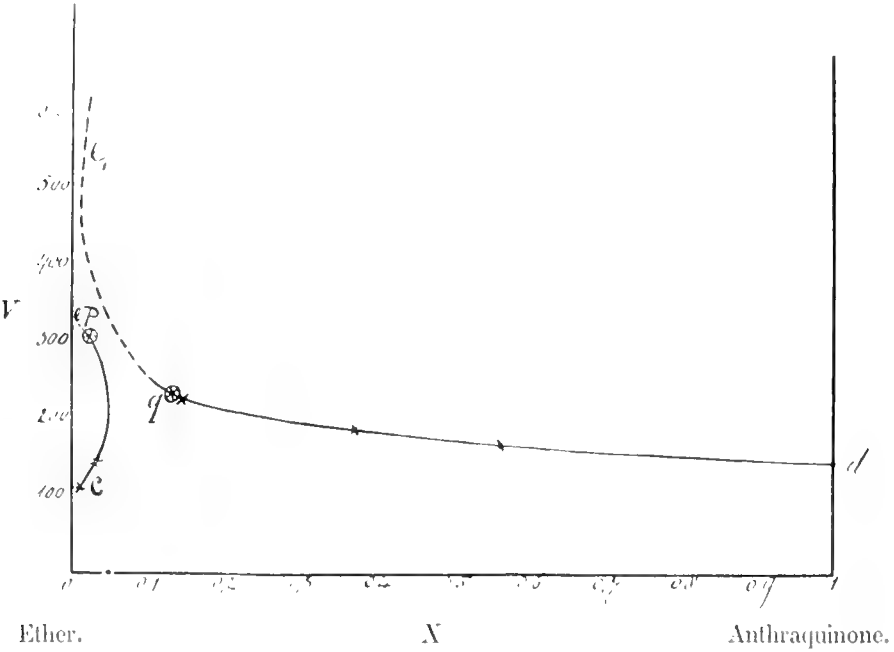

Fig. 8.

the saturated solutions. Here too we have two continuous branches, each of them consisting of a liquid and a vapour branch. dq and cp are the liquid branches and qe_1 and pe are the vapour branches. p and q denote the molecular volumina of the two critical saturated solutions. The dotted vapourcurve qe runs on to the concentration 0.015, so that from this figure also directly follows that at higher temperatures and larger volumina three phases may again be obtained with the concentration with which point p may be realized. Here too the curves cp and qe indicate clearly the phenomenon of retrograde solubility.

So the investigation described here has furnished proof positive of the general points of view which were prominent in the qualitative investigation, and of which the theory of VAN DER WAALS could give a closer description.

The peculiarity of the examined system, which lies in the fact that the vapour pressure of the one substance (ether) far exceeds that of the other (anthraquinone), caused some wholly unexpected phenomena, and made it on the other hand possible to realize retrograde solidification on a much larger scale than had been thought possible till now.

Laboratory for Anorganic Chemistry of the University.
Amsterdam, June 1904.

Chemistry. — "*The preparation of silicon and its chloride.*" By Prof. A. F. HOLLEMAN.

(Communicated in the meeting of June 24, 1904).

The numerous proposals which have been made for the preparation of the element silicon in both the amorphous and crystallised form prove that a simple method has not as yet been found. W. HEMPEL and VON HAASY [1]) have published in 1899 an additional process consisting in the decomposition of silicon fluoride with sodium. They melt this metal in small portions at a time in an iron apparatus and then pass over the mass a current of silicon fluoride, which is then very readily decomposed. The brown porous mass, which has been brought to a faint red heat is allowed to cool for two or three hours in the current of silicon fluoride. An attempt to convert it into silicon chloride by heating the mass without previous purification in a current of chlorine was unsuccessful. It was impossible to remove the $NaFl$ and Na_2SiFl_6 by boiling with water; so in order to obtain pure silicon it was necessary to fuse the mass with sodium and aluminium. The latter dissolves the silicon which is then left insoluble on treating the regulus with dilute hydrochloric acid.

Mr. H. J. SLIJPER who has repeated these experiments in my laboratory showed (1) that by a small modification of the process the crude product may be purified to such an extent by boiling with water that it may be used for preparing silicon chloride; (2) the reason why the crude product on being treated with chlorine does not yield silicon chloride.

1. It is known that sodium fluoride readily absorbs $SiFl_4$ and

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[1]) Zeitschr. f. anorg. Ch. **23**, 32.

passes into $Na_2\,Si\,Fl_6$. By allowing their apparatus to cool for 2 to 3 hours whilst transmitting this gas HEMPEL and VON HAASY practically converted the sodium fluoride, which had been formed according to the equation: $4\,Na + Si\,Fl_4 = 4\,Na\,Fl + Si$, into sodium fluosilicate, which is soluble in water with great difficulty. If, however the action of $Si\,Fl_4$ is stopped as soon as all the sodium has been introduced into the apparatus, it is easy to almost completely avoid the formation of $Na_2\,Si\,Fl_6$. 100 grams of sodium yielded to Mr. SLIJPER 219 grams of crude material ($4\,Na\,Fl + Si$) instead of 213.6 the quantity calculated; 55 grams of the Na gave 119 grams, theory 117.2, and in some further experiments the theoretical quantity was but little exceeded. By washing and boiling with water and with dilute hydrochloric acid the 119 grams were reduced to 20 grams whilst the product may contain 16.7 grams of silicon. The product so obtained is not, however, pure amorphous silicon, only about 40 per cent is volatilised in a current of chlorine and may be condensed as silicon chloride, and a residue is obtained, which is only to a slight extent soluble in water and principally consists of silicon dioxide.

This must have been formed during the washing; for if the crude product is heated in a current of chlorine there remains besides sodium chloride only a very small quantity of insoluble residue. As the crude product when immersed in water causes a visible evolution of gas with the odour of $Si\,H_4$ it is probable that the $Si\,O_2$ has been formed by decomposition of $Si\,H_4$ which may have been produced by the action of water on some sodium silicide. MOISSAN has recently shown that on treating silicon with boiling water the dioxide of that element is formed.

2. In accordance with HEMPEL and VON HAASY, Mr. SLIJPER found that on heating the crude product in a current of chlorine not a trace of silicon chloride is obtained. As the said product consists mainly of $4\,Na\,Fl + Si$, it was surmised that this must be attributed to the fact that the primary formed silicon chloride reacts with sodium fluoride according to the equation

$$Si\,Cl_4 + 4\,Na\,Fl = Si\,Fl_4 + 4\,Na\,Cl$$

It appeared indeed that on heating sodium fluoride or sodium fluosilicate in the vapour of silicon chloride the said decomposition takes place. If, therefore, chlorine is passed over a mixture of Si and Na Fl as is present in the crude product the reaction must proceed in this manner:

$$Si + 4\,Cl + 4\,Na\,Fl = Si\,Fl_4 + 4\,Na\,Cl.$$

That such is practically the case was shown by the fact that the gas evolved consisted of $Si\,Fl_4$ and that the substance left behind in the boat was found to be almost pure sodium chloride.

A better method of preparing amorphous silicon seemed to be the decomposition of silicon chloride by sodium. When boiled in benzene-solution with sodium or potassium no action took place. A reaction, however, took place on heating sodium in the vapour of silicon chloride, but it became very violent; the brown powder obtained could certainly be readily freed from sodium chloride by means of water, but on heating in a current of chlorine a large amount of $Si\,O_2$ (about 30 %) was left behind showing that even this process does not lead to pure amorphous silicon.

Much more simple is the preparation of *crystallised* silicon according to the method recently published by R. A. Kühne (Chem. Centr. 1904, I. 64) if we introduce a slight modification. A mixture of 200 grams of aluminium shavings or powder, 250 grams of sulphur and 180 grams of fine sand is put into a Hessian crucible placed in a bucket with sand. Upon the mixture is sprinkled a thin layer of magnesium powder and this is ignited by means of a Goldschmidt cartridge. The mass burns with a beautiful light and the contents of the crucible become white hot. When cold, the mass is treated with dilute hydrochloric acid, which dissolves the aluminium sulphide and leaves the silicon in a beautifully crystallised state. The yield amounts to about 30 grams. On heating in a current of chlorine $Si\,Cl_4$ is very readily formed, only 3% remaining as non-volatile products. It is a material eminently suited for the preparation of $Si\,Cl_4$, but Mr. Slijper did not succeed in converting it into silicon sulphide by heating with sulphur.

Groningen, Lab. Univers. March 1904.

Crystallography. — "*On the preservation of the crystallographical symmetry in the substitution of position isomeric derivatives of the benzene series*". By Dr. F. M. Jaeger. (Communicated by Prof. A. P. N. Franchimont).

(Communicated in the meeting of June 24, 1904).

Some time ago when engaged in a research as to the connection between molecular and crystallographical symmetry of position-isomeric benzene derivatives¹), I demonstrated, that of the six possible *tribromo-*

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¹) Jaeger, Crystallographic and Molecular Symmetry of position-isomeric Benzene-derivatives. Dissertation, Leiden 1903. (Dutch).

toluenes, the 1-2-4-6 and the 1-2-3-5 derivatives exhibit an isomorphy bordering on identity. I then endeavoured to explain the similar molecular structure of these two substances by referring to the analogy of the (CH_3)-group and *Br*-atom in the positions 1 and 2, particularly in a *spacial* respect. The small differences in crystalline form, melting point etc., are then caused by the difference which of course exists between CH_3 and *Br*.

We may now inquire how matters will be in both molecules as regards the substitution of the two remaining *H*-atoms of the core for instance. It is interesting to notice that as regards the substitution by (NO_2) the two *H*-atoms in each of the two isomers are quite *equivalent* and — what is still more striking — that this substitution does not perceptibly alter the molecular symmetry of the two molecules, so that *the crystallographical relation of the initial products is preserved in the substitution derivatives.*

If we nitrate the 1-2-4-6-tribromotoluene with nitric acid of 1,52 sp. gr. a dinitro-product is obtained, as shown by NEVILE and WINTHER [1]).

WROBLEWSKY [2]) had previously obtained a mono-nitro-derivative which differs in its melting point but little from the dinitro-product.

But notwithstanding many efforts, I have never succeeded in obtaining a mononitro-compound not even as a bye-product, when using fuming nitric acid.

The mere formula of 1-2-3-5-*tribromotoluene* does not at once raise a suspicion that a dinitro-product will be formed in this case. If, however, the analogy of (CH_3) in the position 1 and *Br* in the position 2 is really so great that the difference amounts almost to nothing, we may surmise that the 1-2-3-5-*tribromotoluene* will behave on nitration also nearly quite analogously to the other isomer. The experiment shows that in this case also not a trace of any mononitro-derivative is obtained; we obtain exclusively a *dinitro*-product, which is in all respects quite analogous with the above named *dinitro*-derivative.

After nitration by red fuming nitric acid (sp. gr. 1,516 at 16°) in the cold, separation by adding an excess of water, agitation with benzene and ether and recrystallisation from *benzene,* in which both isomers are very soluble, the two substances are at once obtained pure in large colorless or pale sherry-colored crystals, whose bromine-amount corresponds with that of the dinitro-derivative.

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[1]) NEVILE and WINTHER, Journ. Chem. Soc. Vol. **37**. 438; Berl. Ber. **13**. 974.

[2]) WROBLEWSKY, Ann. d. Chemie **168**. 147.

The 1-2-4-6-*tribromo-3-5-dinitro-toluene* melts at 220°; the 1-2-3-5-*tribromo-4-6-dinitro-toluene* at 210°.

Like the two *tribromotoluenes* themselves, these substances are again quite *isomorphous* and owing to peculiar twin-formation, they so resemble each other, that at first sight we cannot distinguish the two kinds of crystals from each other.

a. 1-2-4-6-*tribromo-3-5-dinitro-toluene.*

$C_6\,\underset{(6)}{Br}\,.\,\underset{(4)}{Br}\,.\,\underset{(2)}{Br}\,.\,\underset{(5)}{(NO_2)}\,.\,\underset{(3)}{(NO_2)}\,.\,\underset{(1)}{(CH_3)}$; melting point 220°.

From benzene this substance crystallises in large apparently quadratic, colorless crystals which are nearly all *twins*, — which may be recognised at once by a very fine diagonal on two of the broadest planes. We also may obtain needle shaped or very elongated thick pillar shaped crystals. The planes are generally angular and give plural

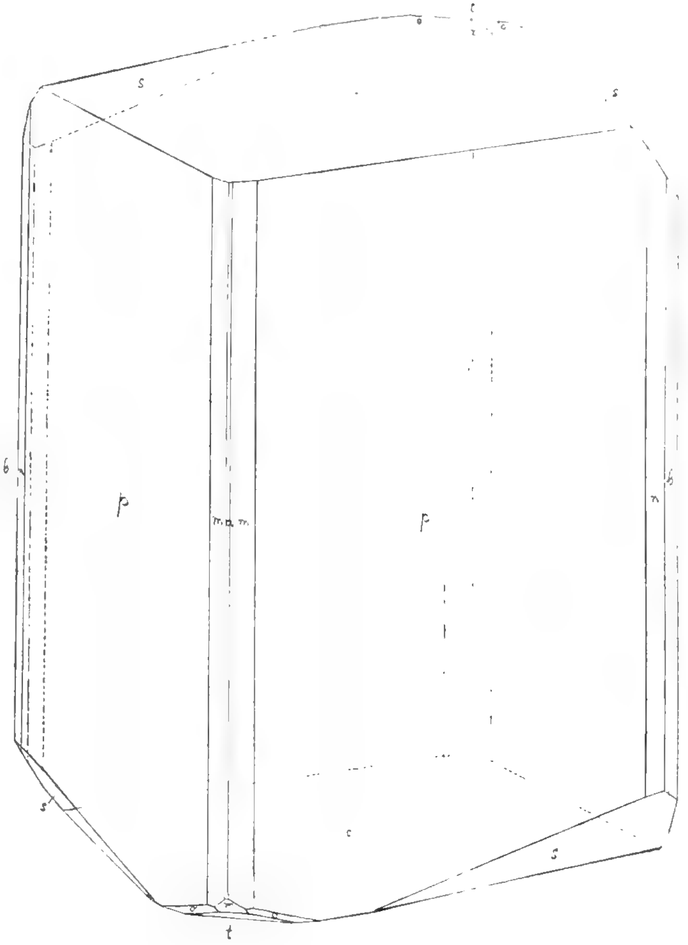


Fig. 1.

reflexes. The crystals are also frequently bordered by curved planes and by vicinal forms in the prism-zone. These circumstances render an accurate investigation very difficult; occasionally, however, I obtained better formed crystals, which gave very sharp reflexes and served for the following accurate measurements.

They are *monoclino-prismatic* with the axial relation:

$$a : b : c = 0.5217 : 1 : 0.7803$$
$$\beta = 85^\circ 12'.$$

Forms observed are: $m = \{110\}$ and $p = \{120\}$, broad and lustrous; $a = \{100\}$ and $n = \{130\}$, very narrow; a is generally hazy; $b = \{010\}$, a little broader, but is generally absent; $c = \{001\}$, large and very lustrous; $r = \{\bar{1}01\}$, well developed and lustrous; $t = \{\bar{1}04\}$, narrower and is often absent; $o = \{\bar{1}12\}$, generally small and dull, occasionally a little broader and better reflecting; $s = \{\bar{1}32\}$, large and lustrous, but generally there are only two parallel planes present.

Combinations of *all* the forms rarely occur. Generally such with m, p, c, r; m, p, b, c, r, t, s and o; m, p, a, b and c, etc. The more typical crystals are shown in figures 1-3.

Fig. 2.

Fig. 3.

In the properly formed crystals, the angular values are very constant; the reflexes are as sharp as possible. The substance has a decided tendency to twin-formation; in this, one form {102} is a twin-plane with a twin-axis normally standing on it. On the plane of *p* may be often observed a delicate line parallel *p* : *c*; in this vertical zone the most important geometrical anomalies are found.

The following are the calculated and observed angular values.

	Observed:	*Calculated:*
$^*m : m = (110) : (1\bar{1}0) =$	54° 56½'	—
$m : a = (110) : (100) =$	27 28¼	27° 28¼'
$m : r = (110) : (\bar{1}01) =$	43 20	43 13
$^*c : r = (001) : (\bar{1}01) =$	59 39	—
$r : a = (\bar{1}01) : (\bar{1}00) =$	35 20	35 33
$c : a = (001) : (100) =$	85 15	85 12
$^*c : m = (001) : (110) =$	85 44½	—
$c : p = (001) : (120) =$	86 40	86 36
$c : n = (001) : (130) =$	87 30	87 25
$c : b = (001) : (010) =$	89 58	90 0
$p : n = (120) : (130) =$	11 12	11 13
$m : p = (110) : (120) =$	18 35	18 39
$p : r = (\bar{1}20) : (\bar{1}01) =$	55 25	55 29
$c : t = (001) : (\bar{1}04) =$	21 12	21 2
$c : o = (001) : (\bar{1}12) =$	41 52½	41 52
$c : s = (001) : (\bar{1}32) =$	55 49	55 54
$m : s = (\bar{1}\bar{1}0) : (\bar{1}32) =$	47 36½	47 35½

A distinct cleavability was not observed.

On *c*, *r*, and *a* the position of the optical elasticity-axis is orientated perpendicularly to the direction of the orthodiagonal; the symmetrical angle of extinction on *m* amounts to 23° with regard to the vertical axis. An axial image could not be observed.

The sp. gr. of the crystals is 2,456 at 15°; the equivalent volume is, therefore: 170,6.

The topical axes are:

$$: \psi : \omega = 3{,}9087 : 7{,}4921 : 5{,}8461.$$

b. 1-2-3-5-*tribromo*-4-6-*dinitrotoluene.*

$C_6 . \underset{(5)}{Br} . \underset{(3)}{Br} . \underset{(2)}{Br} . \underset{(6)}{(NO_2)} . \underset{(4)}{(NO_2)} . \underset{(1)}{(CH_3)}$; melting point: 210° C.

Fig. 4.

This compound crystallises from benzene in very large, colorless, isometrical-developed crystals, which are always twins and of exactly the same form as that of the previous compound with which this substance is isomorphous.

The geometrical anomalies caused by the curvature or angulation of the planes are more considerable with this derivative, than with the previous one; the development of the crystals is less perfect and they also exhibit a smaller number of combining forms. From ether and acetone we obtain besides twin-crystals also single needles which can be measured more accurately.

The symmetry is *monoclino-prismatic*; the axial relation is:

$$a : b : c = 0{,}5392 : 1 : 0{,}7574.$$

$$\beta = 86°28'.$$

Forms observed are: $m = \{110\}$ and $p = \{120\}$, broad and lustrous; $c = \{001\}$, very lustrous and well developed; $r = \{101\}$, smaller but properly measurable; $b = \{010\}$, narrow and often absent. Angular values:

	Observed:	*Calculated:*
$^*p : p = (120) : (1\bar{2}0) =$	94°13′	—
$^*p : c = (120) : (001) =$	87 35½	—
$^*p : r = (\bar{1}20) : (\bar{1}01) =$	56 53½	—
$p : m = (120) : (110) =$	18 50	18°49′
$m : m = (110) : (1\bar{1}0) =$	56 54	56 36
$m : r = (\bar{1}10) : (\bar{1}01) =$	44 57	45 2
$c : r = (001) : (\bar{1}01) =$	57 6	56 55
$m : c = (110) : (001) =$	86 59	86 52½

A distinct cleavability was not observed.

This substance also has a decided tendency to twin-formation towards {102} as twin-plane; single crystals are rare. Owing to this peculiarity, the external resemblance of this isomer with the former is increased in a high degree. It should be observed that these twins and also those of the former substance often also show {010} and symmetrical vertical lines on the prism p, with regard to the twin-section. The sp. gr. of a perfectly homogenous fragment of a crystal was found to be 2,465 at 15°; the equivalent-volume is therefore 169,98 and the topical axes become:

$$\chi : \psi : \omega = 4,0286 : 7,4713 : 5,6580.$$

I have tried, of course, to gain some insight into the progressive course of the binary meltingpoint-line of these two isomorphous derivatives, although the want of sufficient supply of material proved a great obstacle.

This investigation had, however, soon to be abandoned because the mixtures of the two substances assuming a much darker colour are decomposed at their melting point with violent evolution of gas; the temperatures are situated between 210° and 220°. The more the mixture contains of the compound with the higher melting point, the more readily the decomposition takes place, and therefore the only mixtures of which I could sharply determine the melting point, were those containing from 0% to $44\frac{1}{2}\%$ of the derivative with the higher melting point; this melted at 214°, the others between 210° and 214°. I, therefore, suspect that we have here a continuous melting curve; whether an absolute maximum occurs in the meltingpoint-line, such as happens with the two non-nitrated initial products, could not be decided. The mutual behaviour of these two isomorphous derivatives probably corresponds entirely with that of the two tribromotoluenes.

From mixed solutions of the two nitro-derivatives in benzene we obtain large curve-planed and badly formed mixed crystals which exhibit the same typical twin formation as the two components, but which generally possess only {110}, {120} and {001}. They are unsuitable for measuring purposes.

c. 1-3-4-5-*tribromo*-2-6-*dinitro-toluene*.

$$C_6 \,.\, \underset{(5)}{Br} \,.\, \underset{(4)}{Br} \,.\, \underset{(3)}{Br} \,.\, \underset{(6)}{(NO_2)} \,.\, \underset{(2)}{(NO_2)} \,.\, \underset{(1)}{(CH_3)} \quad ; \quad \text{melting point: } 216^\circ \text{ C.}$$

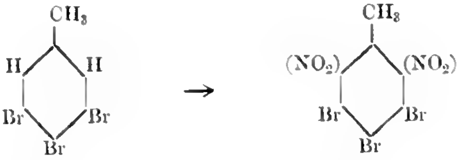
When recrystallised from benzene, in which this compound, which was prepared in the same manner as the preceding ones, is less soluble at the ordinary temperature than the two other isomers, the substance is obtained in thick, quadratically-bounded, crystalline plates, which at first sight appear tetragonal, an occurrence to be expected, when taking into account the slight morphotropical force of the (NO_2)-group, and the previously found tetragonal symmetry of the corresponding tribromotoluene.

The investigation, however, soon showed that the symmetry is *not* tetragonal, and I first thought I had before me a monoclinic compound, — certainly with plenty of geometrical anomalies, — but still reasonably conforming to all the requirements of the monoclinic symmetry. This would also have agreed with everything that I have formerly communicated as to the formrelation of tetragonal and monoclinic crystals.

I hesitated a long time before I could give up this last idea, particularly because the measurement of a very large number of crystals taught me, that in this case just as with the two former compounds, the peculiar softness of the substance causes geometrical disturbances of the crystals during the crystallisation, and because the axial elements of this compound when assuming the monoclinic symmetry exhibited an analogy bordering on isomorphy with those of the two investigated isomers.

The deviations of the angles from the values required for the monoclinic symmetry appeared however, to be so systematical, that there could be no longer a doubt as to the *triclinic* symmetry of these remarkable crystals, even though they were found to represent a *monoclinic limit-form*.

Afterwards, I have also been able to find exceedingly small deviations in the optical orientation of the directions of extinction which again corroborated my belief, that triclinic crystals of a pseudo-monoclinic form are present here. This makes us feel convinced that even if the morphotropical force of the *single* (NO_2) group is generally feeble *two* such groups may cause a comparatively *strong* deformation of the crystal-molecule; and also that the spacial structure of the benzene derivatives is not fully explained by the usual formulation of these substances. For the ordinary schematical manner of writing alone does not explain why a compound of the type 1 should have another symmetry than one of the type II, — even though, owing to the occurrence of the pseudo-monoclinic *limit-form,* the close relation of the two kinds of symmetry is in each case very plainly perceptible:



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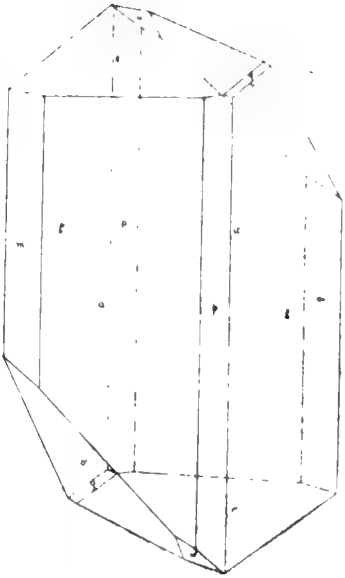

Fig. 5.

The crystals of the 1-3-4-5-*tribromo-2-6-dinitro-toluene* are represented in Fig. 5 in the form in which they crystallise from a mixture of carbon disulphide and benzene. The quadratical looking plate-like crystals, deposited from benzene only, exhibit nearly the same forms; in their case, however, the form *a* is very predominating; then follows *c*, whilst the other forms are narrow and little developed; moreover the form *q* is always and *o* often absent. I also occasionally obtained from benzene, thick prismatic crystals with *a*, *b* and *c* and even *o*.

Triclino-pinacoïdal. The axial relation is:

$$a : b : c = 0{,}5322 : 1 : 0{,}9581$$

$$\alpha = 88^\circ 21'. \qquad A = 88^\circ 26'.$$

$$\beta = 95^\circ\ 4'. \qquad B = 95^\circ\ 2'.$$

$$\gamma = 90^\circ 58'. \qquad C = 90^\circ 50'.$$

Forms observed are: $a = \{100\}$, and $b = \{010\}$ equally strongly developed, *a* generally more lustrous than *b*; $c = \{001\}$ very lustrous; $o = \{\bar{1}22\}$ well developed and lustrous; $\omega = \{\bar{1}12\}$ smaller than *o* but very lustrous; $q = \{012\}$, small and less conspicuous; $m = \{\bar{1}10\}$, narrow, but broader than $p = \{110\}$, which form is often present with a single plane; $s' = \{\bar{3}44\}$ very narrow and not properly measurable [1]).

	Observed:	*Calculated:*
$^*a : b = (100) : (010) =$	89° 10′	—
$^*a : c = (100) : (001) =$	84 58	—
$^*b : c = (010) : (001) =$	91 34	—
$^*o : a = (\bar{1}22) : (\bar{1}00) =$	59 35	—
$^*o : c = (\bar{1}22) : (001) =$	55 25½	—
$a : p = (100) : (110) =$	27 32	27° 45½′
$a : m = (100) : (1\bar{1}0) =$	28 7	28 7

---

[1]) If, in view of the symbol of s' we rather choose $o = \{\bar{2}43\}$, $\omega = \{2\bar{2}3\}$ $s' = \{\bar{3}43\}$, whilst retaining the other symbols, we get $a : b : c = 0{,}5322 : 1 : 0{,}7186$, which agrees better with the other two isomers.

	Observed.	*Calculated.*
$b : o = (010) : (\bar{1}22) =$	54 33	54 34
$b : m = (0\bar{1}0) : (1\bar{1}0) =$	62 40	62 51
$b : p = (010) : (110) =$	61 33	61 $24^1/_2$
$c : q = (001) : (012) =$	26 5	25 50
$b : q = (010) : (012) =$	65 39	65 49
$o : m = (\bar{1}22) : (\bar{1}10) =$	43 21	43 39
$o : s' = (\bar{1}22) : (\bar{3}44) =$	11 52 (circa)	12 8
$\omega : b = (\bar{1}12) : (0\bar{1}0) =$	108 $49^1/_2$	108 47
$\omega : o = (\bar{1}12) : (\bar{1}22) =$	16 51	16 39
$\omega : c = (\bar{1}12) : (001) =$	48 $1^1/_2$	48 $0^1/_2$
$\omega : m = (\bar{1}12) ; (\bar{1}10) =$	47 30	47 $13^1/_2$
$a : \omega = (\bar{1}00) : (\bar{1}12) =$	53 35	53 $35^1/_2$
$a : q = (100) : (012) =$	85 37	85 55
$\omega : q = (\bar{1}12) : (012) =$	40 35	40 $30^1/_2$
$q : o = (012) : (\bar{1}22) =$	38 56	38 54
$m : c = (1\bar{1}0) : (001) =$	84 47	84 $45^3/_4$
$p : c = (110) : (001) =$	86 22	86 19

The position of the optical elasticity-axis on *a* was determined by means of a very thin lamelle, with the aid of a BERTRAND Quartz-Ocular, and found to be 4° with the side (100) : (010); on *b* the angle amounts to more than 45° with respect to the side (110) : (010). An axial image could not be observed.

By means of a THOULET's solution, the sp. gr. of the crystals was found to be 2,459 at 17°; the equivalent volume is, therefore, 170,39, and the topical axial relation becomes:

$$\chi : \psi : \omega = 3{,}6982 : 6{,}9496 : 6{,}6584.$$

The close relation of this triclinic derivative with the two monoclinic isomers is therefore obvious. That there is still an essential difference in the nature of the molecular orientation, which in these three cases determines the crystalline structure, is also shown by the fact, that the first two derivatives exhibit a decided tendency to a similar and typical twin-formation, which is utterly absent in the latter isomer.

I will give lateron some information as to the other nitro-products of the isomeric tribromotoluenes, as these have not as yet been obtainable in measurable crystals.

Mathematics. — Prof. KLUYVER presents a paper: "*Evaluation of two definite integrals.*"

Supposing x to be real the integrals

$$f(x, m) = \int_0^\infty \frac{\cos xt}{(1+t^2)^m}\, dt \quad \text{and} \quad \varphi(x, m) = \int_0^\infty \frac{\sin xt}{(1+t^2)^m}\, dt$$

will have a definite meaning, if only the real part of the parameter m be positive. In what follows we will show how to expand these integrals into rapidly converging power series.

The first of them, the integral $f(x, m)$, is a particular solution of the linear equation

$$x \frac{d^2 y}{dx^2} - 2(m-1) \frac{dy}{dx} - xy = 0,$$

the primitive of which, involving two arbitrary constants A and B, may be written in the form

$$y = A\, L(x, m) + B x^{2m-1} M(x, m),$$

where

$$L(x, m) = \sum_{h=0}^{h=\infty} \frac{\left(\frac{x}{2}\right)^{2h}}{h!\, \Gamma(-m + \frac{3}{2} + h)},$$

$$M(x, m) = \sum_{h=0}^{h=\infty} \frac{\left(\frac{x}{2}\right)^{2h}}{h!\, \Gamma(m + \frac{1}{2} + h)},$$

and the constants A and B must now be determined so that y represents the function $f(x, m)$. To find A, we suppose $m > \frac{1}{2}$ and put x equal to zero. In that case we have

$$f(0, m) = \int_0^\infty \frac{dt}{(1+t^2)^m} = \frac{\Gamma(\frac{1}{2})\, \Gamma(m-\frac{1}{2})}{2\, \Gamma(m)} = A\, L(0, m) = \frac{A}{\Gamma(-m + \frac{3}{2})}$$

and hence

$$A = -\frac{\pi}{2 \cos \pi m} \cdot \frac{\Gamma(\frac{1}{2})}{\Gamma(m)}.$$

For the deduction of the constant B it is convenient to consider first the function $f(x, m)$ in another form. Let the real part of m still be positive, then we have

$$\frac{\Gamma(m)}{(1+t^2)^m}=\int\limits_0^{\infty} e^{-u(1+t^2)}\,u^{m-1}\,du$$

and hence

$$\Gamma(m)\,f(x,m)=\int\limits_0^{\infty} e^{-u}\,u^{m-1}\,du\int\limits_0^{\infty} e^{-ut^2}\cos xt\,dt=\tfrac{1}{2}\sqrt{\pi}\int\limits_0^{\infty} e^{-u-\frac{x^2}{4u}}\,u^{m-\frac{3}{2}}\,du.$$

From the latter integral a simple functional relation is derivable. Changing the variable u into $\frac{x^2}{4v}$ we may write

$$\Gamma(m)\,f(x,m)=\frac{1}{2}\sqrt{\pi}\left(\frac{x}{2}\right)^{2m-1}\int\limits_0^{\infty} e^{-v-\frac{x^2}{4v}}\,v^{-m-\frac{1}{2}}\,dv=$$

$$=\left(\frac{x}{2}\right)^{2m-1}\Gamma(1-m)\,f(x,1-m)$$

and so it follows that the function

$$\frac{\Gamma(m)\,f(x,m)}{\left(\frac{x}{2}\right)^m}=-\frac{\pi}{2\cos\pi m}\,\Gamma\left(\frac{1}{2}\right)\left(\frac{x}{2}\right)^{-m}L(x,m)+$$

$$+\,2^{2m-1}\,B\,\Gamma(m)\left(\frac{x}{2}\right)^{m-1}M(x,m)$$

remains unaltered, if m is replaced by $1-m$.

Now obviously the series L and M are connected by the relation

$$L(x,1-m)=M(x,m),$$

hence we must have

$$2^{2m-1}\,B\,\Gamma(m)=+\frac{\pi}{2\cos\pi m}\,\Gamma\left(\frac{1}{2}\right),$$

$$B=\frac{\pi}{2\cos\pi m}\cdot\frac{\Gamma(\frac{1}{2})}{\Gamma(m)}\left(\frac{1}{2}\right)^{2m-1},$$

and therefore

$$f(x,m)=\int\limits_0^{\infty}\frac{\cos xt}{(1+t^2)^m}\,dt=\frac{\pi}{2\cos\pi m}\cdot\frac{\Gamma(\frac{1}{2})}{\Gamma(m)}\left\{-L(x,m)+\left(\frac{x}{2}\right)^{2m-1}M(x,m)\right\}.$$

Now it will be observed, that the series $L(x,m)$ and $M(x,m)$ converge for all values of x and m, and so we must conclude, that the function $f(x,m)$ exists over the whole x-plane, that its only singularities are $x=0$ and $x=\infty$, and that therefore the integral, we started with, represents the function in a very incomplete manner.

Numerical evaluation of the integral for not too large values of x offers no difficulties, as the series $L(x,m)$ and $M(x,m)$ converge rapidly. Because of the equation

$$\Gamma(m) f(x, m) = \frac{1}{2} \sqrt{\pi} \int_0^{\infty} e^{-u-\frac{x^2}{4u}} u^{m-\frac{3}{2}} du$$

the result will always be a positive number and the integral will not vanish for any real value of x.

A few further remarks may be made. Firstly we may state, that $f(x, m)$ is intimately connected with BESSEL's function $J_n(x)$. In fact, by means of the usual expansion of $J_n(x)$ we may verify the relation

$$f(x, m) = -\frac{\pi}{2\cos\pi m} \cdot \frac{\Gamma(\frac{1}{2})}{\Gamma(m)} \left(\frac{x}{2}\right)^{m-\frac{1}{2}} \left\{ e^{-\frac{\pi i}{2}\left(m-\frac{1}{2}\right)} J_{-m+\frac{1}{2}}\left(xe^{-\frac{\pi i}{2}}\right) - \right.$$

$$\left. - e^{+\frac{\pi i}{2}\left(m-\frac{1}{2}\right)} J_{m-\frac{1}{2}}\left(xe^{-\frac{\pi i}{2}}\right) \right\}.$$

From this we infer, that for positive integer values of m the origin $x = 0$ ceases to be a singular point, and that $f(x, m)$ can be expressed in finite terms. We shall find by actual substitution of the finite expressions for $J_{-m+\frac{1}{2}}\left(xe^{-\frac{\pi i}{2}}\right)$ and $J_{m-\frac{1}{2}}\left(xe^{-\frac{\pi i}{2}}\right)$

$$f(x, m) = \frac{\pi}{2} \cdot \frac{e^{-x}}{(m-1)!} \left(\frac{x}{2}\right)^{m-1} \sum_{h=0}^{h=m-1} \frac{(m-1+h)!}{h!(m-1-h)!} \cdot \left(\frac{1}{2x}\right)^h.$$

However this result may be obtained in a simpler way as follows. It can be shewn, that $f(x, m)$ obeys the relation

$$D^h_{\alpha=1} \left\{ \alpha^{-m+\frac{1}{2}} f(x\sqrt{\alpha}, m) \right\} = \frac{(-1)^h \Gamma(m+h)}{\Gamma(m)} f(x, m+h),$$

and since we have

$$f(x\sqrt{\alpha}, 1) = \int^{\infty} \frac{\cos xt\sqrt{\alpha}}{1+t^2} dt = \frac{\pi}{2} e^{-x\sqrt{\alpha}},$$

we get for all positive values of m

$$f(x, m) = \frac{\pi}{2} \cdot \frac{(-1)^{m-1}}{(m-1)!} D^{m-1}_{\alpha=1} \left\{ \frac{e^{-x\sqrt{\alpha}}}{\sqrt{\alpha}} \right\}.$$

a result that can be identified with that obtained before.

The singularity in the origin $x = 0$ becomes logarithmic, when $2m$ is an odd integer $2k + 1$. The expression of $f(a, m)$ is in this case somewhat intricate. By repeated differentiations it is derived from $f\left(x, \frac{1}{2}\right)$, for we have

$$D^k_{\gamma=1}\, f\left(x\sqrt{\alpha}, \frac{1}{2}\right) = \frac{(-1^k\, \Gamma(k+\frac{1}{2})}{\Gamma(\frac{1}{2})}\, f\left(x, k+\frac{1}{2}\right).$$

To evaluate $f\left(x, \frac{1}{2}\right)$, we put $m = \frac{1}{2} + \delta$ in the general expression for $f(x, m)$, and make δ tend to zero. In this way we get

$$f\left(x, \frac{1}{2}\right) = \operatorname*{Lim}_{\delta=0} \frac{\pi}{2 \sin \pi\delta} \left\{ \sum_{h=0}^{h=\infty} \frac{\left(\frac{x}{2}\right)^{2h}}{h!\, \Gamma(h+1-\delta)} - \left(\frac{x}{2}\right)^{2\delta} \sum_{h=0}^{h=\infty} \frac{\left(\frac{x}{2}\right)^{2h}}{h!\, \Gamma(h+1+\delta)} \right\},$$

$$f\left(x, \frac{1}{2}\right) = \int_0^\infty \frac{\cos xt}{\sqrt{1+t^2}}\, dt = \sum_{h=0}^{h=\infty} \frac{\left(\frac{x}{2}\right)^{2h}}{(h!)^2} \left(\frac{1}{1} + \frac{1}{2} + \frac{1}{3} + \ldots \frac{1}{h} - C - \log\frac{x}{2}\right).$$

We shall now pass on to consider the second integral

$$\varphi\,(x, m = \int_0^\infty \frac{\sin xt}{(1+t^2)^m}\, dt\,,$$

and it will appear that its character is quite similar to that of the first.

Again we transform the integral by the aid of the identity

$$\frac{\Gamma(m)}{(1+t^2)^m} = \int_0^\infty e^{-u(1+t^2)}\, u^{m-1}\, du$$

and obtain

$$\Gamma(m)\, \varphi\,(x, m) = \int_0^\infty e^{-u}\, u^{m-1}\, du \int_0^\infty e^{-ut^2} \sin xt\, dt.$$

A further transformation gives

$$\int_0^\infty e^{-ut^2} \sin xt\, dt = \frac{x}{2u} \int_0^1 e^{-\frac{x^2}{4u}(1-t^2)}\, dt = \frac{x}{4u} \int_0^1 e^{-\frac{x^2 w}{4u}} (1-w)^{-\frac{1}{2}}\, dw.$$

and therefore

$$\Gamma(m)\, \varphi\,(x, m) = \frac{x}{4} \int_0^1 (1-w)^{-\frac{1}{2}}\, dw \int_0^\infty e^{-u-\frac{x^2 w}{4u}}\, u^{m-2}\, du.$$

Comparing this equation with the equality obtained before

$$\Gamma(m)f(x,m)=\frac{1}{2}\sqrt{\pi}\int_0^\infty e^{-u-\frac{x^2}{4u}}u^{m-\frac{3}{2}}\,du,$$

it follows, that we may write

$$\Gamma(m)\,\varphi(x,m)=\frac{x}{2\sqrt{\pi}}\int_0^1(1-w)^{-\frac{1}{2}}\,dw\,\Gamma(m-\tfrac{1}{2})f\left(x\sqrt{w},m-\frac{1}{2}\right)\ ^{1)}.$$

We now expand $\Gamma(m-\tfrac{1}{2})f\left(x\sqrt{w},m-\frac{1}{2}\right)$ and make the substitution

$$\Gamma(m-\tfrac{1}{2})f\left(x\sqrt{w},m-\frac{1}{2}\right)=\frac{\pi}{2\sin\pi m}\cdot\Gamma(\tfrac{1}{2})\left\{-L\left(x\sqrt{w},m-\frac{1}{2}\right)+\right.$$
$$\left.+\left(\frac{x}{2}\right)^{2m-2}M\left(x\sqrt{w},m-\frac{1}{2}\right)\right\}.$$

Then integrating with respect to w, we find the desired expansion of $\varphi(x,m)$ in the form

$$\varphi(x,m)=\int_0^\infty\frac{\sin xt}{(1+t^2)^m}\,dt=\frac{\pi}{2\sin\pi m}\cdot\frac{\Gamma(\frac{1}{2})}{\Gamma(m)}\left\{-N(x,m)+\left(\frac{x}{2}\right)^{2m-1}M(x,m)\right\},$$

where $N(x,m)$ represents the new series

$$N(x,m)=\sum_{h=0}^{h=\infty}\frac{\left(\frac{x}{2}\right)^{2h+1}}{\Gamma(h+\frac{3}{2})\,\Gamma(-m+2+h)}.$$

The same remarks as were made concerning the first integral $f(x,m)$, can here be made again. The integral has only a meaning for real values of x and for positive values of m, but from the expansion is inferred, that the integral incompletely represents a function of x which exists over the whole x-plane, quite independently of the values assigned to the parameter m. Again the origin $x=0$ and $x=\infty$ are the only singularities of the function. The singularities are logarithmic, when m is an integer and the origin becomes a regular point, when $2m$ is equal to an odd integer

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1) It is possible to invert this relation. It may be shewn that we have also

$$\Gamma(m)f(x,m)-\frac{1}{2}\sqrt{\pi}\,\Gamma(m-\tfrac{1}{2})=$$
$$=-\frac{x}{2\sqrt{\pi}}\int_0^6(1-w)^{-\frac{1}{2}}\,dw\,\Gamma(m-\tfrac{1}{2})\,\varphi\left(x\sqrt{w},m-\frac{1}{2}\right).$$

$2k+1$, but in no case is a finite expression by means of elementary functions obtainable.

The function $\varphi(x, m)$ as well as $f(x, m)$ satisfies the relation

$$D^h_{\alpha=1} \left\{ \alpha^{-m+\frac{1}{2}} \varphi(x\sqrt{\alpha}, m) \right\} = \frac{(-1)^h\, \Gamma(m+h)}{\Gamma(m)} \varphi(x, m+h)\cdot$$

and by means of this rule expansions for $\varphi(x, k)$ and $\varphi\left(x, k+\frac{1}{2}\right)$ may be deduced from the equations

$$\varphi(x,1) = \int_0^\infty \frac{\sin xt}{1+t^2}\,dt = \sum_{h=0}^{h=\infty} \frac{x^{2h+1}}{(2h+1)!}\left(\frac{1}{1}+\frac{1}{2}+\frac{1}{3}+\dots\frac{1}{2h+1}-C-\log x\right) =$$

$$= \frac{1}{2}\left\{ e^{-x}\, Li\,(e^{+x}) - e^{+x}\, Li\,(e^{-x}) \right\}.$$

and

$$\varphi\left(x, \frac{1}{2}\right) = \int_0^\infty \frac{\sin xt}{\sqrt{1+t^2}}\,dt = \frac{\pi}{2} \sum_{h=0}^{h=\infty} \frac{\left(-\frac{x}{2}\right)^h}{\Gamma\left(\frac{h}{2}+1\right)^2}.$$

Botany. — On "Leptostroma austriacum OUD., *a hitherto unknown Leptostromacea living on the needles of Pinus austriaca; and on* Hymenopsis Typhae (Fuck.) SACC., *a hitherto insufficiently described Tuberculariacea, occurring on the withered leafsheaths of Typha latifolia.*" By Prof. C. A. J. A. OUDEMANS.

1. LEPTOSTROMA AUSTRIACUM OUD.

(Plate I.)

On the 13th of June 1904 I received from Dr. J. RITZEMA BOS, Professor at Amsterdam, a number of specimens of transplanted seedlings of *Pinus austriaca*, originating from Schoorl, all dead and of which the accompanying letter informed me that the roots showed here and there cushionlike prominences, the surface of which was covered with shuttle-shaped conidia, divided into cells, and the microscopic properties of which resembled most those of conidia of the genus *Fusarium*.

Besides I found, without my attention having been directed to it, that most needles of the dead plantlets were spotted on both sides with small black specks and streaks, the external appearance of which showed most resemblance with the perithecia peculiar to *Leptostroma* or *Leptothyrium*.

The plants sent to me, provided with a here and there ramified tap-root of about 1 decimetre length and 1—3 millimetres thickness, proved on closer inspection to have much suffered, since in various places the bark was loose from the wooden kernel, if it was not entirely lacking. These circumstances justified the supposition that the young pine-trees had succumbed under the attack of the *Fusarium*-plantlets and that the *Leptostroma*- or *Leptothyrium*-individuals had chosen the sickly, lingering or dying needles as the seat of their fatal activity.

The *Fusarium*-cushions that had remained were little numerous, 1—3 mm. in diameter and had a light rosy tint. Lacking suitable objects for investigation, I had to restrict my answer to the communication that here very likely *Fusarium roseum* had been active, and I left the further elucidation of the devastation caused by that fungus to the care of Prof. RITZEMA BOS.

A closer examination of the very numerous specks and streaks found on the needles of *Pinus austriaca*, induced me, on account of their generally elongated, sometimes more, sometimes less hysterium-like shape, their little tendency to loosen at the circumference and to fall off, the fact that nowhere a parenchymatic structure of the perithecium-wall could be distinguished and that the basidia had not developed, to think rather of the genus *Leptostroma* than of *Leptothyrium*, and besides to mark the fungus as non-described and to give the name *Leptostroma austriacum* to it in order to distinguish it from other fungi.

One of the characteristics of *Leptostroma austriacum* is that the perithecia are never united to continuous series, but rather form greater or smaller groups of streaks or small shields, which differ greatly among each other in size, and are rather dull than glossy. Their length varies from $^1/_5$ to 1 mm. and their breadth from $^1/_8$ to $^1/_5$ mm. Their perithecium-wall is "halved", as the term is, does not reach further than the epidermis of the leaf, and consequently has the shape of a cupola. This wall has no foundation or basis. Moreover it is black, carbonaceous and structureless, so that there can be no doubt that we have here a cuticle (Fig. 2 and 3), from which follows that the space, occupied by spores, rests on the epidermis, as is clearly shown by Figs. 2 and 3. By reasoning more even than by observation, one is lead to the conclusion that the spores are produced by a very thin layer of threads extending over the epidermis.

Above this layer the spores form two layers or storeys. A third layer does not exist, as the space, required for it, is occupied by the spores which have loosened themselves and have become entangled.

The spores have an elongated (cylindrical?) shape and are colourless and undivided. Their foot is rounded and encloses (Fig. 4 and 5) a circular or oval, glossy vacuole; their top is more pointed and empty. They measure 7—8 μ in length and $1^1/_2$ μ in breadth.

The difference between *Leptostroma austriacum* and other Leptostromata, peculiar to pine-needles, like *L. Pinorum*, *L. Pinastri* and others, is: that in the latter the perithecia form mostly narrow parallel series; that the spores are not broader than 0.5 μ, and finally, that no vacuoles are found.

The Latin diagnosis of the new species is as follows:

"Peritheciis cuticulam inter et epidermidem occultatis, amphigenis, irregulariter distributis, majoribus et minoribus, item longioribus et brevioribus intermixtis, dimidiatis, nigris, opacis, diu clausis, tandem irregulariter ruptis, persistentibus neque decedentibus nec circumcirca a substrato solutis. Sporulis sessilibus, cylindraceis, hyalinis, continuis, vulgo 7.5 × 1 μ, basi rotundatis guttulaque sphaerica vel ovali, micante, praeditis, apice acutiusculis, vacuis."

EXPLANATION OF THE FIGURES OF PLATE I.

Fig 1. A piece of a needle of *Pinus austriaca* with small heaps of perithecia (*p.*) on them. ($^5/_1$).

„ 2. Vertical section of a not yet fully mature perithecium.
  a. Cuticle.
  b. Epidermis.
  c. The two layers of rod-shaped colourless spores. ($^{500}/_1$).

„ 3. Vertical section of a ripe perithecium which has burst open.
  a. Cuticle.
  b. Epidermis.
  c. Spores, partly undamaged, partly in a displaced position. ($^{500}/_1$).

„ 4. Spores, with a rounded foot and a sharper top. At the foot a vacuole. ($^{1000}/_1$).

„ 5. The same ($^{2000}/_1$).

2. HYMENOPSIS TYPHAE (Fuck.) Sacc.

(Plate II).

This fungus, found for the first time at Nunspeet in July 1904 on the withered leaves of *Typha latifolia*, was sent to me among many others by Mr. C. A. G. Beins.

Unlike the *Sphaerellae* and *Leptothyria* it has not the appearance of small specks but of raised black spots (Figs. 1, 2 and 3) which are spread in the grooves between the nerves and have a length of 1—4 and a breadth of $^1/_2$ mm.

Fuckel described the fungus first under the name of *Myrothecium Typhae* (Symb. 364), in the following words: "Peridiis hemisphaericis, oblongis, $^1/_2$ lineam longis, aterrimis; conidiis oblongo-ovatis, utrimque obtusis, simplicibus, biguttulatis, 18 × 6 μ, pallide fuscis," and gave a not quite satisfactory picture of a conidium in Fig. 21 of Plate I.

He was succeeded by Saccardo (Syllabus IV, 745), who agreed with his predecessor that the fungus belongs to the Tuberculariaceae, but nevertheless removed it to the genus *Hymenopsis*, on account of the spore-bed (sporodochium) of *Myrothecium* being surrounded by a circle of fringes, which is not the case with *Hymenopsis*.

In a very successful drawing by Mr. C. J. Koning of a vertical section of *Hymenopsis Typhae*, (Plate 2), the structure of the fungus is excellently seen, much better than in other pictures, also of other species of the same genus.

Where the black disks or specks rise above the surface of the leaf-sheaths (Figs. 1, 2 and 3), one does not find, as Fuckel writes, a "perithecium" (i.e. a more or less completely occluded fruit-body), but a globular assemblage of reproductive cells or conidia (Fig. 4 *s.s.*), covered by the cuticle and produced by a layer of peculiarly shaped sporophores (Fig. 4 *x.*), collectively called stroma or fruit-bed. Under this stroma the epidermis is found (Fig. 4 *o.*): a layer easily recognisable by the width of its cells. It deserves to be mentioned that the black colour of the prominent little disks (Figs. 1, 2 and 3) must not be ascribed to the colourless cuticle (*c*), nor to the colourless epidermis (*o*), but only to the conidia (Fig. 5 *y*) which have been left uncoloured, however, in Fig. 5, in order not to make the picture too full.

One of the most important Figures of Plate 2 is Fig. 5. At *x* it shows the favoured club-shaped threads or basidia, whose task is the production of the conidia; these latter, let free by their bearers, being seen in their neighbourhood in a free condition (*y*). The conidia have an elongated, cylindrical shape, are more or less asymmetrical or curved, rounded at both ends, somewhat more transparent at the base and of the grey colour of mice. (Sacc. Chromotaxia, pl. I, Fig. 3). They contain 2—4 consecutive vacuoles each and have a length of about 10 and a breadth of about 4 μ.

Comparing the Figures of Plates I and II, one might get the impression that in the Figures 2 and 3 of Plate I a perithecium is lacking as well as in those of Plate II, although this term is usual in descriptions of the Leptostromaceae. Therefore we remark that this latter family of the Sphaeropsideae forms a transition between the perithecium-bearing and the peritheciumless forms and that in judging these two cases weight has been attached to the black colour of the upper half of the shields, which sometimes consists of the cuticle only, sometimes of a combination of the cuticle with the epidermis. In addition to this the Leptostromaceae do not produce well-developed basidia and have remarkably small spores.

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The Latin diagnosis of *Hymenopsis Typhae* is as follows:

"Sporodochiis amphigenis, hemisphaericis, inaequaliter in vaginarum sulcis distributis, majoribus et minoribus, item longioribus et orbicularibus intermixtis, primo cuticulam inter et epidermidem caelatis, 1—18 μ in diam., aterrimis; denique expositis, calvis, thalamo basidiophoro basilari praeditis; basidiis dense fasciculatis, elongato-clavatis, hyalinis, continuis; conidiis oblongis, rectis vel paullo curvatis et utplurimum inaequilateralibus, utrimque obtusis, basi vulgo clarioribus, 10 × 4 μ, murinis (SACC. Chromotaxia Tab. I, f. 3), 2—4-guttulatis, guttulis hyalinis, nunc binis sibi oppositis, tunc iterum ternis (aut quaternis) in seriem dispositis."

EXPLANATION OF THE FIGURES OF PLATE II.

Fig. 1. Piece of a leafsheath of *Typha latifolia*, studded in the grooves between the nerves with sporodochia (spora = spore; docheion = receptacle), (natural size); *p.p.* perithecia.

„ 2. Piece of a leafsheath with two sporodochia, of which one is opened, the other closed ($^{10}/_{1}$).

„ 3. Piece of a leafsheath with two sporodochia, of which one has a groove on the dorsal side ($^{10}/_{1}$).

„ 4. Vertical section of a ripe sporodochium. — *c.c.* cuticle; *o.o.* epidermis; *s.s.* conidia; *vb. vb.* vascular bundles; *x.* club-shaped basidia.

„ 5. A bundle of club-shaped basidia (*x. x.*) with some conidia (*y. y.*), in which two or three vacuoles. The end of the conidia resting on the basidia or turned towards them is always somewhat more transparent than the other.

Fig. 1

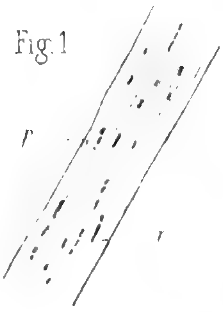

Fig. 2.

Fig. 3

Fig 4

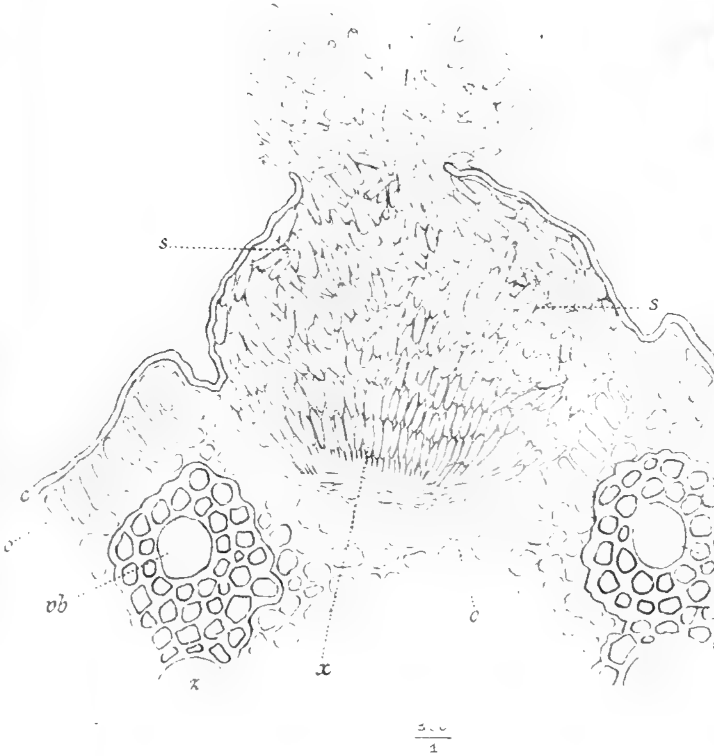

Fig 5

C. J. Koning, del.

J. BIJTEL Lith., P. J. MULDER Impr. Leiden.

Botany. — "*On* Sclerotiopsis pityophila (Corda) Oud., *a Sphaeropsidea occurring on the needles of* Pinus silvestris."
By Prof. C. A. J. A. Oudemans.

In the "Nederlandsch Kruidkundig Archief", 3d series, vol. II, pag. 247, I mentioned a fungus found in 1901 by Mr. C. A. G. Beins at Nunspeet on the needles of Pinus silvestris, which fungus, discovered in 1840 on the same host near Prague by the botanist A. J. C. Corda, was described in vol. IV of his "Icones Fungorum" on page 40, under the name of *Sphaeronema pythiophilum*[1]

The same fungus received a place in Saccardo's "Sylloge Fungorum", vol. III (A° 1884), p. 101, this time under the name of *Phoma pityophila,* whereas on account of a new investigation of fresh specimens I thought it necessary myself, in the article quoted above, to change the name *Phoma* again and to replace it by that of *Sclerotiopsis.*

Besides Saccardo, also Allescher, in the 6th vol. of Winter's Kryptogamen-Flora (1901), page 199, uses the name *Phoma pityophila* for this fungus, which name is changed into *Sclerotiopsis,* by way of improvement, in vol. VII, p. 847 of the same work.

Having been enabled through the kindness of Mr. Beins in January 1904, to examine again some fresh specimens of *Sclerotiopsis pityophila,* I availed myself of this opportunity of testing once more my former experience by facts and had the advantage of having at my disposal the drawings by Mr. C. J. Koning, chemist at Bussum, which accompany this article. I have to thank Mr. Koning for the kindness which he has repeatedly shown in assisting me on former occasions as well as on this. Some particulars supplementing former communications may be mentioned here.

The reason that induced Saccardo in 1884 to change the name *Sphaeronema* into *Phoma* was that some very characteristic properties of the former genus had been passed over silently by Corda, viz. that in his paper no mention is made either of a beak- or brush-shaped prolongation of the peritheciumwall or of spores which, conglomerated to a ball, should have been found at the surface of the perithecia.

The generic name chosen by Corda could not be retained and so no other name seemed more appropriate to the Italian mycologist to replace it than that of *Phoma,* which judgment has not been doubted by any subsequent writer.

[1] The Greek for pine being πίτυς, in what follows Corda's wrong orthography has been corrected.

Meanwhile it was evident as well from the very brief description of *Phoma pityophila* in SACCARDO's Sylloge as from his silence on the microscopic properties of the fungus, that this author had not been able to examine freshly collected specimens, so that mycologists working after him under more favourable conditions might possibly find something to improve.

Having had this opportunity myself it may not be superfluous to return once more to my *Sclerotiopsis pityophila* and to consider more fully the difference between *Sclerotiopsis* and *Phoma*.

First of all it must be mentioned that the perithecia of *Phoma*, when produced by leaves, although they lie concealed below the epidermis, yet are by no means buried deep in the tissue as is the case with *Sclerotiopsis* (Fig. 3—5) and probably on account of this are much more irregularly shaped, sometimes coalesce and come forth with a stronger and less rounded appearance.

Secondly any one who has examined many specimens of *Phoma* must have noticed that with *Sclerotiopsis* stronger and denser perithecia are found which are carbonaceous at the surface, whereas those of *Phoma* belong to the forms that offer little resistance, and are tender and light-coloured; finally that the perithecia of *Sclerotiopsis* have no orifice but decay or burst, whereas with *Phoma* the rule is that a small round ostiolum is found through which the spores are discharged.

In addition to this we remark that the spores of *Sclerotiopsis* do not lie loosely together like those of *Phoma*, but remain long connected by means of a sticky substance (fig. 3 and 4), the consequence of which is that a few drops of water are sufficient to cause *Phoma*-spores to diverge in all directions whereas with *Sclerotiopsis* a slight pressure or friction is required to make them fit for a closer examination.

This latter peculiarity was exactly the reason why CORDA imagined to have found a *Sphaeronema*, overlooking that the beak- or brush-shaped prolongation of the peritheciummouth was absent and that consequently no cluster of spores could be formed at the top of such a prolongation.

The question whether the spores of *Sclerotiopsis* are produced on the top of sporophores is difficult to answer, although analogy pleads for it, since there is no distinct division between the wall of the perithecium and the gleba (the cluster of spores) but a gradual transition of one into the other. Yet not far from the surface of the perithecia ((Fig. 6) a segmentation seems to take place and the formed spores seem to be slowly pushed to the centre.

Sclerotiopsis pityophila (Corda) Oud., a saprophyte, appears as black, fleshy grains (Fig. 1), $^1/_2$ — 2 mm. broad, which are expelled from the tissue of the needles. They consist of polygonal parenchym-cells which at the circumference are larger, harder and darker but in the interior become smaller, softer and colourless and seem to border on a small cavity, which is soon filled with spores. These latter are oval or egg-shaped, straight or slightly curved (Fig. 7), unicellular and undivided and have rounded tops. They vary from $7 - 8 \times 3 - 4\,\mu$, have no polar drops and no appendices. Germinating spores were not found.

The first *Sclerotiopsis* was found by Spegazzini in the Argentine republic on rotting leaves of *Eucalyptus Globulus* and was called *S. australasiaca*. A second and third species (*Scl. Cheiri* Oud. and *Scl. Potentillae* Oud.) were found by myself and Mr. Beins, the former on the stems of *Cheiranthus Cheiri* in the Botanic Garden at Amsterdam, the latter on the leaves of *Potentilla procumbens* at Nunspeet. Finally Corda first mentions *Scl. pityophila* (Corda) Oud. which was collected in 1840 on pine-needles at Prague and 60 years later at Nunspeet.

EXPLANATION OF THE FIGURES.

Fig. 1. A few needles of *Pinus silvestris* studded with perithecia of *Sclerotiopsis pityophila* (Corda) Oud. — Natural size.

„ 2. A needle of *Scl. pityophila* loaded with some perithecia. Cross-Section. Magnification 100.

„ 3, 4 and 5. Vertical sections of *Scl. pityophila*, magnified 400 times. The carbonaceous wall of the perithecium is clearly visible here everywhere. In 3 and 5 the perithecia have broken through the epidermis, in 4 not yet; in the former two also the conglomerated spores are discerned.

„ 6. A piece of a peripheral part of the wall of the perithecium with some stalked spores. Magn. 1000.

„ 7. Single spores, 1000 times enlarged.

Geology. — *"On an equivalent of the* Cromer Forest-Bed, *in the Netherlands."* By Prof. Eug. Dubois. (Communicated by Prof. K. Martin).

On the eastern frontier of the Netherlands, along the middle third part of the province of Limburg, there is the steep west border of a plateau, made up of gravels and sands, which, for the greater part, is enclosed between the valleys of the Meuse, the Niers and the Roer and rises to an average height of about thirty meters above the adjoining low land. That border is falling within the Dutch frontier opposite Venlo, Tegelen and Belfeld, further, east of Swalmen and of Herkenbosch. The plateau is a piece of a formerly coherent, much larger plateau, extending to Nimeguen and Cleves, of which, according to Dr. Lorié, the Veluwe is also a part. This author is inclined to suppose, that the large mass was still entire at the time of the principal extension of the Scandinavian Ice-sheet and that only after the retreat of that ice-sheet, by melting, the great eroding process began, which divided it into a number of pieces and also assailed each of these; so that under consideration was partly divided by the Swalm and the Nette with their affluents. Dr. Lorié showed that the northern and eastern parts of the plateau do not merely consist of "Rhine-diluvium", as Staring supposed for the whole till Nimeguen, but that these northern and eastern parts expose traces of having been reached by the Scandinavian Ice-sheet of the great Glacial Epoch, in consequence of which they consist, at least at the surface, of "Mixed Diluvium". This is not the case with the western piece of the plateau of gravel, which we consider now more particularly. In this only stones are found, which have been transported by the Rhine and its large tributary, the Meuse; further, the horizontal stratification has not been disturbed by an ice-sheet having moved over the plateau.

Nevertheless here too the characteristics of the co-operation of ice in the transport of the sand and the gravel, out which the mass has been made up, are not wanting, but these occur to great depth in it, till 30 metres and more below the surface, and, as already stated above, the horizontal structure has not been disturbed by an ice-sheet having moved over the surface. This stratification, with fluviatile current-bedding, can be observed in a number of places where gravel is dug. At the same time there are repeatedly found, among sand and finer gravel, big angular stones.

So I observed in a gravel-pit in the Jammerdaalsche Heide, opposite Tegelen, the following boulders, which were found on an area of about one hectare, and 2 or 3 M. above the basis of the sand and gravel deposit: A large boulder of *Thonschiefer*, of 1.35 × 0.75 × 0.35 M., and three smaller ones, of about 0.5 M. greatest dimension, a boulder of veined gray quartzite, of 0.80 × 0.75 × 0.50 M., another gray quartzite of 0.67 × 0.36 × 0.20 M., a flint nodule of 0.60 × 0.35 × 0.15 M. Other large stones were knocked into pieces. East of Belfeld boulders are not so frequent in the gravel. Amongst others I observed there a basalt of about 0.40 M. largest dimension. From these observations we are led to suppose a transport on a large scale by floating ice, and we can imagine that ice having had its origin, in the upper-course of the Rhine and the Meuse, from bottom-ice. The basal part of the deposit, 2 M. thick east of Tegelen, 5 M. thick east of Belfeld, is, however, entirely devoid of pebbles, it consists of rather fine sand.

All this induces us to consider this "Rhine-diluvium" as a glacio-fluvial formation of the first Pleistocene Glacial epoch, chronologically the equivalent of the fluvioglacial *Deckenschotter* of the Diluvium of the Middle-Rhine.

This interpretation is now affirmed by the character of the bed underlying the gravels and sands in the plateau in consideration. Save gravel and sand there is dug clay, which furnishes the material for the many tileries and stone-factories, in a great number of places, of the Netherland province of Limburg and of the adjoining region of the Rhine-Province of Prussia, chiefly on the borders and along the transverse valleys, of the Swalm, etc. That clay is lying conformably and with not eroded, rather well horizontal separating plane under the "Rhine-diluvium", the equivalent of the *Deckenschotter*. Her own planes of stratification are also generally horizontal. In the clay-pit of the well-known stone-factory of the firm CANOY-HERFKENS, on the western border of the Jammerdaalsche Heide, her upper surface is at 27 M. + A.P. East of Belfeld, near Maalbeek, 4.5 K.M. S.S.W., I found that surface at 35 M. + A.P. East of Reuver and 8.5 K.M. S.S.W. of the pit opposite Tegelen, it is at 43 M. + A.P. East of Swalmen, near the Dutch Custom-house on the frontier, 14 K.M. south-west of the pit in the Jammerdaalsche Heide, it is at 50.5 + A.P. [1]) The same clay is also dug roundabout Brüggen, on the Swalm, in the Rhine-Province, 5 to 8 K.M. east of the pit near the Custom-house. It is probably also the same clay, which is met with, at the surface, east of the Zwartwater, (north of Venlo), and west of the plateau, in the communes of Tegelen, Belfeld Reuver.

Evidently this clay constitutes a continuous bed underlying the

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[1]) In the Dutch text of this communication the altitudes were only estimated, in this english version they are given from exact determinations by levelling.

"Rhine-diluvium", which has a regular gentle upward slope to the south and probably also to the east, and of which rests appear in the low country bounding the plateau to the west, where the "Rhine-diluvium" has been removed.

There is not much known about the total thickness of the bed, by reason of the under layer of it having not yet been attained in any pit. In the Jammerdaalsche Heide the clay is dug out 6 M. deep, and it has further been ascertained by means of bore holes, that even 2 M. deeper, so at about 19 M. + A.P., the clay makes place for sand. It is however probable that another layer of clay is underlying that sand. In bore holes put down on several places in and about Venlo, some of which approached the last mentioned pit to $2^1/_2$ K.M., they met with similar clay, in a layer of 8 M. thickness, resting, at 4 M.—A.P., on coarse white sand and gravel with much mica, and covered at 4 M. + A.P. by 3 M. sand and about 12 M. of gravel[1]). Along the right bank of the Meuse, south of Venlo, the edge of this very ferrugineous and somewhat consolidated gravel appears, covered by loam, at about 14 M. + A.P. Even at very low watermark, of a few decimeter above 8 M. + A.P., generally the underlying of the gravel cannot be seen in this outcrop. On a few spots however, about 1 K.M. south of the Meuse-bridge and 2 K.M. north-west of the mentioned clay-pit, I observed similar clay as that of Tegelen in the original situation, over 7 M. in horizontal connection, under the gravel. It reaches there upward to 11 M. + A.P. Evidently this clay in the bank of the Meuse belongs to the same bed as that which was met with in the bore holes at Venlo, the bed having been unevenly eroded a long time before the development of the present river channel. In such a way a difference of 7 M. could arise in the upper surface of the clay. In that clay on the right bank of the Meuse I found a tibia of *Rhinoceros*, which is only assimilable with that bone of *R. etruscus* and *R. Mercki.* The bone was still a little fastened in the clay, for the greater part enveloped with the consolidated gravel. This clay is thereby characterised as interglacial or preglacial (prepleistocene). If belonging to the same bed as the Clay of Tegelen, the whole thickness of the latter, including sandlayers, may be estimated at about 30 M. In this computation it has been supposed that its under surface, from Venlo to Tegelen, is horizontal, which seems

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[1]) According to a communication of Mr. DE WAAL MALEFIJT the top of the clay was 5 M. lower in a bore hole put down on the right Meuse-bank at Venlo. Probably the clay which has been met with in bore holes, 24 K.M. south of Venlo, on the east side of the Meuse in the neighbourhood of Roermond, at about 3 M. + A.P., under as much gravel, is geologically identical with that under Venlo.

allowable over such a small distance, in comparison with the great extension of the bed, and with regard to the horizontal structure of the clay. Then we have to regard it as prepleistocene, an interpretation entirely confirmed by the following palaeontological facts. Much more improbable I hold it that the clay under Venlo and on the Meuse near that own, was deposited after the first Pleistocene Glacial epoch, that of the "Rhine-diluvium". In that case we should be obliged to suppose two periods of erosion. In the first one the "Rhine-diluvium", with the underlying Clay of Tegelen in the valley of the Meuse, should have been eroded, afterwards (during an interglacial period) clay should again have been deposited in it, which was attacked in a second period of erosion, on which than in the Second or Great Pleistocene Glacial epoch a deposit of gravel accumulated.

For the chronology of the different beds of the Dutch Pleistocene formations now it is of great importance to ascertain, by means of enclosed fossils, the age of the Clay of Tegelen, which was deposited in the time preceding the accumulation of the "Rhine-diluvium".

I am much obliged to Mr. L. STIJNS, at the time medical student, now physician at Roermond, for having shown me, already in 1897, fossil remains of Mammals (especially *Trogontherium* and Deer) and of Molluscs, together with such of plants, which he had found in the clay-pit of Messrs. CANOY, HERFKENS and SMULDERS, a number of which he has yielded to me for a closer examination. I have further to acknowledge the benevolence of the last named gentlemen for the opportunity of collecting some fine and characteristic fossil remains of Mammals, especially of *Cervus*, *Rhinoceros*, *Equus*, *Hippopotamus* and *Trogontherium* (now in Teyler Museum at Haarlem), by the aid of which the fixing of the geological horizon has been arrived at. The shells and plant remains (especially seeds and wood) and many bones are found at about 5 M. below the upper surface of the clay bed, where this is rather sandy, another, more abundant, ossiferous niveau is at nearly 3 M. below that upper surface, in stiff clay [1]). Opposite Belfeld bones

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[1]) To an average of 2.70 M. below the upper surface, from below which a very stiff clay begins, the clay in this pit has a yellow colour, caused by the action of the atmospherilia on the ferrugineous compounds in the clay, which action is lower down shut off by that stiff clay. The latter itself is of a bluish colour and at the bottom of the pit it is nearly black. Excepted near the upper surface, the yellow clay is on the whole sandy, only at a few places in the pit it is rather stiff. In those places the blue colour continues up to a higher level and the limiting line is not at all right and horizontal, on the contrary the yellow clay, there, is sinking down, in that blue clay, which continues to a relatively higher level. Agatiform wrinkling brown parallel lines, in those yellow insinkings, imitate then contortions,

are mostly found at a depth of 4 M. in the clay; at 1.25 M. below its upper surface it there encloses a layer of sand, 0.30 M. thick. The outside of the bones is always absolutely uningured, they do not look rolled worn at all. The following enumeration of fossil forms will suffice for the determination of the geological horizon. I hope to be able to work out and to complete the list on a later occasion.

As regarding the Molluscs, it is in the first place noteworthy, that these for the most part belong to forms proper to fresh water, and especially to stagnant or very slowly running water; a few land-snails belong to species which may have lived upon the vegetation on the shore. Till now I have recognised:

Fig. 1. — *Cervus tegulìensis,* sp. n. Left antler, lateral aspect. ($^1/_8$).
The figured specimen belongs to the collection of Mr. Stijns. Several other specimen do not possess the strong, curvature of the beam at the origin of the tres-tine, in such a manner that the beam is on the whole straighter.

Paludina, 2 sp., *Planorbis* sp., *Helix hispida* L., *Helix arbustorum* L., *Helix* sp., *Limnaeus* sp., *Pisidium,* 2 sp., *Unio* sp.

Of the Mammals the following species are well determinable:

Trogontherium Cuvieri Owen, *Cervus Sedgwickii* Falc. (= *Cervus dicranius* Nesti), *Cervus teguliensis,* sp. n., *Cervus* (*Axis*) *rhenanus,* sp. n., *Cervus* (*Axis*) sp., *Hippopotamus amphibius* L., *Equus Stenonis* Cocchi, *Rhinoceros etruscus* Falc.

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such as they have been produced elsewhere by the motion of the Pleistocene ice-sheet, but here we have indeed only before us a result of the process of the blue clay to yellow. Elsewhere, as opposite Belfeld, where still the original thick gravel bed covers the clay, and consequently the underground water is at a higher level, has preserved the greyish blue colour up to its upper surface.

There are found too remains of: *Cistudo lutaria* Marsili, of a Frog and of Fishes.

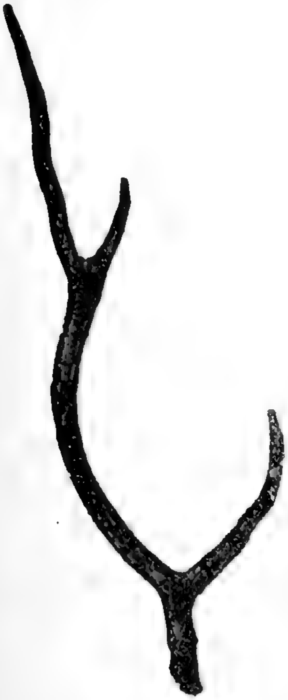

Fig. 2. — *Cervus (Axis) rhenanus*, sp. n. Right antler, lateral aspect. ($^{1}/_{8}$).

Of great importance are the remains of plants, from which especially seeds were carefully collected by Mr. Stijns. They enable us to form a conclusion concerning the climate and thereby concerning the time in which the plants lived. And that is so much the more desirable as remains of Elephants have not yet been encountered, among the mammalian remains. The species already determined are:

Viburnum sp., *Prunus* sp., *Trapa natans* L., *Cornus mas* L., *Vitis vinifera* L., *Staphylea pinnata* L., *Juglans tephrodes* Ung., *Nuphar luteum* L., *Stratiotes Websteri* Pot., *Abies pectinata* DC., *Chara* sp.

That is an assemblage of animals and plants which can only be preglacial in the sense of prepleistocene. The group of Mammals is distinguished from that of the Sands of Moosbach, which are now generally regarded as a deposit of the interglacial period before the great or second Pleistocene Glacial epoch, by the possession of *Equus Stenonis* [1]), of two species of Deer of the *Axis* type and an other species belonging to a type not represented by any living Deer. They give to the whole a Tertiary character and make, for themselves, the equivalence of the Clay of Tegelen with the Cromer Forest-Bed probable. From the last mentioned deposit we know one species Deer of the *Axis*-group (*C. etueriarum*, probably nearly related to the new species from Tegelen), a second species has been described from the somewhat older Norwich Crag; from the Pliocene of central France there are described as many as six species. *Cervus teguliensis* closely resembles *C. tetraceros*, Boyd Dawkins, from the youngest beds of that Pliocene, characterised by *Elephas meridionalis*, and from the Cromer Forest-Bed, but the antler of the large Deer of Tegelen never obtained more than three tines. The other Mammals of the Clay of Tegelen are all known from the Cromer Bed. The presence of *Equus Stenonis* and *Rhinoceros etruscus* together with *Trogontherium Cuvieri* and *Hippopotamus amphibius major* leaves no doubt on that equivalence.

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[1]) Of this species it is the variety distinguished by Mr. M. Boule as the one with great dimensions, which he believes to be the immediate ancestor of *E. caballus*.

What is known from the species of plants in the Clay of Tegelen, points even to a somewhat warmer climate than that indicated by the flora of the Cromer Bed, and so, seemingly, to a somewhat older age. The *Prunus*-species is certainly different from *P. spinosa* L., which belongs to the Cromer fossil flora, and which is now also indigenous in northern Europe. The seed is only assimilable with that of species, which now appear to be spontaneous in Turkey, south of the Caucasus, in Armenia and northern Persia. Amongst the plants of the Cromer Bed *Vitis vinifera* is also wanting, which grows now spontaneously in temperate West-Asia, especially in Armenia and south of the Caucasus and the Caspian Sea, also in southern Europe, Algeria and Marocco. Remains are also found in Pleistocene travertines of Tuscany and southern France, where the species, with *Ficus carica* L., is considered to be a remnant of the Tertiary flora, further in Italian lake-dwellings. Amongst the numerous species of plants of the Cromer Bed is wanting too *Staphylea pinnata*. In wild state this species does not grow now more northerly than southern Germany, it is especially indignous in the Pontine countries and also in Asia Minor. No species of *Juglans* has been found in the Cromer Bed, *Juglans tephrodes*, the nut of which, like that of some nearly related forms, is hardly discernable from the present American *Juglans cinerea* L., is a Tertiary species of Italia and the middle of Germany. The seed of the *Stratiotes* is very different from that of *S. aloides*, on the contrary strikingly similar to that of *S. Websteri* from the Upper Miocene of the Wetterau. In the Cromer Bed as yet no *Viburnum* was found. The seed of the species from the Clay of Tegelen closely resembles that of *V. Opulus* L., it is only larger and a little less flat. The circumstance, that the genus *Viburnum* played an important rôle among the Tertiary flora seems to me not to be without bearing, in connexion with the above mentioned facts. A similar consideration applies to the genus *Cornus*, of which another species, *C. sanguinea* L. is found in fossil state on the coast of Norfolk. *C. mas* appears to grow, besides in Asia, only in southern and central Europe. *C. sanguinea*, on the other hand is also indigenous in northern Europe.

It wants no demonstration that the flora from the Travertines of Taubach, to which, on conclusive grounds, the same age as that of the Sands of Moosbach is now attributed, is a much younger one than that of the Clay of Tegelen. The former contains arctic and alpine forms, which are wanting here, on the other hand the fossil flora of Taubach lacks the mentioned Tertiary forms and those pointing to a warmer climate. From the fact that the flora of Tegelen apparently lived in a somewhat warmer climate than that of Cromer we are, however, not obliged to conclude that the former is older than the latter. For we have to consider, that the situation of Tegelen is about 2° of latitude more south than Cromer, but especially, as PRESTWICH and CLEMENT REID have shown, that local circumstances must have made the climate of Cromer relatively a less genial one. Of the Mammals, by which the older Pliocene deposits of Norfolk are distinguished from the *Cromer Bed* none are found in the Clay of Tegelen.

Taking all these facts into serious consideration, there seems to me hardly to remain any room for doubting the equivalence of the latter with the Cromer Forest-Bed. Like this celebrated fluviatile and estuarine deposit and like the undermost gravel beds of Saint-Prest near Chartres, the alluvia characterised by *Elephas meridionalis* in central-France and the lignite beds of Leffe near Gaudino, not far from Bergamo, they must be placed at the top of the Pliocene.

On good reasons it is generally accepted, that at the end of the Pliocene period the continual subsidence during that period, the unmistakable proofs of which have been found as well in the Netherlands and Belgium as in England, has been interrupted by an uprising of the region, properly a flattening of that great concave zone or geosynclinal, in which the marine Pliocene sediments were deposited. In consequence the southern half of the North Sea was converted into land and England united with the continent. The great river of that sedimentation basin, the Rhine, as has been shown by CLEMENT REID and by HARMER, then poured its waters over the east of England into the North Sea, and in Norfolk the Cromer Forest-Bed is a deposit of that river. Also HARMER rightly remarked, already in 1896, that this river, before it reached England must have passed somewhere over the Netherlands; so we should perhaps one day find the equivalent of the ossiferous beds of Cromer in our Country. In the Clay of Tegelen we now have really met with such a bed, which evidently accumulated in a shallow fresh-water lake, flow through by the Rhine.

On good reasons it is also accepted that with the beginning of the Pleistocene period the geosynclinal became steeper, in consequence of which, over the greater part of the present Netherlands, sand, gravel and clay could accumulate, attaining a thickness, in Holland, up to more than 150 M. But, at the same time, on the border of the steeper basin, in consequence of its larger angle of slope and the increased transporting capacity of the running waters there, first deposition of coarser material, the "Rhine-diluvium", took place and, as the slope increased still more, an important erosion. By this erosion the Meuse could excavate a broad valley through the Rhine-diluvium and deep in the Upper Pliocene clay, in which, the slope having somewhat decreased, probably already in the second or great Pleistocene Glacial Epoch, there accumulated a mighty deposit of gravel.

Physics. — *Contributions to the knowledge of* VAN DER WAALS' *ψ-surface. IX. The conditions of coexistence of binary mixtures of normal substances according to the law of corresponding states.* By Dr. H. KAMERLINGH ONNES and Dr. C. ZAKRZEWSKI. Supplement N°. 8 to the communications from the Physical Laboratory at Leiden.

(Communicated in the meeting of February 27, 1904).

1. *The graphical treatment of the conditions of coexistence.* In this paper where the theory of mixtures of VAN DER WAALS is illustrated, as in the former contributions we have placed in the foreground the law of corresponding states.

The data required calculating VAN DER WAALS' ψ-surfaces for all temperatures may be defined in the following way from the point of view of this law:

1°. An equation of state agreeing with reality, must be given for one normal substance over the whole range of temperatures and pressures to be obtained, (comp. § 2).

2°. For the different mixtures of the two substances considered, as well as for these substances themselves, the deviations from the law of corresponding states must be known (comp. § 3).

3°. We must know the critical temperature T_{xk} and pressure p_{xk} of each mixture taken as homogeneous [1]) with the molecular proportion x of one of the components, derived from the law of corresponding states, as functions of those of the simple substances and of x (comp. § 4).

With these data at our disposal VAN DER WAALS' theory will teach us all possible cases of coexisting phases of those substances if we roll tangent planes over the ψ-surfaces of each pair of substances for different temperatures.

In the treatment of the problems concerning conditions of coexistence

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[1]) Whenever we speak of critical temperature, a maximum vapour tension etc. of a mixture without more, we always mean "taken as homogeneous".

which have been solved in general by VAN DER WAALS, the following simplifications have been made:

1°. The first form with two constants a and b, in which VAN DER WAALS has written the equation of state, is used instead of the real equation of state;

2°. The supposition has been made that also the equation of state of each mixture with the proportion x has the same form with two constants a_x and b_x, whereby the law of corresponding states is rigorously satisfied;

3°. it has been supposed that the critical quantities determined by a_x and b_x are related to those of the simple substances determined by a_{11} and b_{11}, a_{22} and b_{22} by means of the relations

$$a_x = a_{11} x^2 + 2 a_{12} x (1 - x) + a_{22} (1 - x)^2$$
$$b_x = b_{11} x^2 + 2 b_{12} x (1 - x) + b_{22} (1 - x)^2,$$

so that the entire behaviour of the mixtures of two known substances is determined by two additional constants a_{12} and b_{12};

and 4°. it has often been assumed that the vapour phase satisfies the laws of ideal gases.

In this way VAN DER WAALS has obtained important approximation formulae. Though they do not always represent numerically accurately the behaviour of the mixtures, most of the particularities of the conditions of coexistence are sufficiently explained by these in general valid formulae [1]).

If in the treatment of these problems we want to use equations of state which over the whole range of temperatures and pressures agree accurately with the observations, if therefore we do not require the simplifications ad 1°, 2° and 3°, and if finally we want to consider other than rarefied vapour phases, so that the neglection of the deviations from the law of BOYLE-GAY LUSSAC-AVOGADRO mentioned ad 4° is not allowed, an analytical treatment of the conditions of coexistence in general becomes impossible.

Such problems we come across, for instance, when we derive the conditions of coexistence for mixtures of oxygen and nitrogen (critical state of air and relation between composition and pressure in the boiling off liquid air) from equations of state which also at the ordinary temperature accurately represent the compressibility of these substances and of their mixtures. An instance of an entirely different kind is given by the following group of problems: determine at ordinary temperature the absorption of hydrogen in ether and the

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[1]) VAN DER WAALS, Die Continuïtät etc. II p. 52.

deviations from the law of HENRY for this pair of substances, investigate the variations of this absorption with a small variation of temperature and finally find for the same temperature the pressure to which KUNDT ought to have gone in his experiments [1]) on the removal of the capillary ascension of liquid by pressing gas on it in order to see the meniscus of ether disappear under the pressure of hydrogen, which, as has been remarked in VAN ELDIK's thesis for the doctorate p. 7, comes to a determination of the plaitpoint pressure of the mixture of ether and hydrogen of which the plaitpoint lies at this temperature [2]).

In such cases we can only obtain solutions by means of the graphical treatment described in Comm. N°. 59*t* (Sept. 1900). It is true that the graphical method lacks the general character of the approximate solutions just mentioned, yet by means of it a better numerical agreement may be obtained for each special case. [3]) By a proper choice of special cases some data may also be derived for the qualitative characters of phenomena in mixtures [4]).

If we only aim at such qualitative results we may simplify the graphical treatment as well as the analytical by introducing different approximations according to the nature of the problem, while it lies at hand to derive wanting experimental data or results of calculations from empirical formulae on a larger scale than in the analytical treatment. For instance, everything that may be neglected in the analytical treatment may also be neglected in the graphical method. Occasion for this exists only, however, with problems which neither qualitatively are solved by means of the analytical method.

If we do not want to neglect to such an extent as in the analytical treatment, we might for instance retain the neglection of the deviations mentioned sub 2° of different normal substances and mixtures of normal substances from the law of corresponding states, which first occurs in Comm. N°. 59*a* and is kept up in this whole series of contributions.

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[1]) Repeated by VAN ELDIK (thesis for the doctorate; Leiden 1898) for hydrogen-ether and ethylene-methylchloride.

[2]) Comp. also VAN DER WAALS, Die Continuität etc. II, p. 136.

[3]) For instance, one of us and REINGANUM have derived (Comm. N°. 59*b* Sept. 1900) a numerical fairly approximate representation of the retrograde condensation observed by KUENEN with mixtures of methylchloride and carbon dioxide from the isothermals observed by him at other temperatures.

[4]) So for instance the character of the retrograde condensation (comp. note 2), and also the peculiarity in the conditions of coexistence in mixtures of which the critical temperature varies almost linearly with the composition, far below the critical temperature. Comp. these contributions Comm. N°. 59*a* § 8 at the end and III, Comm. N°. 64. HARTMAN, Livre jubil. LORENTZ, p. 640.

The simplifications relating to the case that one of the two coexisting phases as compared with the other has a very small density, will be considered in the sections 7 and 8 of this Communication.

§ 2. *Empirical reduced equation of state.* As to the supposition mentioned in § 1, we are now under much more favourable circumstances than at the time when Comm. N°. 59*a* was written.

The beauty of VAN DER WAALS' theory lies above all in the fact that it brings under one point of view phenomena in mixtures which are distributed over a large range of temperatures and densities. Hence for a satisfactory illustration of this theory we require first of all an equation of state which holds true over a large range of temperatures and densities. Now most of the equations of state — this has been made clear especially by D. BERTHELOT — hold only for a limited range. For considerations as are meant here probably only those equations of state can serve which are developed in series and made to agree with the observations over a very large range. Such equations of state which are very suitable for the calculation have been obtained in Comms. N°. 71 (June '01) and N°. 74 (Livre jubil. BOSSCHA p. 874) by combining as well as possible the known pieces of reduced equations of state for substances with different critical temperatures. As now we neglect the deviations from the law of corresponding states in the different substances and in their mixtures, we may without more base our considerations on a similar empirical reduced equation of state.

We have used a form which does not differ much from the more preliminary one given in Comm. N°. 74, which was indicated by *V* 2. We obtained it by making it agree with hydrogen 0° C. [1]), oxygen and nitrogen 0° C. (all of AMAGAT) and ether 0° C., 100° C., 195° C. (AMAGAT, RAMSAY and YOUNG). This polynomial, which contains for instance all the reduced temperatures which occur on the ψ-surface for ether and hydrogen at 0° C., will be designated by *VI* 1. As in Comms. N°. 71 and 74 we have for a substance with the critical temperature T_k and pressure p_k, if v is expressed in the theoretical normal volume,

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} + \frac{E}{v^6} + \frac{F}{v^8} \quad . \quad . \quad . \quad . \quad . \quad (I)$$

where at an absolute temperature of $t°$ above freezing-point

$$A = 1 + 0.0036625\, t$$

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[1]) For hydrogen the critical quantities of OLSZEWSKI are still used in the calculation.

[2]) Comp. Comm. No. 71 form. (10).

$$B = \frac{T_k^2}{p_k}\mathfrak{B}, \quad C = \frac{T_k^3}{p_k^2}\mathfrak{C}, \quad D = \frac{T_k^5}{p_k^4}\mathfrak{D}, \quad E = \frac{T_k^7}{p_k^6}\mathfrak{E}, \quad F = \frac{T_k^9}{p_k^8}\mathfrak{F}$$ [2]

and the reduced virial coefficients $\mathfrak{B}$, $\mathfrak{C}$, $\mathfrak{D}$, $\mathfrak{E}$, $\mathfrak{F}$ with $\mathfrak{t} = \frac{T}{T_k}$ are determined by

Reduced virial coefficients VI. 1.

$10^8\,\mathfrak{B}$	$189.523\,\mathfrak{t}$	-465.197	$-\ 21.291\frac{1}{\mathfrak{t}}$	$-184.410\frac{1}{\mathfrak{t}^3}$	
$10^{11}\,\mathfrak{C}$	$58.598\,\mathfrak{t}$	$+\ 23.55$	$-\ 14.451\frac{1}{\mathfrak{t}}$	$+159.936\frac{1}{\mathfrak{t}^3}$	$+\ 21.692\frac{1}{\mathfrak{t}^5}$
$10^{18}\,\mathfrak{D}$	$482.544\,\mathfrak{t}$	-379.527	$-\ 562.94\frac{1}{\mathfrak{t}}$	$+203.384\frac{1}{\mathfrak{t}^3}$	$-158.215\frac{1}{\mathfrak{t}^5}$
$10^{25}\,\mathfrak{E}$	$-1910.43\,\mathfrak{t}$	$+6797.37$	$-\ 5322\frac{1}{\mathfrak{t}}$	$+1143.47\frac{1}{\mathfrak{t}^3}$	
$10^{32}\,\mathfrak{F}$	$2052.16\,\mathfrak{t}$	-7742.41	$+7204.66\frac{1}{\mathfrak{t}}$	$-1843.03\frac{1}{\mathfrak{t}^3}$	$+\ 192.55\frac{1}{\mathfrak{t}^5}$

The calculations which show the systematical deviations of different normal substances from a similar equation of state are progressing.

§ 3. *Validity of the law of corresponding states for mixtures.* We can judge of this much better now than when Comm. No. 59*a* was written. The different applications given in this series of Contributions to the knowledge of VAN DER WAALS' ψ-surface [1]) seem to indicate that the deviations in mixtures of normal substances are not much larger than those which occur in normal substances inter se.

This is very striking, especially if we look for the basis of the law of corresponding states in the mechanical similarity of the movements, as a mixture even geometrically is not at all similar to a simple substance. It would seem to follow from this, that the linear quantity which determines the geometrical scale of similarity is a mean value of very different linear quantities, which play parts in different collisions. In that case we should have to attach to the "volume of a molecule" not so much a physical meaning and rather the geometrical meaning of a sphere drawn with this linear quantity as a radius.

To establish a systematical relation in the deviations of the mixtures of normal substances from the law of corresponding states is not likely to be feasible until this has been done for the devia-

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[1]) Comm. No. 59*b* KAMERLINGH ONNES and REINGANUM. Comm. No. 64, HARTMAN. Comms. Nos. 65, 81, Suppls. Nos. 5, 6, 7 VERSCHAFFELT. Comms. No. 75 and No. 79 KEESOM.

tions of the normal substances themselves. Still a beginning has been made with calculations which aim at a representation of those deviations.

§ 4. *Determination of the critical quantities of the mixtures taken as homogeneous.* As we neglect the deviations from the law of corresponding states, we may derive these quantities (occurring in the unstable region and hence not to be determined directly) from any observed range of the equation of state of any mixture.

The most obvious means is the shifting of logarithmical or partly invariant diagrams of isothermals in the area near the critical state. In Comm. N°. 59*b* it was applied to $\frac{pv}{T}$ isothermals with regard to $log\, v$, in Comm. N°. 65 to $log\, p$-isothermals with regard to $log\, v$, in Comm. N°. 88 to $log \frac{pv}{T}$-isothermals with regard to $log\, p$ and to $log \frac{pv}{T}$-isothermals with regard to $log\, v$. We may also imagine, however, that we have at our disposal a sufficient number of observations of another range. Thus, to give a simple instance, we know the critical temperature of a mixture if the temperature is found, at which under relatively small pressures it does not deviate from the law of BOYLE. And it is also possible that we may derive the data from observed conditions of coexistence. If the critical quantities for some mixtures are found, it will in graphical solutions be preferable to derive the T_{xk} and p_{xk} as a function of x also graphically. For the experiments of KUENEN have made us doubt whether the supposition made ad 3° is in general possible, and this doubt is strengthened by KEESOM's experiments.

If on the other hand we confine ourselves to qualitative investigations of mixtures of substances about which all the data which belong to the mixing are lacking, the supposition first lies at hand that $a_{12} = \sqrt{a_{11}\, a_{22}}$ [1]) and $b_{12} = \frac{1}{2}(b_{11} + b_{22})$.

§ 5. *The reduced* ψ*-curves.* In Comm. N°. 59*a* is briefly set forth how the different ψ_x-curves can be derived from those that have been calculated once for all for a simple substance. If we write a little more extensively, and if v_1 indicates such a large volume that with this the mixtures are in the ideal gaseous state,

$$\psi_{xv} = -\int_{v_1}^{v} p dv + RT\,\{x \log x + (1-x) \log (1-x)\}$$

omitting a temperature function linear in x. This with

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[1]) GALITZINE and D. BERTHELOT.

$$\frac{p_k v_k}{RT_k} = \frac{1}{C_4}, \quad \mathfrak{p} = \frac{p}{p_k}, \quad \mathfrak{v} = \frac{v}{v_k}\,.$$

may be easily transformed into:

$$\frac{\psi_{xv}}{RT} = -\frac{1}{C_4}\frac{1}{\mathfrak{t}}\int\limits_n^{\mathfrak{v}} \mathfrak{p}_{\mathfrak{t}}\,d\mathfrak{v} - \log\frac{p_{xk}}{T_{xk}} + x\log x + (1-x)\log(1-x) \quad . \quad (1)$$

if we put n a certain large number and neglect other temperature functions.

For convenience we may call $\int\limits_n^{\mathfrak{v}} \mathfrak{p}_{\mathfrak{t}}\,d\mathfrak{v}$ as function of $\mathfrak{v}$ the *curve of reduced free energy* for $\mathfrak{t}$. In the construction of each given ψ-surface occurs the group of curves of reduced ψ that lie between the extreme values of reduced temperature which occur on this surface.

On the planes $x = 0$ and $x = 1$ of the ψ-model we can draw the ψ-curves of higher and lower temperature. In passing over to a ψ-surface of higher temperature the ψ-curves (at least in the most common case) are moved on the surface from the side of the highest reduced temperature to that of the lowest, while the linear dimensions in the two directions ψ and v undergo a certain variation.

§ 6. *The ψ-surface for mixtures of methylchloride and carbon dioxide at* — 25° C. As an example of the application of the graphical method and the empirical reduced equation of state we have now chosen the prediction of the composition of the coexisting phases and the coexistence pressure for mixtures of methylchloride and carbon dioxide at — 25° C. We were led to this choice by the following considerations:

1°. we can derive the critical quantities from the experiments of KUENEN [1]), they lie tolerably far from each other, are given in Comm. N°. 59*b*, while for + 9.°5 C. a model has been constructed by HARTMAN;

2°. — 25° C. corresponds to the lowest reduced temperature for methylchloride for which the empirical reduced equation of state has been calculated;

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[1]) As critical quantities are used, comp. Comm. N°. 59*b*,

	x	T_{xk}	p_{xk}
carbon dioxide	0	303	72.2
	$^1/_4$	336	73
	$^1/_2$	363	71.8
	$^3/_4$	391	68.9
methylchloride	1	416	64.8

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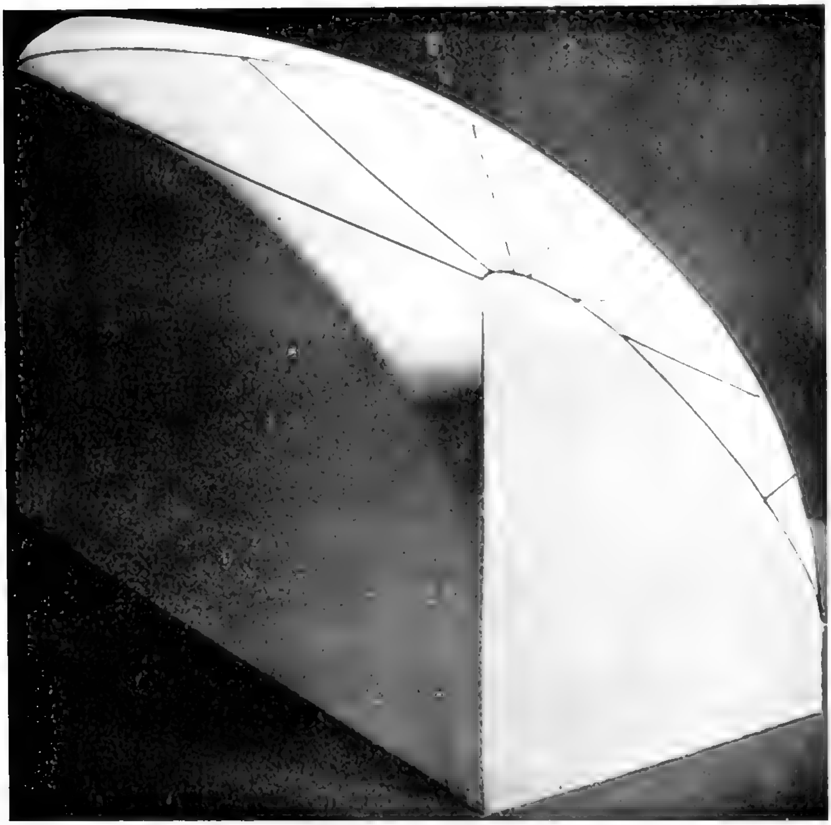

Fig. 1.

3°. with no other equation of state suitable for a calculation we can reach such a low temperature;

4°. VAN DER WAALS, for similar circumstances as are found on this surface, has also derived analytically the particularities in the coexistence-phenomena (Contin. II, p. 146, sqq.), and the agreement between these results and the observations of carbon dioxide and methylchloride, found partly already by HARTMAN at + 9.°5 C., will probably appear even more clearly at — 25° C.,

5°. finally that a paper on an experimental determination of these conditions of coexistence, which also VAN DER WAALS thinks very desirable (Contin. II, p. 154) will, as we hope, soon be published.

The numerical agreement becomes less accurate because methyl-chloride is not similar to ether, with which substance the empirical reduced equation of state for the reduced temperature of the methylchloride on this ψ-surface is made to agree whereas this is the case with carbon dioxide at the reduced temperature, which it has on this ψ-surface. An empirical reduced equation of state in good harmony for the reduced temperature of 0.6 with methylchloride of — 25° C., for the reduced temperature of 0.8 with carbon dioxide of — 25° C., would have been more favourable for the obtainment of a numerical agreement.

The plaster model obtained is represented on the annexed plate fig. 1, it is 0,7 m. long (v-axis), 0.4 m. high (ψ-axis), 0,3 m. broad (x-axis). The large dimension in length was made necessary by the great difference in density of the vapour phase between carbon dioxide and methylchloride.

The binodal curve and the tangents which connect two coexisting phases, the nodal lines, are found by rolling a piece of plate-glass. Fig. 2 shows the binodal curve with nodal lines, and also sections $v =$ const. projected on the $x\psi$-plane, fig. 3 the same on the xv-plane; fig. 4 shows the values of the pressure as function of the composition of the coexisting phases.

It is obvious that:

1°. the liquid ridge, i.e. that part of the surface which lies on the side of the small volumes, when the dimensions of the surface are not taken extraordinarily large, becomes very thin and the construction is practically possible only if we take for it a plate of uniform thickness (for instance a sheet of tin);

2°. while the tangent plane is rolled over the ridge of the liquid part and over the convex vapour surface, as the ridge near the pure methylchloride rapidly changes its direction, the point of contact moves a long way on the vapour branch of the binodal line, while the node on the liquid branch moves only a little. Hence in the directions of the tangents the double fan-shape is very prominent.

3°. the vapour branch of the binodal line in the projection is almost a straight line, and in agreement with this, according to VAN DER WAALS, the law of HENRY holds over the whole area of composition variation, while the vapour branch on the px-diagram is again almost a hyperbola.

§ 7. *Simplification of the determination of conditions of coexistence when the liquid phase is far below its*[1]) *critical temperature.* In order to determine the binodal line of the transverse plait we need only know two zones on either side of the plait. Let the *border curve of the homogeneous mixtures* be that curve which on the ψ-surface connects the vapour and the liquid phases in which the mixture, with the composition x taken as homogeneous, would be in equilibrium, then the binodal line wanted lies beyond [2]) this border curve, which it meets for the compositions 0 and x. Therefore it is more or less indicated, which zone on the vapour side we have to calculate.

If, as in the case of methylchloride and carbon dioxide at — 25° C. (or with ether and hydrogen at the ordinary temperature for the part of the ether side) the zone on the liquid side is shrunk to a plate, we need only calculate a single curve on the liquid side. For then the point of contact is so near the rim curve — that for which ψ is a minimum — that this curve may be substituted for the ψ-surface. The v of this curve may be easily derived for each x from the equation of state because $\left(\frac{d\psi}{dv}\right)_x = -p = 0$. With the value $v_{p=0}$ or $v_{p=0}$ we then find by integration $\psi_{p=0}$, while in the way as described in Comm. n° 66 § 5, [3]) the tangent through the point $\psi_{p=0}$, $v_{p=0}$ to the curve ψ_x on the vapour surface is drawn graphically and the vapour tension of the homogeneous mixture is obtained.

If we only wish to determine the pressure and the composition of the coexisting phases we have also a neglection of little importance in the supposition that $v_{liq x} = v_{liq_1}\, x + v_{liq_2}\, (1-x)$, in other words that the rim curve lies in a plane, while in many cases we may suppose that this plane coincides with the ψv-plane.

In order to find the conditions of coexistence we roll a plane (piece of plate-glass) over the rim of a thin plate cut after the calculated rim curve $\left(\text{better still the rim curve for } \frac{\psi}{RT}\right)$ and over a model

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[1]) Comp. § 1 footnote.

[2]) VAN DER WAALS Continuität II p. 100.

[3]) Arch. Néerl. Livre jubil. LORENTZ, p. 665.

(made for instance of plaster) of the vapour surface (which if we choose $\frac{\psi}{RT}$ and if we neglect the deviations from the law of BOYLE is always the same).

Instead of executing this process, which directly expresses the theory of VAN DER WAALS, on the plastercast, it may also be done entirely by a drawing on the plane as indicated in Comm. 59*a* § 6. The given construction now becomes much simpler if only we neglect the thickness of the ridge. In fig. 2 is drawn the rim curve of the liquid plate and the different sections $v =$ const. Then we combine the points where the sections have the same $\frac{d\psi}{dx}$ (or s comp. Comm. 59*a* § 8) as certain points of the rim curve to the *substitution curves* (comp. Comm. 59*a* § 5) which therefore always belong to the point with the given $\frac{d\psi}{dx}$ (or s) value on the rim curve (with mixtures taken as perfectly gaseous the substitution curves on the $x\psi$ projection are straight lines at right angles to the x-axis), connect the point on the rimcurve with different points of the substitution curve in the vapour zone, rotate the section with a plane at right angles with the xv-plane passing through the connecting line with the latter on the ψv-plane. The point where the section touches the connecting line gives the phase wanted, which is in equilibrium with the first.

The construction becomes still simpler if we neglect the distance from the rim curve to the plane $v = 0$. Then we need only transfer in fig. 2 the sections $v =$ const. by $A + \frac{B}{v} + \ldots$ lower, and draw a common tangent to the rim curves and each of these transferred lines in order to find x_{vap} and x_{liq}.

If finally we neglect the deviations from the law of BOYLE, we have only to move down unvaried the entire sections $v =$ const. of the vapour phase in fig. 2 in order to obtain the just mentioned system of curves, to which with the rim curves common tangents must be drawn in order to find x_{vap} and x_{liq}.

§ 8. *Application of the empirical law of reduced vapour tension of pure substances to the phenomena of coexistence in mixtures.* In § 7 we drew the attention to the circumstance that the liquid branch of the binodal line is obtained sufficiently accurately by substituting the rim curve, the points with $\left(\frac{d\psi}{dv}\right)_x = 0$, for the points with

$\left(\frac{d\psi}{dv}\right)_x = -p_{x coëx}$; in the same way we can put instead of these the points of the border curve with $\left(\frac{d\psi}{dv}\right)_x = -p_{x\, max}$, where $p_{x\, max}$ indicates the maximum vapour tension of the mixture x, called by VAN DER WAALS the coincidence pressure.

According to (1) the liquid branch of the binodal $\left(\frac{\psi}{RT}\right)$ as function of x is obtained as the sum of three terms.

The first

$$\varphi_{\alpha x} = x \log x + (1-x) \log (1-x) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is only determined by the molecular composition.

The second term is derived from the function

$$\varphi_{\beta\mathfrak{t}} = -\left[\frac{1}{\mathfrak{t}C_4}\int_n^{\mathfrak{v}} \mathfrak{p}\, d\mathfrak{v}\right]_{\mathfrak{v}=\mathfrak{v}_{liq.}\mathfrak{t}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

if as the higher limit in the integral we take the reduced liquid volume $\mathfrak{v}_{liq}$ of a simple substance at the reduced temperature $\mathfrak{t}$. We imagine that the function $\varphi_{\beta\mathfrak{t}}$ has been graphically represented once for all as a function of $\mathfrak{t}$.

The properties of mixtures of a given pair of substances are determined by

$$\varphi_{\gamma x} = -\log \frac{p_{xk}}{T_{xk}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

as a function of x and by $\frac{1}{T_{xk}}$ as a function of x. By combining the graphical representation of the latter with the graphical one of $\varphi_{\beta\mathfrak{t}}$ we obtain $\varphi_{\beta x}$, the graphical representation of the value which the quantity φ_{β} adopts with the value of $\mathfrak{t}$, which belongs to x. Then the liquid branch of the connodal line, and hence also the rim curve and the border curve are satisfactorily given by:

$$\varphi_{\alpha x} + \varphi_{\gamma x} + \varphi_{\beta x} = \frac{\psi}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The quantity μ, which plays such an important part in the theory of VAN DER WAALS about the coexisting phases is, while neglecting pv, determined for the liquid phase by $\varphi_{\beta x} + \varphi_{\gamma x} = \frac{\mu}{RT}$ and the ζ of VAN DER WAALS also with the same neglection (for which moreover a correction may easily be applied) $= \psi$.

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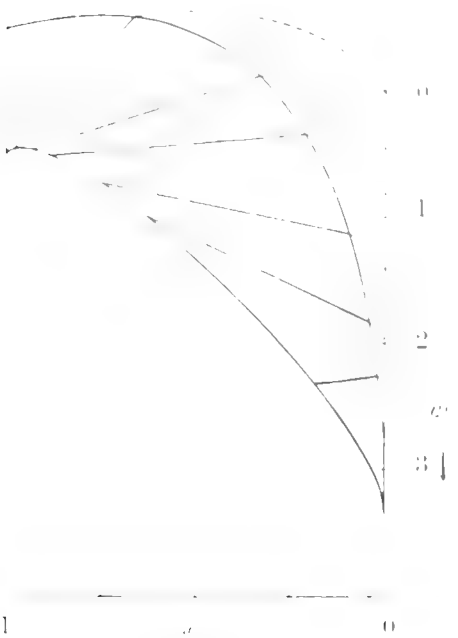

fig. 2.

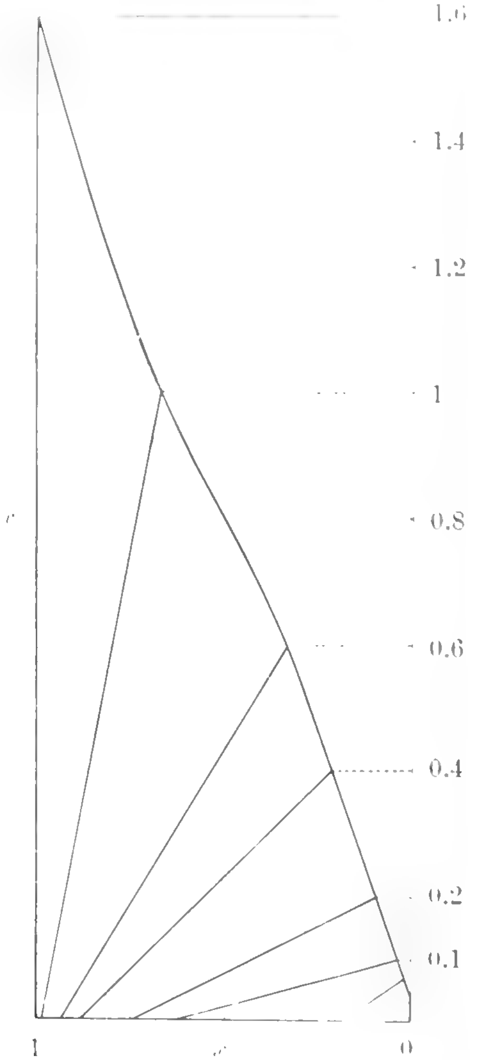

fig. 3.

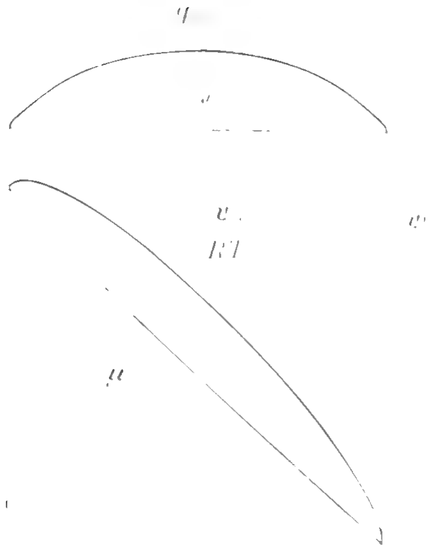

fig. 5.

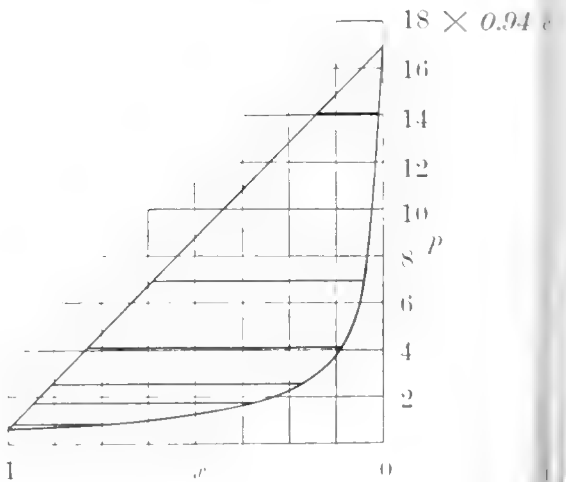

fig. 4

The considerations, constructions and figures given seem therefore suited to illustrate this part of the theory of VAN DER WAALS. $\frac{\mu}{RT}$ is in the case of carbon dioxide and methylchloride a curve slightly bent downwards. Fig. 5 shows how the liquid branch of the binodal line (the rim curve of the liquid part) $\frac{\psi}{RT}$ (comp. also the other figures) follows from the curve $\frac{\mu}{RT}$ and the curve φ_{xv}.

As to the calculation of $\varphi_{\mathfrak{xt}}$ it should be remarked that $\mathfrak{p}_{max}$ as function of $\mathfrak{t}$ is known through the vapour tension law, and hence also from the empirical equation of state $\mathfrak{v}_{vcp}$, and that $\int_{\mathfrak{v}_{liq}}^{n} \mathfrak{p} d\mathfrak{v} = \int_{\mathfrak{v}_{vap}}^{n} \mathfrak{p} d\mathfrak{v} + \mathfrak{p}_{max} (\mathfrak{v}_{vap} - \mathfrak{v}_{liq})$. Especially if $\mathfrak{v}_{liq}$ is small and hence $\mathfrak{v}_{vap}$ large, (so that at the utmost $\frac{B}{v}$ comes into consideration for the deviation from the ideal gas laws) this, when at the same time neglecting $\mathfrak{v}_{liq}$, leads to an important shortening of the calculations.

Neglecting entirely the deviation of the vapour phases from the ideal gaseous state and accepting for a simple substance $log\, \mathfrak{p}_{max} = - f \frac{1 - \mathfrak{t}}{\mathfrak{t}}$ we return to the developments given by VAN DER WAALS in his theory of the ternary mixtures [1]) in which theory many problems about the binary mixtures are developed more in detail.

Physics. — *"The determination of the conditions of coexistence of vapour and liquid phases of mixtures of gases at low temperatures."* By Dr. H. KAMERLINGH ONNES and Dr. C. ZAKRZEWSKI. Communication N°. 92 from the Physical Laboratory of Leiden by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of June 25, 1904).

§ 1. *Introduction.* The two methods for the determination of the molecular coexistence compositions x_l and x_v of the liquid and vapour phases of substances which are gaseous in normal conditions, it is known, can be described as follows. Following the first method we separate small quantities from the two phases at a series of coexistence

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[1]) Proceedings, May 31, 1902, p. 1, sqq.

pressures p and determine each time the composition of those two quantities either by chemical or by physical means.

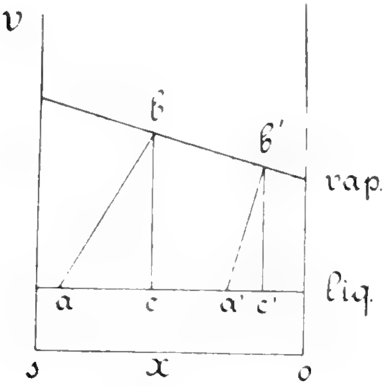

Fig. 1.

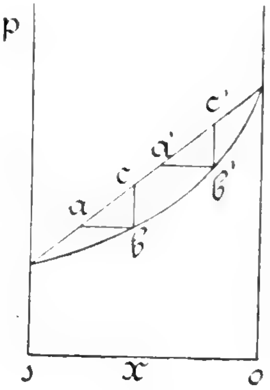

Fig. 2.

On the $v\,x$-projection of the binodal curve of the transverse plait on VAN DER WAALS' $\psi x v$-surface for a given temperature T, fig. 1, and also on the $p\,x$ diagram of that binodal line, fig. 2, two such phases are indicated by a and b, for instance. The determination of several pairs of values $a\,b$, $a'\,b'$ etc. gives then the whole course of p, x and v over the transverse plait for T.

If we follow the second method we observe in a series of mixtures with a known composition x, the beginning- and endcondensation phase and determine for them p and v, hence p_{lxT} and p_{cxT}, and v_{lxT}, and v_{cxT}. This investigation comprises each time the phases represented in fig. 1 and 2 by b and c. By combining the results $b\,c$, $b'\,c'$ etc. we can derive again the binodal line and hence the values for x_{lpT}, x_{vpT}, v_{lpT} and v_{vpT}. The application of this last method to low temperatures especially under moderate pressures, forms the subject of this paper.

It is possible to follow also the first method in the case of low temperatures as it has been applied by HARTMAN in Comm. N°. 43 (June '98) for ordinary temperatures. Yet as a rule the analysis of a gaseous mixture is much more difficult than the preparation of a mixture of a definite composition (among others, by means of the mixing apparatus of Comm. N°. 84, Dec. '02) and it is difficult to obtain certainty whether the quantities of vapour and liquid run off have the same composition as the phases which are brought to equilibrium by stirring.

Therefore it is important to solve the difficulty which accompanies the second method for temperatures below 43° (melting-point of mercury). When we made a first trial in this direction, a high degree of accuracy was not aimed at. In order to answer several questions the accuracy we have reached is sufficient and for the calculation of corrections for more accurate determinations it is quite sufficient.

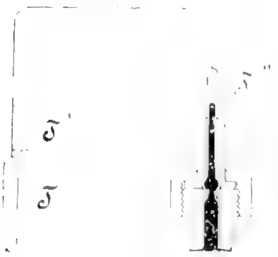

Fig. 3.

In our measurements we have used the apparatus which is represented schematically in fig. 3. It is in principle a twice bent tube of CAILLETET, of which one end is immersed in the cryostat of the temperature T and filled with a known quantity of a mixture of known composition x, which by forcing up mercury at the ordinary (or higher) temperature T'' is brought to condensation at T.

The mixture of which the quantity and the composition x are known, is then only partly contained in the vessel T at the temperature of investigation. Another part is necessarily in a tube at the ordinary or higher temperature T'' which is connected with the vessel by means of a capillary tube. This involves complications, not with regard to the measurement of the begin condensation pressure p_{cx} for the composition x; for until the condensation of the first traces of liquid, with respect to which the vapour is a phase of equilibrium, the composition of the vapour phase in the space at low temperature remains as it was originally, and hence the composition of the vapour phase of equilibrium is perfectly known; but with regard to the determination of the end condensation pressure p_{lx} of the mixture with the composition x. For we cannot condense the whole quantity of the mixture at low temperature. Hence the composition of the liquid phase at T, above which there is a vapour phase of a composition differing in the main from this or the original composition, is no longer indicated by the latter and therefore unknown.

We can, however, find this composition by applying a correction to the original composition x which, as long as the vapour phase occupies only a small volume and remains under a moderate pressure, is not very large (comp. § 5).

§ 2. *General arrangement of the measurements.*

A schematical representation of it will be found on Pl. I, fig. 1. The letters are the same as those used on the plates to which we shall refer.

The volumenometer E (with manometer M, comp. Comm. N°. 84, March '03, Pl. II, figs. 1 and 2) contains the gaseous mixture which has been prepared in it by means of the apparatus connected at r_6 and r_8 (comp. Comm. n°. 84). Through the cock r_9, the steel capillary g_1' and the steel three-way stopcock k (see Comm. N°. 84, Pl. I, fig. 2) it is led to the pressure tube b with calibrated stem (see Comm. N°. 69, April '01, Pl. II) placed in the pressure cylinder $\mathfrak{A}_1'$ (Comm. N°. 84, Pl. I) in order to be compressed by means of mercury from the pressure reservoir C_1' (comp. Comm. N°. 84). Thence through the three-way stopstock k and the steel capillary g_1'' it can be brought under pressure into one of the two apparatus $\mathfrak{D}$ or $\mathfrak{P}$. For the present, according as we wanted to determine either the begin or end condensation pressure p_{cxT} or p_{bxT}, we have connected either the capillary of $\mathfrak{D}$, $\mathfrak{D}_{b_2}$ or that of $\mathfrak{P}$ $\mathfrak{P}_{p_2}$ to the capillary g_1'' by means of sealing wax.

Different from Comm. N°. 84 Pl. I fig. 1 the mercury of the pressure cylinder (see our plate fig. 1) is also connected by means of n with that of a manometer to determine the pressure in $\mathfrak{D}$ or $\mathfrak{P}$.

By means of the three-way stopcock k the apparatus $\mathfrak{D}$ or $\mathfrak{P}$ may also be connected directly with the volumenometer and then the pressure is measured by means of M.

A detailed representation of the apparatus $\mathfrak{D}$ and $\mathfrak{P}$ is given in figs. 2 and 3 of Pl. I and a description in §§ 4 and 5. In both cases the glass tube to which the mixture which is to be investigated is conducted by means of the capillary g_1'', p in $\mathfrak{P}$ and a in $\mathfrak{D}$, is immersed in a cryostat where the desired temperature is kept in the same way as described in Comm. N°. 83 (Feb. and March '03).

The regulation is brought about for $\mathfrak{P}$ through the exhaust-tube T_{12} and for $\mathfrak{D}$ through the tubes f_4' and m_2. In our measurements we brought liquid methylchloride into the cryostat and the temperature was regulated according to the indications of an alcohol thermometer.

By means of the cock r_8 the volumenometer E is connected not only with the gasreservoirs but also with the mercury airpump so that also the pressure-tube and the test-tube in $\mathfrak{D}$ and $\mathfrak{P}$ can be exhausted. We shall not expatiate on the process of filling the apparatus with a definite quantity of the desired mixture and of measuring any quantity of gas which we allow to escape from them. For the rest we refer to Comm. N°. 84 for the volumenometer and the mixing apparatus, to Comms. N°. 69 and N°. 84 for the pressure cylinder and its appurtenances, to §§ 4 and 5 and Comm. N°. 83 for the cryostats.

§ 3. *Determination of the molecular volume of the coexisting phases.* As we did not aim at a very high degree of accuracy a few remarks will be sufficient. As to the liquid phase: with the limitations and conditions to be treated in § 5, part of the gaseous mixture in the apparatus 𝔓, called for shortness the piezometer, may by condensation attain a liquid phase of a composition which, as said in § 1, is derived from x of the original gaseous mixture by a correction. Measurements with the volumenometer yield the volume that the liquid phase would occupy in its gaseous state. And by means of the divisions at p_5 and p_6 Pl. I fig. 3 we read the volume of the liquid phase itself. The molecular volume of the gaseous phase may best be derived from the coexistence pressure and from isothermals which with not too small pressures can be determined after the method of Comm. N°. 78, April '02, if necessary with the dew-point apparatus 𝔇 itself. With not too large pressure it will in most cases be possible to apply the correction for the deviation from the law of BOYLE-GAY-LUSSAC-AVOGADRO by means of the empirical reduced equation of state (Comm. N°. 71, June '01) according to the law of corresponding states.

§ 4. *Beginning of the condensation.* In order to determine this we have applied the principle of REGNAULT's hygrometer [1]). To this end we observe the first condensation which is formed in a part of the apparatus of which the temperature is a little below that of the surrounding gaseous mixture when the gaseous mixture is brought to the begin condensation pressure. In order to be able to observe a very small condensation we have taken for the place of the lowest temperature a shining mirror, and next to it is placed another mirror which is not cooled.

The apparatus is blown of one piece in the same way as an ice calorimeter of BUNSEN. The outer space a has a capacity of about 20 c.c. and is provided with a capillary to which the steel capillary g'_1, through which the gaseous mixture is led, may be sealed on. One of the mirrors d is sealed on to the bottom. The inner tube c_2 carries at c_1 the second reflecting surface and serves at the same time as a cryostat to keep the temperature of this surface constant, a little below the temperature of the gaseous mixture.

To this end we have devised in the same way as for the outer cryostat the cover m_1, fitting hermetically on the tube c_3, the small stirrer h_1 of which the rod h_2 projects through an india-rubber tube

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[1]) BATTELLI, (Ann. de Chim. et de Phys. ser. 6, vol. 25, p. 59, 1892), has found that for pure substances the deposition of liquid on a not cooled mirror placed in the vapour is a suitable means for the determination of the condensation point.

as in Comm. N°. 83, and the thermometer i sealed on to m_1 while the vapour of the liquid gas in e_2 is exhausted through m_2.

On the tube e at e_1 the glass cap f_1 is sealed on, through which with an india-rubber stopper the capillary connected to c passes at f_2. This cap forms the cover of the larger cryostat. Through this the apparatus has become very firm and very easy to handle. The capillary b_1 is protected against the stirrer by a metal frame n.

Through the cover at f_3 pass the wires by which the stirrer is suspended. At f_4 the vapour of the bath of liquefied gas is exhausted.

The surfaces of d and e_1 are made reflectors by platinizing them at a redhot temperature with platinum chloride in camomileoil. Though the platinum surface is not so shining as that of a silver mirror, yet the advantages of platinum for this purpose are evident.

The regulation of the temperature in the two cryostats of the apparatus is performed by means of the same exhaust-pump that keeps the pressure constant by means of a pressure regulator (according to the principle of Comm. N° 87, § 3, March '04) in a main tube which branches off into two exhaust-tubes, each shut with a cock.

By adjusting these cocks we can take care that the temperature in the inner cryostat is a little below that of the outer cryostat. What difference of temperature can be kept constant in the two depends on the temperature itself and on the liquid gas.

In measurements to be described in the continuation of this paper the temperature of the large cryostat was — 25°.0 C., that of the small one — 25°.1 C. The required decrease of pressure in the main exhaust-tube could be easily kept up (boiling-point methylchloride — 23° C.) with a water airpump.

The pressure regulator was adjusted at about the pressure belonging to — 25° C. By means of the regulating cocks an assistant took care, as signs were given by another assistant according to the thermometer readings, that both temperatures, hence also the difference between them, remained constant. This could be attained to within 0°.05 C.

The accuracy which we can reach in the determination of the dew-point with our apparatus depends in the first place on the difference of temperature in the two cryostats. As a matter of course it is smaller as the temperature coefficient of the begin condensation pressure is larger. At a given difference of temperature it increases according to the difference of the pressures at which the condensation appears or disappears. The amount of this difference is also determined by the illumination and this is much impaired by the two walls of the cryostat. In our experiments, observations made with the naked eye with side-illumination of the mirror proved to be the best. The difference ranged between limits which amounted to $2\,^{0}/_{00}$ of the pressure. The optical part of the method may certainly be much improved. The accuracy attained will, however, be sufficient in many cases.

Adiabatic pressure-variation must naturally be avoided. Yet all such difficulties arise also with measurements at ordinary temperature. With a view to the large dimensions of the vapour space a we have not made use of a stirrer and have tried as much as possible to surmount the difficulties by operating slowly.

§ 5. *Determination of the end condensation pressure.* For this determination the mixture, after the begin condensation pressure is measured, is led back to the volumenometer, the dew-point apparatus is disconnected from the steel capillary and in its place the piezometer p in 𝔓 Pl. I figs. 1 and 3 is connected with the steel capillary q''_1. The piezometer consists of a wide glass tube p_5 Pl. I fig. 3 fastened to a capillary, both graduated and calibrated. The dimensions are chosen with regard to the quantities of gas that may be intended for the measurements. If these are decided upon, the exact quantity of gas, necessary for filling the piezometer at a suitable position of the mercury in the pressure tube b with liquid to near the end of the capillary, must be determined before each determination by means of a preliminary experiment.

The equilibrium of the phases in p_5 is reached by means of a magnetic stirrer q moved by the coil S. The immediate effect of this coil is not sufficient to move the stirrer forcibly through the liquid meniscus. Therefore a soft iron tube z_1 with a groove z_2 which enables us to read on p_6, is moved up and down at the same time with the coil.

This movement ought to be independent from that of the stirrer in the cryostat. But as we did not require a very high degree of accuracy in our experiments we have for simplicity devised the iron tube z as a connection between the upper and the lower part χ_{02} and χ_{04} of the ringshaped valved stirrer (comp. Comm. N⁰. 83). This is moved up and down mechanically and with the hand in turns, one time to stir the liquid bath, the other time to establish equilibrium between the liquid and the vapour while we simultaneously move the magnetizing coil S.

The essential difference between a determination of the end condensation pressure in our apparatus and that in a CAILLETET tube does not lie so much in the circumstance that we do not liquefy the whole quantity of gas, as in the fact that, as remarked in

§ 1, the temperature is different in the different portions of the gaseous mixture. The portion (see fig. 3 § 1) at the temperature of investigation T is separated from that at ordinary (or higher) temperature T''' by a series of layers (in the capillary) of which the temperatures range from the highest T''' to the lowest T. One of these temperatures we shall call T''.

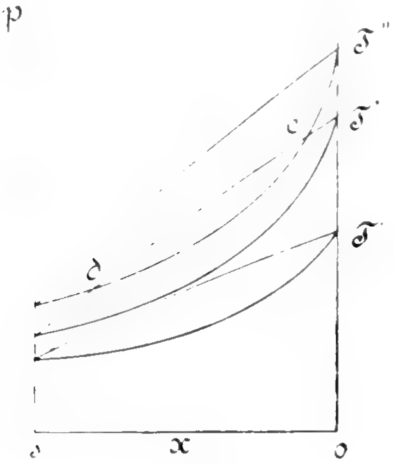

Fig. 4.

This circumstance involves several restrictions and conditions in the application of the method.

In order to make measurements possible for all compositions x the temperature T''' must be taken or raised so high above T, that on the px-diagram (fig. 4) the vapour branch of the binodal curve of T''' does not intersect the liquid binodal curve T. Then we need not fear that condensation begins at T''' while condensation takes place during the transfer of the mixture from the compression tube (or perhaps the volumenometer) to the piezometer. At T''' we then always have a gaseous mixture of the original composition. When the above-mentioned curves intersect, as is represented in fig. 4 for the case of T'', we can make measurements only for the compositions represented by points outside the region included approximately between d and e.

Even if, without condensation taking place in the compression apparatus (or perhaps volumenometer) the gaseous mixture can be transferred to the piezometer, the part of the capillary where the temperature falls from T''' to T still offers another difficulty of the same kind. Here we necessarily find temperatures T'' at which the vapour branch of the binodal curve of T''' intersects the liquid branch of T''. If drops are formed at T'', the composition x_{lpT} of the liquid belonging to the observed coexistence pressure can no longer be indicated. By flowing down and by distillation (the effect of capillarity exceeds that of gravitation) the drops gradually pass over into the liquid phase at T, if care is taken by means of the cock k (see Pl. I fig. 1) and by adjustment of the pressure in b (see Pl. I fig. 1)) that gas streams only into and not out of the piezometer, until finally when we stir with open cock k it appears that equilibrium is reached and the capillary contains vapour only.

In order to further the distillation and the disappearance of the condensation, it is desirable that the capillary at the place where the temperature is between T' and T''' should not be too narrow. Moreover the capillary is surrounded by an air jacket p_4, made of a glass tube tightly closed with india-rubber rings p_8 and fish-glue. To avoid diffusion the other portion of the capillary g''_1 must be narrow.

If by previous determinations with the dew-point apparatus we have determined x_{vpT} (as a first approximation it will in some cases be possible to use a preliminary ψ-surface as constructed in Supplement N°. 8 see p. 222), it is easy to apply the correction necessary to derive the composition of the investigated liquidphase at T from x_1, the original composition. On the piezometer divisions the volume of the vapour is read. Let V_v be this volume reduced to normal circumstances and corrected for the first virial coefficient B (comp. for instance the continuation of this paper), let V be the entire volume of vapour and liquid, measured and corrected in the same way, then $V_l = V - V_v$ is the volume of gas, measured and corrected in the same way, which would form the liquid phase.

Hence:

$$X_{lpT} = \frac{X_1 V - X_{vpT} V_v}{V - V_v} = X_1 + \frac{V_v}{V} (X_1 - X_{vpT}) + \ldots$$

If we operate under moderate pressures, the correction will be always small and even if x_{vpT} is not very accurately known, it can be applied in a satisfactory way.

Astronomy. — "*A new method of interpolation with compensation applied to the reduction of the corrections and the rates of the standard clock of the Observatory at Leyden,* HOHWÜ 17, *determined by the observations with the transit circle in* 1903." By J. WEEDER. Communicated by Dr. H. G. VAN DE SANDE BAKHUYZEN.

§ 4. In the Proceedings of Nov. 29, 1902 occurs a paper "On interpolation based on a supposed condition of minimum," of which the present paper is to be considered as a continuation; this explains the numbering of the sections. In order to interpolate between the ordinates S belonging to the abscissae $t = a, b \ldots y, z$, I have there determined the interpolating curve for which the total sinuosity $Is = \int_a^z \left(\frac{d^2S}{dt^2}\right)^2 dt$ has the least value. I found that between two successive points which are well defined by observations this curve satisfies an equation of the third degree $S_t = S_q + g_q\,T + c_q\,T^2 + e_n\,T^3$, where $T = t - q$ and $q < t < r$, and has moreover the properties that besides S also $\frac{dS}{dt}$ and $\frac{d^2S}{dt^2}$ are continuous, while at the ends of this curve $\frac{d^2S}{dt^2}$ is zero; these data appeared to be sufficient for a definite determination of such an interpolating curve.

In the same paper in § 3 I have referred to the problem of compensation for the case that the results of the observations S are affected with errors.

Now I shall describe how that problem was solved and I shall apply this method of compensation to the corrections and the rates of the clock Honwü 17 during the period Jan. 14, 1903—Jan. 14, 1904.

For the sake of the compensation I have used instead of the supposition on which my interpolation was based, another hypothesis which covers more, and for this purpose I have accepted that the probability of a group of corrections S is proportional to $e^{-\lambda I_S}$, where the factor λ is independent of the intervals between the observations; the original condition of minimum is a result of this hypothesis, if we accept as interpolated for the time t that value which (considered as result of observation) makes the expression $e^{-\lambda I_S}$ as large as possible.

As formerly I have called the error of observation in S_q: f_q and the real clock correction L_q, so that $L_q = S_q - f_q$, meanwhile, I venture to use the same letters f_q and L_q in the sense of most probable values of the errors and measured quantities, although there is naturally a difference between the latter quantities and the real values.

As soon as we have to do with errors of observation we must substitute I_L for I_S in the expression for the probability of a group.

The probability that the errors $f_a, \ldots f_p, f_q, f_r, \ldots f_z$ respectively, occur in the observations, must in those cases where the continuity of the observed quantity agrees with the hypothesis made above, be proportional to the product of $e^{-\lambda I_{S-f}}$ and $e^{-\frac{1}{2}\Sigma\frac{f_q^2}{\mu_q^2}}$; in the latter expression μ_q represents the value of the mean error in S_q. The system of errors of greatest probability satisfies the condition:

$$\lambda\, I_{S-f} + {}^1/_2\, \Sigma \frac{f_q^2}{\mu_q^2} = \text{minimum},$$

whence for each of those most probable errors the relation:

$$\lambda \frac{\partial I_{S-f}}{\partial f'_q} + \frac{f'_q}{\mu_q^2} = 0.$$

Theoretically $\frac{\partial I_{S-f}}{\partial f'_q}$ contains all the unknown quantities f', practically, however, besides f'_q only the 3 or 4 preceding and following ones, since, owing to the small coefficients, the other terms may be neglected. The most probable errors occur in it in a linear form, and hence the complete system of error-equations is sufficient to determine them all.

§ 5. In this manner I have treated 61 clock corrections determined by observations made from Jan. 14, 1903 to Jan. 14, 1904 by E. F. van de Sande Bakhuyzen and A. Pannekoek. This problem was somewhat complicated because the observed rates depend on the pressure and the temperature of the air in which the pendulum moves. An increase of atmospheric pressure of 1 mm. mercury gives to the clock rate a retardation of 0.015 seconds a day, while an increase of temperature of 1 deg. C. accelerates the rate by about 0.030 seconds a day.

I have found that also the differences of temperature observed in the clockcase have a perceptible influence on the rate[1]).

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[1] This temperature gradient forms a new element in the reduction of the clock rates, in so far as at the Leyden Observatory it was not accounted for until 1903. Although in the clockcase of Hohwü 17 two thermometers have been suspended at different heights since 1866, the influence of the temperature gradient did not clearly appear from the earlier observations owing to the inaccuracy of those readings. Although Dr. E. F. van de Sande Bakhuyzen detected a yearly periodicity in the differences between those thermometers, which might explain the phenomenon of the yearly periodicity in the rates (Proc. Kon. Ak. v. W. 1902) yet at that time he still doubted of their reality, because the thermometers were graduated according to Réaumur and the accuracy of the reader in estimating the tenth parts was insufficient to warrant an inequality of 0.1° R. in the monthly means of the difference in temperature.

In order to obtain certainty on this point, two thermometers were placed into the clockcase in January 1903, which were divided into tenth parts of a centigrade and had been compared with each other beforehand by the director of the Observatory; since that time they have been read with accurate estimation to a hundredth part of a centigrade.

The vertical distance between these thermometers is 63 cm. It soon appeared that in the clockcase there is a variable temperature gradient, which cannot but cause a considerable variation of rate.

In July 1903 it was derived from observations that a difference between the

A temperature gradient in vertical direction of 1 centigrade per meter causes, roughly calculated, a variation in rate of $0^s.25$.

thermometers (upper—lower) of one centigrade corresponds with a retardation of $0^s.30$ a day.

This difference of temperature, apart from variations in connection with meteorological conditions, clearly shows a yearly periodicity; in winter it is small, in summer on some days it increases to above 0°.50 C. It can hardly be doubted that, at least to begin with December 1898, the yearly periodicity must be ascribed to the temperature gradient; for it is since that date that the standard clock has been placed in the vestibule in a niche cut out from the pier of the 10-inches refractor. Since about March 1899 the place on the Eastern pier in the transit room where the standard clock hung during the former periods 1862—'74 and 1877—'98, treated by E. F. VAN DE SANDE BAKHUYZEN, has been occupied by the clock Hohwü 46 with a Riefler-pendulum.

In order to obtain accurate data about the temperature gradient also for this place, two thermometers, which had been compared with each other and were graduated to tenth parts of a centigrade were suspended in the case of Hohwü 46 at a vertical distance of 65 cms. on February 27, 1903. It appeared that here the differences in temperature were in general greater than in the pier-niche, and in July 1903 it was derived from the observations that a difference of temperature between the thermometers of 1 centigrade corresponded with a variation of $0^s.40$ in the daily rate of this clock.

A yearly periodicity in the temperature gradient appeared also distinctly in Hohwü 46, as will be seen from the following monthly means, which are given by the side of those of Hohwü 17.

		Hohwü 17.	Hohwü 46.
1903	March	+0°.14	+0°.25
„	April	+ 0.09	+ 0.16
„	May	+ 0.31	+ 0.42
„	June	+ 0.28	+ 0.37
„	July	+ 0.29	+ 0.32
„	August	+ 0.18	+ 0.22
„	September	+ 0.16	+ 0.26
„	October	+ 0.06	+ 0.12
„	November	+ 0.02	+ 0.10
„	December	+ 0.01	+ 0.03
1904	January	— 0.02	+ 0.08
„	February	+ 0.05	+ 0.12

Moreover in the temperature gradient in the clockcase in the transit room a daily inequality was observed, which was hardly perceptible in the niche.

In the case of Hohwü 46 the mean values of the temperature gradient from 0^h to 12^h mean time, are regularly greater than the mean values from 12^h to 24^h mean time. From the differences between these mean values in connection with the differences in the relative rates of the two clocks for the corresponding half days I could derive the influence of a variation in the temperature gradient on the rate of Hohwü 46 for a shorter period.

The investigation is not yet finished, but in connection with the theoretical

A 4th inequality in the rates was due to the difference between the personal equations of the observers. From direct determinations we have obtained the following differences in the clock corrections:

	B — P
1 April 1901	— $0^{s}.201$
18 March 1903	— 0.275
15 March 1904	— 0.224

For the time being I have adopted for this difference during the period Jan. 14, 1903—Jan. 14, 1904: — $0^{s}.250$ and have reduced the clock corrections determined by P. to B.'s system. Besides the corrections for atmospheric pressure, temperature and difference in temperature I introduced a correction for the assumed personal equation; these 4 unknown quantities are introduced into the equations and will be derived from the observations. I represented them by x, y, z and u and chose the following units so that these quantities should have about the same values: for atmospheric pressure (B) the unit $= {}^1/_4$ mm. mercury of 0° C., for temperature (ϑ) the unit $= {}^1/_{10}$ degree Celsius, for difference in temperature (V) the unit $= {}^1/_{100}$ degree Celsius, for clock rates per day the unit $= {}^1/_{1000}$ second of time; x, y and z represent the influence of each of the three units on the daily rate, expressed in thousandth parts of a second of time, while u is the 10th part of the correction for the assumed difference in the personal equations of the observers during the same unit of time, viz. $B - P = -250 - 10\,u$.

§ 6. The observed clock corrections were reduced beforehand to midnight of the data of observation. This was done with clock rates according to a preliminary formula with due regard to atmospheric pressure, temperature and temperature difference in the period from the instant for which the clock correction was determined to midnight. This formula is derived from observations during the first half of 1903, it has been regularly tested by each new determination of the clock error, and has proved very satisfactory for the purpose set here.

$$\text{Constans} = \text{daily rate} - \overset{s}{0}.0157\,(\text{bar.} - 760) + \overset{s}{0}.032\,(\text{temp.} - 10^\circ\,\text{C.})$$
$$- \overset{s}{0}.31\,(\text{temp. difference}).$$

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development of B. WANACH of Potsdam on the influence of the temperature-gradient on clocks (A. N. Nrs. 3967—68) I think it worth mentioning that in this way I found that per 1 centigrade difference in temperature between the thermometers, there was a variation in rate of about $0^{s}.80$, twice the amount derived from the before mentioned observations.

From readings of the barometer and the thermometers, daily means of atmospheric pressure, temperature and difference of temperature from midnight to midnight have been derived. Let the clock corrections at midnight be S, and the mean daily rates in the intervals between the successive determinations of the clock corrections be Q, in accordance with the letters previously used by me. From the said daily means, the mean values of the atmospheric pressure, of the temperature and of the difference in temperature were derived for the same intervals. In the interpolation these quantities correspond with Q, hence I call them Q^B, Q^ϑ, Q^V. For the barometer readings I used the deviations from 76 cms. The temperatures ϑ are those of the upper thermometer.

In this paper I shall also use the letters S^B, S^ϑ, S^V to indicate quantities that can be computed for each observation by taking the sum of the daily means of B, ϑ and V, to begin with a certain date, say Jan. 14, 1903 till midnight of the day for which the clock correction is determined. S^P denotes a value which is + 10 for each observation of PANNEKOEK, and zero for each observation of BAKHUYZEN, and the series Q^P relates to the series S^P in the same way as each series Q relates to the series S according to the formula $Q_n = \dfrac{S_r - S_q}{n}$. S_r and S_q are two successive quantities of the series, and n is the interval between them expressed in days.

$$L = S - x\,S^B - y\,S^\vartheta - z\,S^V - u\,S^P - f$$

must then be considered as a formula for a reduced and compensated clock correction.

Each of the letters L, S, f represents a series of discrete values, one for each observed clock correction, but by means of the interpolation along the least sinuous line they can also be taken as continuous variable quantities of which the derivatives of the first and second order also vary continuously, but of which the derivatives of the third order vary abruptly. To determine such a variable, say S^B, for the instant $t = q + T$ between the epochs q and r of the determinations of the clock correction, we use according to § 4 the formula

$$\overset{B}{S}_{q+T} = \overset{B}{S}_{q} + \overset{B}{g}_{q}\,T + \overset{B}{c}_{q}\,T^2 + \overset{B}{e}_{n}\,T^3,$$

where q is the epoch of the observation which immediately precedes t. The coefficients g^B c^B e^B can be derived from the series Q^B if we use the formulae C in § 2 of the previous paper on this method of interpolation.

Taking the quantities L, S, f in the sense as explained above we can develop the total sinuosity of the reduced and compensated correction as follows:

$$I_L = \int_a^z \left(\frac{d^2 L}{dt^2}\right)^2 dt = \int_a^z \left[\frac{d^2(S-f)}{dt^2} - x\frac{d^2 S^B}{dt^2} - y\frac{d^2 S^\vartheta}{dt^2} - z\frac{d^2 S^V}{dt^2} - u\frac{d^2 S^P}{dt^2}\right]^2 dt.$$

In order to give the greatest probability to the series L we must choose x, y, z and u so, that the partial derivatives of I_L with regard to each of these are zero; i.e. that they satisfy the following relation:

$$\int_a^z \left[\frac{d^2(S-f)}{dt^2} - x\frac{d^2 S^B}{dt^2} - y\frac{d^2 S^\vartheta}{dt^2} - z\frac{d^2 S^V}{dt^2} \quad u\frac{d^2 S^P}{dt^2}\right] \frac{d^2 S^B}{dt^2} = 0\,,$$

and 3 others, which we obtain by substituting for the last factor $\frac{d^2 S^B}{dt^2}$, successively $\frac{d^2 S^\vartheta}{dt^2}$, $\frac{d^2 S^V}{dt^2}$ and $\frac{d^2 S^P}{dt^2}$.

Definite integrals, such as $\int_a^z \frac{d^2 S^B}{dt^2} \cdot \frac{d^2 S^\vartheta}{dt^2}\, dt$, which here occur as coefficients, can be computed in the following way:

$$\int_a^z \frac{d^2 S^B}{dt^2}\, d \cdot \frac{dS^\vartheta}{dt} = \left[\frac{d^2 S^B}{dt^2} \cdot \frac{dS^\vartheta}{dt}\right]_a^z - \int_a^z \frac{dS^\vartheta}{dt}\, \frac{d^3 S^B}{dt^3}\, dt =$$

$$= 2\, [e^B\, g^\vartheta]_a^z - 6\, \Sigma\, e_n^B\, (S_r - S_q)^\vartheta = 2\, [e^B\, g^\vartheta]^z - 6\, \Sigma\, n\, e_n^B\, Q_n^\vartheta.$$

If in the last term we also substitute for

$$3\, n\, e_n^{\;B}\,,\ (c_r - c_q)^B\,,\ \text{we have}$$

$$\tfrac{1}{2}\int_a^z \frac{d^2 S^B}{dt^2}\, \frac{d^2 S^\vartheta}{dt^2}\, dt = [e^B\, g^\vartheta]^z + \Sigma\, Q_n^\vartheta\, (c_q - c_r)^B$$

and after interchanging the indices B and ϑ in the second member also

$$[e^\vartheta\, g^B]^z + \Sigma\, Q_n^B\, (c_q - c_r)^\vartheta.$$

I have computed these coefficients according to both formulae, and thus obtained a rigorous test.

At the beginning and the end of the interpolation the quantities e are always zero, so that products such as $e^B g^\vartheta$ would be zero at either end. With a view, however, to the continuation of this computation for next year, I have not closed the interpolation-computation for the atmospheric pressure, the temperature, etc. on January 14, 1904. Hence on Jan. 14, 1904 c^B, c^z, c^V, c^P differ from zero and in the formula I had to retain the term for the end.

In integrals such as $\int_a^z \frac{d^2\,SB}{dt^2}\,\frac{d^2\,(S-f)}{dt^2}\,dt$ I first put all errors equal to zero and computed the known terms of the four equations according to formulae of the form:

$$\tfrac{1}{2}\int_a^z \frac{d^2\,SB}{dt^2}\,\frac{d^2\,S}{dt^2}\,dt = [c^B\,g]^z + \Sigma\,(c_q - c_r)^B\,Q.$$

By solving these equations, I have obtained preliminary values for x, y, z and u, and in the way to be explained in § 7, also for the most probable errors f; from the mean daily rates computed with these preliminary values, using the formula

$$Q_L = Q - x\,Q^B - y\,Q^z - z\,Q^V - u\,Q^P - \frac{f_r - f_q}{n}$$

I have derived as a second approximation the corrections x, y, z and u to these preliminary values. The influence of those corrections on the most probable errors was of little importance.

Integrals such as $\int_a^z \left(\frac{d^2\,S}{dt^2}\right)^2 dt$ have been computed twice, first according to the formula for $\tfrac{1}{2}\int_a^z \frac{d^2SB}{dt^2}\,\frac{d^2S^z}{dt^2}\,dt$

$$\tfrac{1}{2}\int_a^z \left(\frac{d^2\,S}{dt^2}\right)^2 dt = [c\,g] + \Sigma\,Q_n\,(c_q - c_r)$$

and secondly according to the formula, deduced in § 2

$$\int_a^z \left(\frac{d^2\,S}{dt^2}\right)^2 dt = \frac{4}{3}\,\Sigma\,n\,(c_q^2 + c_q\,c_r + c_r^2)$$

The following are the 4 equations expressed in numbers:

$$\begin{array}{rrrrrrr}
5460\,x & -\ 252\,y & -\ 14\,z & +\ 59\,u & = & +\ 21664 & -\ 145 \\
-\ 252\,x & +\ 952\,y & +\ 512\,z & -\ 8\,u & = & -\ 1757 & -\ 88 \\
-\ 14\,x & +\ 512\,y & +\ 571\,z & -\ 22\,u & = & +\ 383 & +\ 87 \\
+\ 59\,x & -\ 8\,y & -\ 22\,z & +\ 101\,u & = & -\ 101 & -\ 21
\end{array}$$

The second members are written in 2 parts. The first part is derived from the observed rates Q, the second from the preliminarily reduced compensated rates Q_L. The solution of the two sets yielded :

$$
\begin{aligned}
x &= +3.90 - 0.04 = +3.86 \\
y &= -2.30 - 0.34 = -2.64 \\
z &= +2.72 + 0.46 = +3.18 \\
u &= -2.86 - 0.09 = -2.95
\end{aligned}
$$

According to these results the influence on the daily clock rates of the atmospheric pressure per 1 mm. mercury of 0° C. is $+ 0^{s}0154$, of the temperature per 1 centigrade (upper thermometer) $- 0.0264$, and of the difference in temperature per 1 centigrade (upper—lower) $+ 0{,}318$, while for the personal difference BAKHUYZEN—PANNEKOEK in the clock corrections is found $- 0^{s}.220$.

Table I contains the values required for the said computations: for each interval between two consecutive determinations of the clock correction : the number of days n, the observed clock rate Q, the values Q^B, Q^ξ, Q^V and Q^P, and also the values $(c_q - c_r)^B$, $(c_q - c_r)^\xi$, $(c_q - c_r)^V$, $(c_q - c_r)^P$. To this must be added in order to render the computation possible the values for the last epoch Jan. 14, 1904, :

$$
\begin{array}{llll}
g^B = -14.0 & g^\xi = +57.7 & g^V = -3.1 & g^P = +2.4 \\
c^B = +1.09 & c^\xi = +2.01 & c^V = +0.76 & c^P \quad +0.54
\end{array}
$$

$g = - 146$, adopted in case we use the series of the observed clock rates Q.
$G = - 194$, ,, ,, ,, ,, ,, preliminarily reduced Q_L.

§ 7. Here follows the reduction of the relations between the most probable errors and the determination of the latter according to these relations.

Sub § 5 I have derived for each error f_q the relation :

$$
\lambda \frac{\partial I_L}{\partial f_q} + \frac{f_q}{\mu_q^2} = 0 \quad \text{or} \quad \frac{\partial I_L}{\partial f_q} + \frac{1}{\lambda \mu_q^2} f_q = 0
$$

I have thought myself justified in adopting the same value for the mean errors in the determinations of the clock correction, although for 1 of those corrections only 2 stars, for 13 corrections 4 stars, and for all the others 3 stars were observed, since the difference in accuracy resulting from the different numbers of stars is relatively

TABLE I.

Intervals in days.	Observed clock rates.	Atmospheric pressure (B).		Temperature (ϑ).		Temperature difference (V).		Personal equation (P).	
	Q	Q^B	$(c_q-c_r)^B$	Q^ϑ	$(c_q-c_r)^\vartheta$	Q^V	$(c_q-c_r)^V$	Q^P	$(c_q-c_r)^P$
3	$+0^{s}.230$	+52.9	+ 2.45	49.3	+1.88	+16.0	+3.62	−3.3	−1.78
3	+ .126	+40.5	+ 0.13	42.0	−2.12	+ 1.3	−3.46	+3.3	+2.33
8	+ .036	+23.3	− 4.15	49.6	−2.69	+ 1.1	−1.89	0.0	−0.14
3	+ .050	+25.5	+ 3.98	71.3	+3.23	+12.3	+2.83	−3.3	−1.57
6	− .034	+14.2	− 3.21	74.7	−1.44	+ 7.7	−1.22	+1.7	+1.91
10	+ .024	+31.2	− 3.47	80.9	+2.76	+ 7.9	−0.20	−1.0	−1.63
3	+ .164	+60.8	+11.39	72.0	−2.95	+10.7	+0.72	+3.3	+1.77
7	− .067	+ 4.9	− 2.99	80.4	+0.84	+ 8.9	−0.65	−1.4	−1.06
8	− .235	−31.0	−14.05	88.3	+0.54	+10.6	+0.18	0.0	−0.51
3	.000	+23.2	+14.22	87.7	+1.48	+12.3	−0.45	+3.3	+2.81
3	− .063	+10.7	− 0.90	81.7	−1.73	+13.0	+1.95	−3.3	−3.41
4	− .117	− 2.9	− 9.97	81.8	−0.34	+ 7.5	−1.91	0.0	+1.70
6	− .042	+17.4	+14.57	89.5	−1.36	+11.8	−1.00	0.0	−0.95
5	− .201	−23.1	−12.98	105.0	+1.62	+22.8	+1.99	+2.0	+1.16
7	− .139	− 2.7	+ 6.05	108.3	+1.19	+19.1	+0.38	−1.4	−0.98
7	− .150	+ 0.6	− 3.54	98.9	−0.21	+10.2	−1.17	0.0	+0.50
10	− .106	+ 4.2	+ 7.51	85.3	+0.38	+ 7.8	+1.32	0.0	−0.39
7	− .291	−46.1	− 6.63	77.0	−3.77	+ 2.9	−3.58	+1.4	+0.63
10	− .245	−37.9	− 0.51	107.8	+1.81	+27.2	+3.15	−1.0	−0.82
12	− .192	− 2.7	+ 0.67	126.6	+1.63	+25.3	−0.24	+0.8	+1.22
3	− .104	+22.1	− 5.19	125.7	−3.82	+21.7	−2.84	−3.3	−2.91
3	− .052	+40.1	+14.67	138.3	+1.92	+32.3	+1.41	+3.3	+3.22
5	− .190	+ 3.4	− 9.29	153.8	−2.61	+44.2	−1.20	0.0	−1.38
5	− .225	+ 5.0	− 4.61	174.0	+7.85	+53.2	+6.93	0.0	+0.29
4	− .139	+30.8	+12.40	157.3	−5.25	+30.2	−5.55	0.0	+0.30
10	− .311	−14.8	−10.09	156.7	+2.97	+27.0	+2.44	−1.0	−0.90
4	− .278	− 1.7	− 1.00	144.2	−2.21	+16.2	−2·17	+2.5	+1.25
4	− .153	+24.4	+ 4.82	147.8	−2.51	+20.8	−1.94	0.0	−0.81
4	− .158	+26.1	+ 0.10	167.0	+0.57	+36.2	+1.84	0.0	+0.09
4	− .209	+20.3	+ 0.39	180.8	+4.27	+40.5	+2.88	0.0	+0.42

Intervals in days.	Observed clock rates.	Atmospheric pressure (B).		Temperature (ϑ).		Temperature difference (V).		Personal equation (P).	
	Q	Q^B	$(c_q-c_r)^B$	Q^ϑ	$(c_q-c_r)^\vartheta$	Q^V	$(c_q-c_r)^V$	Q^P	$(c_q-c_r)^P$
6	$-0\overset{s}{.}243$	+ 9.1	+ 0.49	171.0	—1.93	+27.7	—2.55	—1.7	—0.65
7	— .324	— 4.9	— 2.28	168.6	—0.63	+27.4	+0.05	0.0	+0.36
8	— .344	— 5.1	+ 2.15	175.0	+0.61	+29.6	+1.07	0.0	—0.09
11	— .379	—12 0	— 3.95	175 9	+0.29	+21.7	—0.88	0.0	+0.02
8	— .338	+ 1.8	+ 7 33	173.3	—0.56	+20.8	+0.12	0.0	+0.02
6	— .436	—30.0	— 8.03	173.5	+1.46	+19.8	+0.80	0.0	—0.13
12	— .365	— 2.1	+ 3.51	167.1	—1.73	+14.6	—1.81	+0.8	+0.23
3	— .288	+10.5	— 2.83	174.0	—0.84	+22.7	+0.02	0.0	—0.11
4	— .271	+13.9	+ 8.68	180.5	+3.45	+27.0	+2.10	0.0	—0.16
8	— .363	—12.2	—13.53	163.4	+0.22	+17.1	—0.13	0.0	+0.61
4	— .196	+28.2	+ 9.11	143.8	—2.04	+ 6.8	—1.10	—2.5	—1.05
5	— .209	+26.9	— 1.18	146.2	—0.55	+ 7.6	—0.56	0.0	+0.81
4	— .237	+16.4	+ 2.75	152.8	—0.70	+13.0	—0.04	0.0	—0.49
7	— .373	—13.5	— 1.14	160.7	+2.46	+17.4	+1.53	+1.4	+0.42
8	— .429	—35.0	— 5.03	149.5	—0.06	+10.0	—0.34	0.0	+0.09
11	— .333	—16.4	+ 6.18	131.4	—0.72	+ 2.2	—0.45	—0.9	—0.91
3	— .447	—37.3	— 2.68	124.7	—1.02	+ 0.3	+0.24	+3 3	+1.87
2	— .395	—35.4	—11.48	126.0	+1.47	0.0	—0.90	0.0	—1.31
6	— .193	+19.6	+12.15	121.2	—0.37	+ 2.2	+1.25	0.0	—0.01
12	— .147	+22.9	— 0.56	111.9	+0.15	+ 0.8	—1.68	0.0	+0.53
3	— .135	+ 8.1	+ 1.55	104.0	—0.34	+ 7.7	+2 82	—3.3	—0.70
10	— .243	—18.0	— 0.58	95.2	+1.54	+ 0.2	—3.65	0.0	—0.05
3	— .274	—40.5	— 1.52	77.0	+0.02	+ 9.0	+3.96	+3.3	+0 96
7	— .265	—43.7	— 0.09	66.7	—3 31	— 1.4	—2.59	0.0	—0.85
3	— .309	—41.5	— 3.32	73.7	+0.29	— 2.7	+0.81	0.0	+0.29
4	— .235	—20.1	— 1.54	80.5	+1.48	— 2.5	—0.86	0.0	—0.07
5	— .067	+12.2	+ 5.15	78.2	+1.12	+ 0.8	+0.58	0.0	+0.03
7	— .008	+18.1	— 0.81	61.3	+0.89	+ 2.6	—0.26	0.0	—0.09
5	+ .060	+15.9	+ 3.28	39.6	—2.13	+ 3.2	+1.31	0.0	+0.34
12	— .101	—11 3	— 3.04	42.2	—2.16	— 5.0	—1.79	— 0.8	—0.81

small as compared with that depending on other causes which are difficult to account for. But the computation would not become much more difficult if we should assign different weights to the determinations.

I now use the following thesis for the interpolation with regard to the smallest sinuosity that is proved in § 3 of my previous paper viz.: the partial derivative of the total sinuosity I_S of a series of clock corrections with regard to one of the corrections S_q, is equal to twice the abrupt variation which occurs in the derivative of the third order of the interpolation curve near the abscissa q and the ordinate S_q. Hence according to § 4

$$\frac{\partial I_S}{\partial S_q} = 12\,(e_n - e_m).$$

I apply this relation to the interpolating curve after compensation determined by the corrections L, and I obtain

$$\frac{\partial I_L}{\partial L_q} = 12\,(E_n - E_m) = 12\,\Sigma_q\,,$$

in case that each part of that curve is represented by an equation:

$$L_t = L_q + G_q\,t + C_q\,t^2 + E_n\,t^3.$$

In accordance with the previous paper I have used capitals for the interpolation coefficients belonging to the corrections which are freed from errors. Also the meaning of Σ for this interpolation corresponds entirely with that of σ used for the interpolation without compensation.

For $\frac{\partial I_L}{\partial L_q}$ we may substitute $-\frac{\partial I_L}{\partial f_q}$, because $L_q + f_q$ is invariable, hence $\partial L_q = -\partial f_q$.

After the substitution of $\frac{\partial I_L}{\partial f_q} = -12\,\Sigma_q$, each relation $\lambda \frac{\partial I_L}{\partial f_q} + \frac{f_q}{\mu_q^2} = 0$ takes the form: $\Sigma_q = \frac{1}{12\lambda\mu^2}\,f_q$.

The first member of this relation depends on x, y, z, u and the errors f, and all these quantities occur in it in a linear form:

$$\Sigma_q = \sigma_q - x\sigma_q^{B} - y\sigma_q^{\vartheta} - z\sigma_q^{V} - u\sigma_q^{P} - \sigma_q^{f}\,.$$

If we use the approximate values obtained for x, y, z and u in the supposition $f = 0$, we can compute the expression:

$$\psi_q = \sigma_q - x\sigma_q^{B} - y\sigma_q^{\vartheta} - z\sigma_q^{V} - u\sigma_q^{P}\,.$$

I have made this computation by determining the differences between the successive coefficients of t^3 for the reduced clock rates

$$Q - xQ^B - yQ^{\xi} - zQ^V - uQ_P,$$

according to the new method of interpolation.

σ_q^f may be developed in the following way:

$$\sigma_q^f = \ldots + K_q^o f_o + K_q^p f_p + K_q f_q + K_q^r f_r + K_q^s f_s + \ldots$$

We have also $\sigma_q^f = \dfrac{1}{12}\dfrac{\partial I_f}{\partial f_q}$ where $I_f = \displaystyle\int_a \left(\frac{d^2 f}{dt^2}\right)^2 dt.$

Hence:

$$K_q^o = \frac{\partial \sigma_q^f}{\partial f_o} = \frac{1}{12}\frac{\partial^2 I_f}{\partial f_q \partial f_o} = \frac{\partial}{\partial f_q}\left(\frac{1}{12}\frac{\partial I_f}{\partial f_o}\right) = \frac{\partial \sigma_o^f}{\partial f_q} = K_o^q$$

therefore the coefficient of f_o in the expression for σ_q^f is equal to the coefficient of f_q in the expression for σ_o^f.

Let us consider the case that $f_q = 1$ and all the other values of $f = 0$ then $\sigma_q = K_q$, $\sigma_p = K_p^q$ or $= K_q^p$, $\sigma_r = K_r^q$ or $= K_q^r$, etc. The series of the quantities σ^f for that case gives us directly all the coefficients K which are required for the development of σ_q^f. In this manner an interpolation was made between the numbers ..., 0, 0, 100,0, 0 . . . as many times as there were observations, each time moving the number 100 further over one interval between two successive determinations of the clock correction.

If this computation is properly arranged, it can be made in a very short time and the accuracy can be tested by the results themselves as the coefficients are derived twice independently of each other.

I shall now describe in detail how I have arranged the computation of those coefficients for a determination of the clock correction.

According to § 2 of my paper "On interpolation etc." of Dec. 10, 1902 we have the relations;

$$\sigma_q = e_n - e_m \qquad e_n = \frac{g_q + g_r - 2\,Q_n}{n^2} \qquad e_m = \frac{g_p + g_q - 2\,Q_m}{m^2}$$

which allow us, once the series of the g being found, to deduce the series of the σ from the series of the g and Q.

The series of the g is determined by the equations (C) of § 2 viz.

$$g_q = \frac{n\,Q_m + m\,Q_n}{m+n} + \frac{n\,(Q_m - g_p)}{2\,(m+n)} + \frac{m\,(Q_n - g_r)}{2\,(m+n)},$$

which for the first and the last epochs a and z become:

$$g_a = Q_\mu + \frac{Q_\mu - g_b}{2} \qquad g_z = Q_\nu + \frac{Q_\nu - g_y}{2}$$

where μ and ν refer to the intervals at both ends.

In the example given here, also one of the latter relations occurs, i. e. that for the observations of January 20, 1903. The successive intervals with the values of Q belonging to them are here:

$$\begin{array}{cccc|ccccl} \infty & 3 & & 3 & 8 & 3 & 6 & 10 & \ldots\ (l, m, n, o) \\ & 0 & & +\,{}^{100}/_{3} & -\,{}^{100}/_{8} & 0 & 0 & 0 & \ldots\ (Q) \end{array}$$

The line separates what precedes this observation and what follows.

As a first approximation for the quantities g I have adopted $\frac{n\,Q_m + m\,Q_n}{m+n}$, only three of these values differ from zero, namely:

$$g_p = \frac{l}{m+l}\,Q_m \quad ; \quad g_q = Q_m - Q_n \quad ; \quad g_r = \frac{o}{n+o}\,Q_n.$$

In my example: $Q_m = +\,33$; $Q_n = -\,12$; $l = 3$, $m = 3$, $n = 8$, $o = 3$; hence $g_p = +\,17$; $g_q = +\,21$; $g_r = -\,3$. With these three values begins the annexed scheme, in which the successive corrections of the g are computed. (see p. 255 sq.)

Annexed to this paper is a table (II) (p. 256 sq.) containing the coefficients $100\,K$ for this computation; under the heading "Sum of the squares...." have been given the sums of the squares of the coefficients for each date, and to the first and second approximations the values of $100\,\psi$ which belong to the observations.

Each equation of errors is reduced to the form:

$$\ldots.\ K_q^o f_o + K_q^p\ f_p + (K_q + \mathfrak{K}) f_q + K_q^r f_r + K_q^s\ f_s + \ldots. = \psi_q$$

where $\mathfrak{K} = \frac{1}{12\,\lambda\,\mu^2}$, is constant for all equations, and must be determined in order to enable a solution.

In the relation:

$$\Sigma_q + \ldots + K_q^o f_o + K_q^p f_q + K_q\, f_q + K_q^r f_r + K_q^s f_s\ + \ldots = \psi_q$$

which is independent of the hypothesis of the probability of a group of clock corrections, the quantities f represent real errors of observation, of which the mean value is μ. The error of interpolation φ_q in the interpolation with regard to the least sinuosity, i. e. the difference between the real clock correction L_q and the interpolated correction for the same instant is $\frac{\Sigma_q}{K_q}$. From the expression of pro-

```
                                    0   +17     + 21       3      0 . . . . . . .   1. (g. first approximation)
                                       ↙                 ↘
                                      0     +33        12      0 . . . . . . . .    2. (Q).
                                     ↙
                                  +17   —12     +  9       0   ↘  0 . . . . . . .   3. (subtract obliquely to the left)
                                ∞      3      3       8      3      6 . . . . . .   4. (intervals)
                                         0      16     +33      3 . . . . . . . .   5. (subtract 2 from 1 obliquely to the right)
                           divide by 2
                         and change sign —36    + 27       0      0 . . . . . . .   6  intervals × numbers to the right above
                                         0     128     +99     18 . . . . . . . .   7. intervals × numbers to the left below

                                        36     101     +99     18 . . . . . . . .   8. take the sum of 6 and 7
                                   12      22      22      18 . . . . . . . . . .   9.take the sum of twice two successive intervals
first corrections . — 8   + 3     +  5     — 4    + 1     0     0 . .               10. divide 8 by the numbers to the left
                                                                                        below and change sign
                     ∞   .       3       3      8      3      6     10. .           11. intervals
                         .              8    + 3    + 5     4   + 1 . .             12. row 10 moved to the right by two places

                         .      + 15      12    + 8     0     0 . .                 13. repeat these operations beginning with
                         .        24     +24   +15   — 24   +10                         the multiplications, until the last cor-
                                                                                        rections are small enough.
                         .         9     +12   +23     24   +10
                         .    12       22    22     18    32
second corrections . . .   — 2    + 1    — 1   — 1   + 1     0
first corrections . . .    — 8    + 3    + 5   — 4   + 1     0
to the first approximation . . .   0    + 17   +21   — 3     0     0

true values of g . . .    —10    + 21    +25   — 8   + 2     0
```

TABLE II.

	Coefficients for the compensation.									Sum of the squares of the preceding numbers for each date.	$100\,\psi$ in first approximation.	$100\,\psi$ in second approximation.
			$100\,K_q^o$	$100\,K_q^p$	$100\,K_q$	$100\,K_q^r$	$100\,K_q^s$					
1903	+	—	+	—	+	—	+	—	+			
Jan. 14					1.0	2.1	1.2	0.2	0.1	6.8	— 30	— 20
» 17				2.1	5.1	3.5	0.9	0.4	0.0	43.1	+ 27	+ 4
» 20			1.2	3.5	2.9	1.3	0.8	0.1	0.0	24.2	+ 30	+ 43
» 28		0.1	0.9	1.3	2.5	2.4	0.6	0.2	0.1	14.6	— 80	— 79
» 31	0.1	0.4	0.8	2.4	2.8	1.0	0.4	0.2	0.0	15.7	+ 59	+ 57
Febr. 6	0.0	0.1	0.6	1.0	0.7	0.6	0.4	0.0	0.0	2.4	— 1	— 3
» 16	0.0	0.2	0.4	0.6	1.9	1.9	0.5	0.2	0.1	8.0	— 9	+ 2
» 19	0.1	0.2	0.4	1.9	2.3	0.9	0.4	0.3	0.1	10.3	— 15	— 25
» 26	0.0	0.0	0.5	0.9	0.7	0.8	0.6	0.1	0.0	2.6	+ 61	+ 57
Mrch. 6	0.0	0.2	0.4	0.8	2.8	3.8	1.8	0.3	0.1	26.9	— 301	— 320
» 9	0.1	0.3	0.6	3.8	7.2	5.1	1.5	0.3	0.1	95.7	+ 543	+ 580
» 12	0.1	0.2	1.8	5.1	5.6	2.7	0.8	0.2	0.0	68.3	— 380	— 405
» 16	0.0	0.3	1.5	2.7	2.3	1.2	0.5	0.1	0.0	16.8	+ 121	+ 122
» 22	0.0	0.2	0.8	1.2	1.5	1.0	0.3	0.1	0.0	5.5	— 48	— 40
» 27	0.1	0.2	0.5	1.0	1.2	0.6	0.2	0.0	0.0	3.2	+ 21	+ 14
Apr. 3	0.0	0.1	0.3	0.6	0.7	0.4	0.1	0.0	0.0	1.2	+ 14	+ 14
» 10	0.0	0.1	0.2	0.4	0.4	0.3	0.1	0.0	0.0	0.5	— 14	— 12
» 20	0.0	0.0	0.1	0.3	0.4	0.3	0.1	0.0	0.0	0.4	+ 9	+ 8
» 27	0.0	0.0	0.1	0.4	0.4	0.2	0.2	0.1	0.0	0.4	— 21	— 17
May 7	0.0	0.0	0.1	0.2	0.2	0.3	0.3	0.1	0.0	0.3	+ 20	+ 14
» 19	0.0	0.0	0.1	0.3	2.1	3.2	1.6	0.2	0.1	17.4	— 3	+ 4
» 22	0.0	0.1	0.3	3.2	6.6	4.5	1.2	0.3	0.1	76.2	+ 8	— 6
» 25	0.0	0.1	1.6	4.5	4.4	2.1	0.8	0.2	0.0	47.6	— 42	— 27
» 30	0.0	0.2	1.2	2.1	2.1	1.6	0.6	0.1	0.0	13.2	+ 70	+ 69
June 4	0.1	0.3	0.8	1.6	2.3	1.5	0.4	0.2	0.1	11.2	— 45	— 60
» 8	0.1	0.2	0.6	1.5	1.3	0.6	0.4	0.1	0.0	4.8	— 5	+ 7
» 18	0.0	0.1	0.4	0.6	1.3	1.7	0.9	0.2	0.0	6.3	+ 51	+ 46
» 22	0.0	0.2	0.4	1.7	3.3	2.7	1.1	0.3	0.0	22.4	— 82	— 80
» 26	0.1	0.1	0.9	2.7	3.7	2.7	1.0	0.2	0.0	30.0	+ 41	+ 47
» 30	0.0	0.2	1.1	2.7	3.5	2.2	0.6	0.1	0.0	26.0	+ 55	+ 48
July 4	0.0	0.3	1.0	2.2	2.1	1.0	0.3	0.1	0.0	11.4	— 101	— 102

	Coefficients for the compensation.									Sum of the squares of the preceding numbers for each date.	100 ξ in first approximation.	100 ξ in second approximation.
			100 K_q^o	100 K_q^p	100 K_q	100 K_q^r	100 K_q^s					
1903-04	+	—	+	—	+	—	+	—	+			
July 10	0.0	0.2	0.6	1.0	0.9	0.5	0.2	0.0	0.0	2.5	+ 63	+ 67
» 17	0.0	0.1	0.3	0.5	0.6	0.3	0.1	0.0	0.0	0.8	— 4	— 5
» 25	0.0	0.1	0.2	0.3	0.3	0.2	0.1	0.0	0.0	0.3	— 28	— 30
Aug. 5	0.0	0.0	0.1	0.2	0.3	0.4	0.2	0.0	0.0	0.3	+ 50	+ 51
» 13	0.0	0.0	0.1	0.3	0.6	0.5	0.2	0.2	0.0	0.8	— 91	— 89
» 19	0.0	0.0	0.2	0.5	0.5	0.4	0.4	0.0	0.0	0.8	+ 83	+ 80
» 31	0.0	0.0	0.2	0.4	1.9	2.6	1.0	0.2	0.1	11.6	— 64	— 58
Sept. 3	0.0	0.2	0.3	2.6	4.2	2.2	0.6	0.3	0.1	29.6	+ 35	+ 26
» 7	0.0	0.0	1.0	2.2	1.7	0.9	0.5	0.1	0.0	9.8	— 6	0
» 15	0.0	0.2	0.6	0.9	1.6	1.6	0.7	0.2	0.0	7.0	+ 27	+ 25
» 19	0.1	0.3	0.5	1.6	2.5	1.8	0.7	0.1	0.0	13.0	— 2	— 2
» 24	0.1	0.1	0.7	1.8	2.5	1.7	0.4	0.1	0.0	13.1	— 58	— 56
» 28	0.0	0.2	0.7	1.7	1.7	0.7	0.2	0.1	0.1	6.9	+ 63	+ 61
Oct. 5	0.0	0.1	0.4	0.7	0.6	0.3	0.2	0.2	0.0	1.2	— 25	— 24
» 13	0.0	0.1	0.2	0.4	0.4	0.5	0.4	0.1	0.0	0.7	— 16	— 17
» 24	0.0	0.1	0.2	0.5	2.5	4.5	2.5	0.1	0.0	32.8	+ 249	+ 254
» 27	0.1	0.2	0.4	4.5	11.6	8.3	1.0	0.2	0.2	225.7	— 619	— 629
» 29	0.0	0.1	2.5	8.3	7.1	1.4	0.4	0.2	0.0	128.8	+ 448	+ 455
Nov. 4	0.0	0.1	1.1	1.4	0.6	0.5	0.3	0.0	0.0	3.8	— 60	— 64
» 16	0.0	0.2	0.4	0.5	1.5	1.5	0.5	0.3	0.0	5.2	— 8	+ 10
» 19	0.1	0.2	0.3	1.5	1.7	0.9	0.6	0.1	0.0	6.2	+ 6	— 17
» 29	0.0	0.0	0.5	0.9	2.0	2.0	0.8	0.4	0.1	9.9	+ 70	+ 97
Dec. 2	0.0	0.3	0.6	2.0	2.5	1.6	0.9	0.2	0.0	14.4	— 123	— 142
» 9	0.0	0.1	0.8	1.6	3.1	3.4	1.2	0.2	0.0	25.7	+ 146	+ 150
» 12	0.0	0.4	1.0	3.4	4.9	2.8	0.8	0.2	0.0	44.9	— 54	— 65
» 16	0.1	0.2	1.2	2.8	2.7	1.4	0.4	0.1	0.0	19.0	— 95	— 90
» 21	0.0	0.2	0.8	1.4	1.3	0.8	0.3	0.0		4.9	+ 101	+ 101
» 28	0.0	0.2	0.4	0.8	1.0	0.6	0.1			2.3	— 96	— 84
Jan. 2	0.0	0.1	0.3	0.6	0.5	0.1				0.8	+ 64	+ 55
» 14	0.0	0.0	0.1	0.1	0.0					0.0	— 9	— 12

bability $e^{-\lambda I_L}$ we may deduce the mean value of φ_q. Let us suppose that all the real clock corrections remain unaltered with the exception of that for the instant q. Then I_L will be a minimum for $L_q - \varphi_q$; and for any other clock correction adopted for the same instant, which differs from this interpolated value by ε, I_L is equal to its least value augmented by $6\,\bar{K}_q\,\varepsilon^2$.

Hence the probability of the group of clock corrections contains the factor $e^{-6\lambda \bar{K}_q \varepsilon^2}$, whence follows that the mean value of ε, or also that of φ_q is equal to $\frac{1}{\sqrt{12\lambda \bar{K}_q}}$. Then the mean value of $\varphi_q \sqrt{\bar{K}_q}$ is constant and equal to $\frac{1}{\sqrt{12\lambda}}$; this constant is called $\mathbf{r}$.

Hence the 2nd power of the mean value of the first member of the above relation is:

$$\bar{K}_q\,\mathbf{r}^2 + \mu^2\,[\ldots.\,\bar{K}_q^{o^2} + \bar{K}_q^{p^2} + \bar{K}_q^{2} + \bar{K}_q^{r^2} + \bar{K}_q^{s^2} + \ldots].$$

The 2nd member ψ_q computed with approximative values of x, y, z and u is known. I had no direct data for the determination of μ^2. It consists of one part which is independent of the number of stars observed for the clock correction, and another part which is in inverse proportion to this number. For one star observed by BAKHUYZEN, the latter part amounts to about 900 and for PANNEKOEK it is a little less. I wished to avoid a too large value for μ^2 for fear of exaggerating the regularity of the clock at the cost of the accuracy of the observations, and therefore I have put for each of those parts of μ^2 300, together $\mu^2 = 600$.

According to the value given above for $\mathfrak{K}$ we have $\mathbf{r}^3 : \mu^2 = \mathfrak{K}$ and the mean value of the expression:

$$\psi_q : \sqrt{\bar{K}_q\,\mathfrak{K} + \ldots.\,\bar{K}_q^{o^2} + \bar{K}_q^{p^2} + \bar{K}_q^{2} + \bar{K}_q^{r^2} + \bar{K}_q^{s^2} + \ldots.}$$

will be equal to μ.

With different suppositions for $\mathfrak{K}$, I could derive from this relation the corresponding value μ^2. My result was that for $\mathfrak{K} = {}^1/_{50}$ the value of μ^2 is 592 and therefore I have retained this value of $\mathfrak{K}$ in the further computation.

The hypothetical expression of the probability was tested in two different ways.

In the first place I investigated whether indeed $\mathbf{r}^2$ might be regarded as equal for the different intervals of the period treated. Therefore I have arranged the observations according to their coefficients $\bar{K}_q$, and have derived from the half with least $\bar{K}_q$ separately the value of μ^2 belonging to $\mathfrak{K} = {}^1/_{50}$. The result was $\mu^2 = 591$.

In the second place I have investigated whether also for intervals of longer duration, the constancy of $\mathbf{r}^2$ remains the same. In that case I could derive $\mathbf{r}^2$ from the total sinuosity I_L of the real clock corrections.

If we imagine that from the series of those clock corrections one is dropped, which deviates from the interpolated value by φ_q, then I_L is diminished by $6\ K_q\,\varphi_q^2$. 59 times we can drop successively one observation from the 61 observations at our disposal, and thus each time diminish the total sinuosity of the remaining clock corrections by $6\ K\varphi^2$. At the end I_L is zero and hence I_L may be considered as consisting of 59 parts, each of a mean value of $6\ \mathbf{r}^2$. Hence the mean value of I_L is $354\ \mathbf{r}^2$.

From the reduced rates $Q - x\,Q^B - y\,Q^{\Xi} - z\,Q^V - u\,Q^P$ I deduced the total sinuosity of the clock corrections $L+f$ and obtained $I_{L+f} = 8756$.

In my previous paper on this interpolation it is demonstrated that if the errors f and the clock corrections expressed by I are independent of each other $I_{L+f} = I_L + I_f$. Instead of the formula derived there:

$I_f = \Sigma 6 \varepsilon_n (f_q - f_r)$ I now write $I_f = \Sigma 6 f_q (\varepsilon_n - \varepsilon_m) = \Sigma 6 f_q \sigma_q{}^f$

and substitute for σ_q^f its value expressed in terms of the errors f.

In this way we get:

$$I_f = \Sigma\ 6\ f_q\,[\ldots K_q^o\,f_o + K_q^p\,f_p + K_q\,f_q + K_q^r\,f_r + K_r^s\,f_s\ldots]$$

In the 2nd member occur under Σ many products of real errors. The mean value of these terms is zero. I omit them, substitute μ^2 for the square of each error and find as mean value for I_f $6\ \mu^2\ \Sigma\ K_q$.

The computation of $\Sigma\ K_q$ yielded 1.39.

In this way I have found the following relation between $\mathbf{r}$ and μ:

$$8756 = 354\ \mathbf{r}^2 + 8{,}34\ \mu^2$$

whence, if μ^2 is equal to 600, $\mathbf{r}^2 = 11$, which result is in good harmony with the value first found for $\mathfrak{K}$.

The set of equations by which the most probable errors are connected is readily solved, if we use as a first approximation $f_q = 0.45\,\dfrac{\psi_q}{K_q + \mathfrak{K}}$. After I had found by the substitution of these values that the 2nd member required still another correction $\Delta_1\,\psi$, I used $0.80\,\dfrac{\Delta_1\,\psi_q}{K_q + \mathfrak{K}}$ as a correction for the first approximation.

When computed according to the empirical formula

$$f_q = \frac{0.45\ \psi_q + 0.80\ \Delta_1\,\psi_q}{K_q + \mathfrak{K}}$$

the errors appeared to satisfy fairly well the set of equations. Where it was necessary I took away the last differences by adding $\frac{\Delta_2 \psi_q}{K_q + \mathfrak{K}}$ to the errors.

Table III contains the results of the compensation which are necessary to compute the clock correction at any instant between the observations. Let this instant be $q + T$, the epoch of the immediately preceding clock correction being q; if moreover during the interval from q to $q + T$:

the mean atmospheric pressure, expressed in mms. of mercury of 0° C. is $760 + B_T$,
the mean temperature in centigrades $10° \text{C} + \vartheta_T$,
the mean difference in temperature in centigrades V_T,

then we can compute the clock correction S_{q+T} according to the following formula:

$$S_{q+T} = S_q - f_q + \frac{T}{1000}(G_q + 15{,}4 B_T - 26.4 \vartheta_T + 318 V_T + C_q T + E_n T^2).$$

The values of S, f, G, C, E, occurring in this formula can be derived from table III.

The 5th column shows the mean rates for each interval between two successive determinations of the clock correction after the reduction and the compensation. From this we may judge of the constancy of the rate of the clock. It must be remarked that the small yearly inequality occurring in these values is very probably due to a little inaccuracy in the coefficient of temperature obtained as described above.

The last column of table III shows the quantities Σ, the differences between the successive values of E. They give us a simple test for the computation of the compensation, because they must be equal to the errors f multiplied by 20, or $f_q = \Sigma_q : 20$. The adopted series of errors satisfies tolerably well this relation, if we admit small differences, which in thousandth parts of a second of time do not exceed the intervals m or n expressed in days, and hence give rise to a difference less than $0^s{,}001$ in the mean daily rates.

TABLE III.

Date	Observers	Clock corrections reduced to B S	Error according to the compensation f	Compensated daily rates Q_L	G	C	E	Σ
1903					—			
Jan. 14	P	— 3ᵐ 28ˢ.222	—0ˢ.008		171	0 0		— 0.14
				—0ˢ.173			— 0.14	
„ 17	B	27.561	+ .004		176	— 1.3		+ 0.12
				— .180			— 0.02	
„ 20	P	27.153	+ .010		184	— 1.5		+ 0.14
				— .188			+ 0.12	
„ 28	P	26 864	— .014		184	+ 1.5		— 0.21
				— .180			— 0.09	
„ 31	B	26.744	+ .006		177	+ 0.7		+ 0.04
				— .175			— 0.05	
Febr. 6	P	26.921	+ .004		175	— 0.2		+ 0.07
				— .174			+ 0.02	
„ 16	B	26.710	— .004		171	+ 0.5		— 0.08
				— .170			— 0 06	
„ 19	P	26.189	— .001		170	0.0		+ 0.02
				— .171			— 0.04	
„ 26	B	26.690	+ .005		174	— 0.8		+ 0.12
				— .176			+ 0.08	
Mrch. 6	B	28.568	— .029		173	+ 1.0		— 0.50
				— .174			— 0.42	
„ 9	P	28.539	+ .038		179	— 2.8		+ 0.80
				— .184			+ 0.38	
„ 12	B	28.757	— .021		186	+ 0.6		— 0.36
				— .183			+ 0.02	
„ 16	B	29.225	.000		180	+ 0.9		— 0.02
				— .174			0.00	
„ 22	B	29.475	— .004		168	+ 0.9		— 0 09
				— .166			— 0.09	
„ 27	P	30.449	+ .002		166	— 0.5		+ 0.05
				— .172			— 0.04	
Apr. 3	B	31.453	+ .007		180	— 1.4		+ 0.12
				— .186			+ 0.08	
„ 10	B	32.506	— .004		189	+ 0.2		— 0.07
				— .186			+ 0.01	
„ 20	B	33.565	+ .001		183	+ 0.4		+ 0.02
				— .178			+ 0.03	
„ 27	P	35.575	— .007		172	+ 1.1		— 0.12
				— .169			— 0.09	
May 7	B	38.051	+ .007		175	— 1.6		+ 0.13
				— .189			+ 0.04	
„ 19	P	40.326	+ .002		197	— 0.3		— 0.01
				— .198			+ 0 03	
„ 22	B	40.667	— .004		198	0.0		— 0.10
				— .199			— 0.07	
„ 25	P	40.794	— .002		200	— 0.6		+ 0.02
				— .205			— 0.05	
„ 30	P	41.746	+ .014		214	— 1.4		+ 0.24
				— .213			+ 0.18	
June 4	P	42.872	— .010		210	+ 1.4		— 0.21
				— .205			— 0.02	
„ 8	P	43.427	— .002		200	+ 1.2		— 0.04
				— .194			— 0.06	
„ 18	B	46.570	+ .008		194	— 0.5		+ 0.17
				— .194			+ 0.11	
„ 22	P	47.654	— .012		193	+ 0.8		— 0.25
				— .192			— 0.14	
„ 26	P	48.265	+ .009		194	— 0.9		+ 0.20
				— .196			+ 0.06	
„ 30	P	48.896	+ .006		198	— 0.2		+ 0.09
				— .196			+ 0.15	

Date	Observers	Clock corrections reduced to B S	Error according to the compensation f	Compensated daily rates Q_L	G	C	E	Σ
1903-04					—			
July 4	P	$-3^m\ 49^s.732$	$-0^s.020$		192	+ 1.6		− 0.37
				$-0^s.190$			− 0.22	
„ 10	B	51.220	+ .016		196	− 2.3		+ 0.29
				− .209			+ 0.07	
„ 17	B	53.488	+ .002		219	− 0.9		+ 0.05
				− .219			+ 0.12	
„ 25	B	56.236	− .011		212	+ 1.9		− 0.23
				− .204			− 0.11	
Aug. 5	B	-4^m 0.408	+ .015		210	− 1.8		+ 0.30
				− .212			+ 0.19	
„ 13	B	3.115	− .026		202	+ 2 7		− 0.51
				− .198			− 0.32	
„ 19	B	5.734	+ .024		206	− 3.1		+ 0.47
				− .221			+ 0.15	
„ 31	P	10.082	− .012		215	+ 2.3		− 0.25
				− .209			− 0.10	
Sept. 3	P	10.946	− .001		204	+ 1.4		− 0.02
				− .200			− 0.12	
„ 7	P	12.029	+ .005		198	− 0.1		+ 0.05
				− .203			− 0.07	
„ 15	P	14.936	+ .008		212	− 1.7		+ 0.25
				− .216			+ 0.18	
„ 19	B	15.752	− .003		217	+ 0.4		− 0.13
				− .214			+ 0.05	
„ 24	B	16.795	− .010		210	+ 1.1		− 0.21
				− .208			− 0.16	
„ 28	B	17.744	+ .013		209	− 0.8		+ 0.27
				− .209			+ 0.11	
Oct. 5	P	20.328	− .009		204	+ 1.5		− 0.17
				− .196			− 0 06	
„ 13	P	23.762	+ .001		192	+ 0.1		0.00
				− .198			− 0.06	
„ 24	B	27.460	+ .020		212	− 1.9		+ 0.40
				− .214			+ 0.34	
„ 27	P	28.771	− .024		213	+ 1.2		− 0.69
				− .212			− 0.35	
„ 29	P	29.561	+ .021		212	− 0.9		+ 0.42
				− .215			+ 0.07	
Nov. 4	P	30.720	− .004		215	+ 0.4		− 0.05
				− .207			+ 0.02	
„ 16	P	32.482	− .004		195	+ 1.3		− 0.13
				− .192			− 0.11	
„ 19	B	32 918	+ .002		190	+ 0.3		+ 0.09
				− .188			− 0.02	
„ 29	B	35.348	+ .014		187	− 0.2		+ 0.16
				− .187			+ 0.14	
Dec. 2	P	36.141	− .020		185	+ 1.1		− 0.30
				− .186			− 0.16	
„ 9	P	37.998	+ .026		195	− 2.3		+ 0.43
				− .199			+ 0.27	
„ 12	P	38 926	− .005		201	+ 0.1		− 0.05
				− .197			+ 0.22	
„ 16	P	39.866	− .021		190	+ 2.8		− 0.49
				− .182			− 0.27	
„ 21	P	40.201	+ .019		181	− 1.2		+ 0.39
				− .183			+ 0.12	
„ 28	P	40.254	− .017		179	+ 1.3		− 0.32
				− .178			− 0.20	
Jan 2	P	39.953	+ .015		182	− 1.7		+ 0.25
				− .195			+ 0.05	
„ 14	B	41.200	− .005		201	0.0		− 0.05

(October 20, 1904).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday October 29, 1904.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 29 October 1904, Dl. XIII).

CONTENTS.

The following papers were read:

Mathematics. — “*The congruence of the conics situated on the cubic surfaces of a pencil.*” By Prof. JAN DE VRIES.

(Communicated in the meeting of September 24, 1904).

1. On each cubic surface S^3 of a pencil lie 27 systems of conics, of which each system has one of the 27 right lines for common chord. Through any point P of space passes one S^3 of the pencil; so P bears 27 conics C^2 of the congruence formed by the C^2 of all S^3.

The pairs of lines of the congruence evidently form the skew surface of the trisecants of the basecurve R^9; for the points of intersection of a right line of one of the S^3 with a second S^3 belong to all S^3 of the pencil. Quite independent of this consideration we can find the degree of the above mentioned skew surface in the following way.

Let u_k be a homogeneous function of degree k in x, y, z. If we take a point of R^9 to be the origin of the system of coordinates, the pencil has for equation

$$u_3 + u_2 + u_1 = 0,$$

where the coefficients contain a parameter λ to the first degree.

If a right line through O must lie on S^3, for all values of m the equation

$$m^3 u_3 + m^2 u_2 + m u_1 = 0$$

must be satisfied, so we have simultaneously

$$u_3 = 0\,, \qquad u_2 = 0\,, \qquad u_1 = 0.$$

By eliminating x, y, z out of these three equations a relation is found containing the coefficients, so λ too, in degree

$$3 \times 2 + 3 \times 1 + 2 \times 1 = 11$$ [1].

The basecurve R^9 is thus an *elevenfold curve* on the skew surface of the right lines lying on the surfaces S^3 of the pencil.

Each surface S^3 bearing 27 right lines, its section with the indicated skew surface is of degree $27 + 9 \times 11 = 126$; the skew surface is thus of degree 42 [2].

2. Any right line l is a chord of 42 conics, whose planes are determined by the 42 right lines of the skew surface ϱ^{42} resting on l.

Let us now consider the surface (P) formed by the C^2, the planes

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[1] See a.o. CLEBSCH, *Leçons sur la géométrie*, II, 13.

[2] See a.o. KLUYVER, *Kenmerkende getallen der algebraïsche ruimtekromme* (*Characteristic numbers of the algebraic twisted curve.*) Versl. K. A. v. W., 3rd series vol. VII, page 152, 1889.

of which pass through the point P. An arbitrary ray through P is intersected outside P in 84 points. As P bears 27 C^{12} the degree of (P) is $84 + 27 = 111$.

According to the notation of SCHUBERT we have thus

$$\mu^2 = 42 \qquad \text{and} \qquad \mu\nu = 111.$$

From the well known relations[1]

$$3\nu = 2\eta + \delta + 4\mu \qquad \text{and} \qquad 3\varrho = \eta + 2\delta + 2\mu.$$

where in our case η is equal to 0 we deduce by symbolic multiplication the following system of relations:

$$\begin{aligned} 3\mu\nu &= \delta\mu + 4\mu^2\,, & 3\mu\varrho &= 2\delta\mu + 2\mu^2\,,\\ 3\nu^2 &= \delta\nu + 4\mu\nu\,, & 3\nu\varrho &= 2\delta\nu + 2\mu\nu\,,\\ 3\nu\varrho &= \delta\varrho + 4\mu\varrho\,, & 3\varrho^2 &= 2\varrho\delta + 2\mu\varrho\,. \end{aligned}$$

We have here six equations for nine characteristic numbers of which we have already determined two.

But the number $\delta\nu$ we can find directly. For on the arbitrary right line l rest 42 right lines of ϱ^{12}; each of these right lines is intersected bij 10 right lines of the surface S^3 to which it belongs; so it furnishes 10 pairs of lines resting on l. Consequently

$$\delta\nu = 420.$$

We now find successively

$$\begin{aligned} \nu^2 &= 288\,, & \delta\mu &= 165\,, & \nu\varrho &= 354\,,\\ \mu\varrho &= 138\,, & \delta\varrho &= 510\,, & \varrho^2 &= 432\,. \end{aligned}$$

3. Out of $\nu^2 = 288$ follows *that the surface A formed by the conics cutting the right line l is of degree* 288.

Evidently l is a 27 fold right line of A and a chord of 42 conics lying on A. It is evident that on A lie 462 right lines, which are situated three by three in 210 planes.

If l is a trisecant of R^9, thus a right line of a surface S_1^3, then A^{288} breaks up into the surface S_1^3 counted double and the loci of the conics passing through each of the three points of intersection of the trisecant.

The conics having a point of the basecurve R^9 in common, form thus a surface of degree 94.

The surfaces T^{94} belonging to the points of intersection T_1 and T_2 of the trisecant have evidently the 10 conics in common which are determined by the 10 trisecants through the third point of intersection T_3.

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[1] SCHUBERT, *Kalkül der abzählenden Geometrie*, p. 92.

If l is a chord of R^9 then A degenerates into two surfaces T^{94} and a surface of degree 100.

If l is a line cutting R^9 once then A consists of two parts, which will be successively of degree 94 and 194.

4. The numbers $\delta\varrho = 510$ and $\delta\mu = 165$ furnish well known results.[1]) The first tells us that the skew surface ϱ^{42} of the trisecants of R^9 possesses a double curve of degree 255; for each plane through a double point of a pair of lines is to be regarded two times as tangent plane. The second number furnishes the property that the threefold tangent planes of the surfaces S^3 of a pencil envelop a surface of class 55.

The surface (P) contains thus 165 right lines lying three by three in 55 planes.

The numbers $\nu\varrho$ and $\mu\varrho$ furnish with reference to the plane at infinity the following properties:

The parabolae of the congruence form a surface of degree 354, *their planes envelop a surface of class* 138.

Each S^3 contains 108 parabolae.[2]). As a definite S^3 can cut the parabolae on the other S^3 only in points of the basecurve R^9 the locus of the parabolae passes $(3 \times 354 - 2 \times 108) : 9 = 94$ times through R^9.

So through each point of R^9 pass 94 parabolae.

Chemistry. — "*The nitration of disubstituted benzenes.*" By Prof. A. F. Holleman.

(Communicated in the meeting of September 24, 1904).

If we introduce into a benzene derivative C_6H_5X a second atom or group this takes up in respect to X a position either chiefly meta or para-ortho depending chiefly on the nature of X. The cause of this is as yet obscure. The efforts for elucidating this phenomenon are totally inadequate, first of all because they are too vague, secondly because they do not take into account the relative quantities which are formed from the isomers; in fact they could not do so, as these were still unknown at the time that these "explanations" were given. A better insight into this problem can only be rendered possible by the quantitative study of the substitution process, which has

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[1]) Kluyver, page 152.

[2]) J. de Vries, *La configuration formée par les vingt-sept droites d'une surface cubique*, Arch. Néerl., sér. 2, t. VI, p. 148.

already been made in a number of cases of nitration of the substances C_6H_5X.

For the present we must content ourselves with accepting the results of those quantitative studies as facts. Doing this, we may put the following question: Given a benzene derivative C_6H_4XY, in which a third group Z is introduced. If now we know the relative quantities of the isomers of both C_6H_4XZ and C_6H_4YZ which are formed by the introduction of Z into C_6H_5X and into C_6H_5Y; can we then deduce from this the structure and relative quantities of the isomers C_6H_3XYZ which are formed by the introduction of Z into C_6H_4XY?

Suppose (by way of an example) that we have determined how much para- and ortho-compound is formed in the nitration of chlorobenzene and how much meta- and ortho-benzoic acid in the nitration of benzoic acid; can we then determine beforehand which and how much of the possible nitrochlorobenzoic acids will be formed in the nitration of chlorobenzoic acid?

Qualitatively this problem has been studied rather fully, but as a rule not very systematically. In a great many cases it has been determined which of the possible isomers C_6H_3XYZ are formed by the introduction of Z into C_6H_4XY and one has tried to draw conclusions therefrom which render it possible to predict what may be expected in unknown cases. BEILSTEIN has summarised these as follows: "In the introduction of a group Z into a substance C_6H_4XY both X and Y exert an influence but that of one of these groups is predominant and directs Z."

Undoubtedly, this rule is correct in a great many cases, but not in a good many others. For instance it cannot be applied to the nitration of m-nitroanisol, which I have investigated. In any case it shows that the groups X and Y do not exert their directing influence independently of each other but that this is modified by their simultaneous presence. This has been fully confirmed by a quantitative investigation in the case of a number of nitrations of the compounds C_6H_4XY.

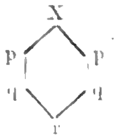
If the groups X and Y exerted a directing influence on a third substituent independently of each other we ought to have the following: If we call the proportion in which the three isomers are formed when Z is introduced into C_6H_5X

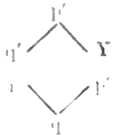
$$p_{ortho} : q_{meta} : r_{para}$$

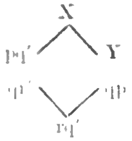
and that of the three isomers when Z is introduced into C_6H_5Y

$$p'_{ortho} : q'_{meta} : r'_{para}$$

the quantity of the isomers, when introducing Z into C_6H_4XY, would be expressed by products as pq′ etc. as shown by the subjoined scheme:



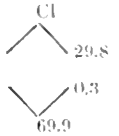




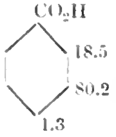
In this it has been supposed that on introducing a second group into a monosubstituted benzene derivative all the three possible isomers are formed, which in practice will most likely be the case even if the quantity of one of these should be so small as to be generally overlooked. In fact, in a number of cases where at first only two substituents had been found, such as in the nitration of nitrobenzene, a careful investigation also revealed the presence of a third one.

The quantitative investigation as to the relative quantities of the isomers which are formed in the nitration of substances C_6H_4XY now showed that those quantities generally differ very considerably from the products pq′ etc. so that a serious diversion of the directing influence on the third substituent must be admitted. This diversion was found to depend not only on the nature of the substituents but also on their place in the molecule as proved by the following example.

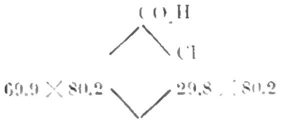
In the nitration of chlorobenzene at 0° para-, ortho- and meta-nitrochlorobenzene are formed in the following quantities:



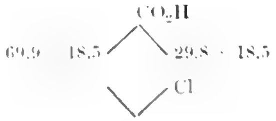
In that of benzoic acid the nitrobenzoic acids in the following proportion:



If CO_2H and Cl did not modify each other's directing influence, nitro-derivatives obtained in the nitration of ortho- and metachlorobenzoic acid would be formed in the quantities indicated in the subjoined schema:

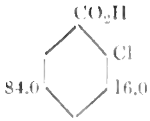


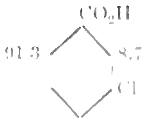
and



;

of the other possible isomers only very insignificant quantities. These were in fact so trifling that they were not found. Of the two isomers to be expected in both cases, the relative quantity ought to be just as large as that which is formed in the nitration of chlorobenzene itself. Instead of this was found:





In the subjoined table a number of such observations have been collected. By "diversion" is meant the quotient of the quantity of the byeproduct actually found and that of the quantity calculated.

Nitration of	Amount of byeproduct on 100 parts of main prod.		Diversion of the directing influence of the halogen		of carboxyl.	
	at —30°	at 0°	at —30°	at 0°	at —30°	at 0°
C_6H_5Cl	36.4	42.0				
C_6H_5Br	52.7	60.5				
$C_6H_5CO_2H$	16.9	23.1				
o-$C_6H_4Cl.CO_2H$	16.3	19.1	0.448	0.455	—	—
o-$C_6H_4Br.CO_2H$	20.6	24.4	0.391	0.403	—	
m-$C_6H_4Cl.CO_2H$	9.1	9.5	0.250	0.226	0.539	0.411
m-$C_6H_4Br.CO_2H$	13.4(?)	12.9	0.254(?)	0.213	—	0.601
o-$C_6H_4Cl_2$	5.5	7.8	0.151	0.186	—	--
m-$C_6H_4Cl_2$	2.7	4.1	0.074	0.098	—	—

In the nitration of o-halogenbenzoic acid and of o-dichlorobenzene the NO_2-group in the byeproducts places itself *adjacent* to the halogen; in that of the m-dichlorobenzene *between* the carboxyl and the halogen. On comparing the diversion figures of the directing influence of the halogen in these acids and dihalogen-compounds, those of the meta-compounds amount to about half of the ortho-compounds. This is one of the many cases which show that the introduction of a substituent between two others meets with a particularly great resistance.

Groningen, Lab. Univers. Aug. 1904.

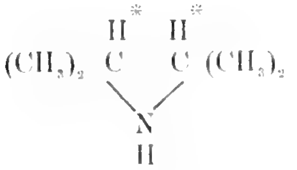
Chemistry. — *"On αα'-tetramethylpiperidine."* By Prof. A. P. N. Franchimont and Dr. H. Friedmann.

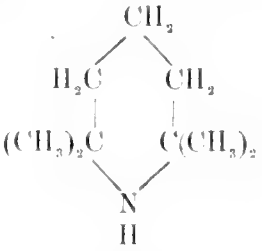
(Communicated in the meeting of September 24, 1904).

This substance, which was obtained in 1885 by Canzoneri and Spica but in an impure condition, was prepared by us in another manner, namely, by reduction of γ-bromotetramethylpiperidine with a copper-zinc couple (Gladstone-Tribe's method) in absolute alcoholic solution.

It is a liquid boiling at 155,°5—156°5 at 760 m.m. pressure having a sp. gr. of 0.8367. With water it yields a crystalline compound which melts at 28° and loses its water totally or partially in a dry atmosphere. The compounds with hydrogen chloride, hydrogen bromide and sulphuric acid form very beautiful crystals; those with the two first-named acids sublime on heating without previous fusion, those with sulphuric acid melt: the acid one at 174°, the neutral one at 270°.

Compared with piperidine, this amine reacts remarkably slowly on acid chlorides such as benzoyl chloride, chloro-formic esters, picrylchloride etc. In aqueous solutions the reaction takes place hardly at all, in ethereal solutions extremely slowly. However, there were obtained: methylurethane as a liquid with a strong mint-like odour boiling at 227° at a pressure of 760 m.m.; sp. gr. 0.9848 and the benzoyl derivative as crystals melting at 41°—42°; the picryl derivative melts at 225°. An effort to prepare a urea from the hydrogen chloride compound and potassium isocyanate has resulted as yet in failure. This reminds us of experiments of Dr. K. H. van der Zande in 1889 with di-isopropylamine, where urea could only be obtained with difficulty and in very small amount, whereas dinormalpropylamine presented no difficulties [1]). If we compare the formulae of di-isopropylamine and αα'-tetramethylpiperidine we notice that they only





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[1]) Some years before, I had already noticed an analogous phenomenon when treating propyl- and isopropylmalonic acid with nitric acid; the first compound is much more readily attacked than the second.

differ in this way that the two hydrogen atoms of the first compound (indicated by asterisks) have been replaced in the second one by the bivalent group $CH_2-CH_2-CH_2$; piperidine and tetramethylpiperidine differ because the first one contains hydrogen atoms where the other possesses methyl groups, namely at the *α C* atoms in regard to the nitrogen.

As piperidine reacts strongly with the above substances and tetramethylpiperidine does not do so and as there exists an analogous difference between dinormalpropylamine and di-isopropylamine it is natural to look for the cause of this in the methyl groups. As, however, their nature does not explain this difference we are bound to consider their mass and their position in space in regard to the nitrogen. This is then a case of so-called sterical obstacle which is to a certain extent comparable with a number of other cases which have been chiefly observed in the aromatic compounds; a case which may, perhaps, affect the views held as to the nitrogen atom.

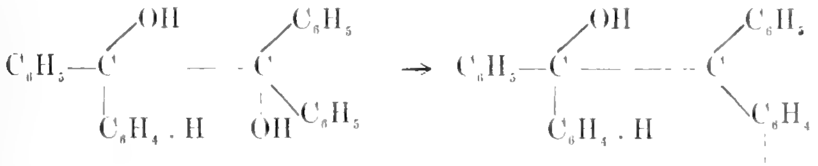
It must be finally observed that tetramethylpiperidine yields like di-isopropylamine a crystalline compound with nitrous acid, which is fairly stable and is only decomposed at a higher temperature into water and the nitroso-compound.

Chemistry. — "*On intramolecular atomic rearrangements in benzpinacones.*" By P. J. Montagne. (Communicated by Prof. A. P. N. Franchimont).

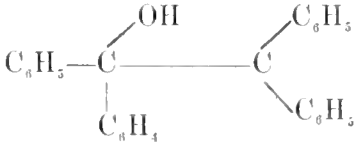
(Communicated in the meeting of September 24, 1904).

The following research originated in an effort by Nef[1]) to explain the intramolecular atomic rearrangement in the conversion of benzpinacone into benzpinacoline by assuming the presence of an intermediate product. His explanation when put into formulae is as follows:

Benzpinacone is dissociated into water and unsaturated hydrocarbon:



then addition to:



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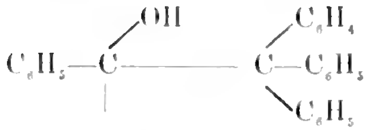
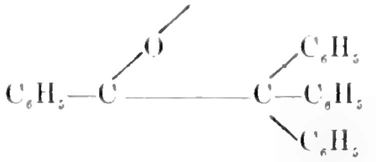
[1]) Ann. 318 p. 38.

then dissociation:



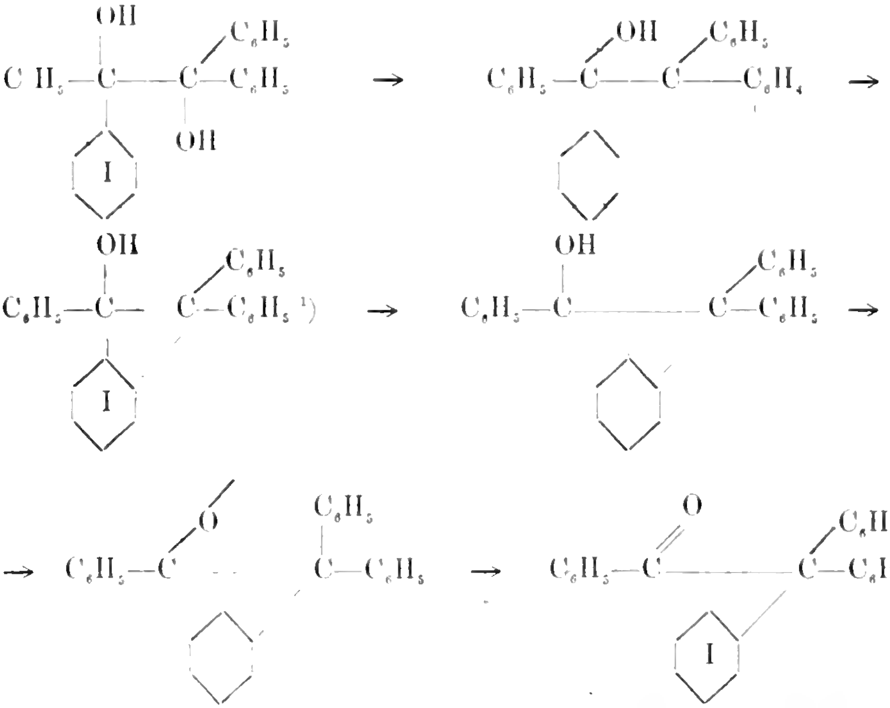
then addition to:



then formation of 

$C_6H_5—\overset{O}{\overset{\|}{C}}——C(C_6H_5)_3$.

If, however, we represent the matter by structural formulae we get:



This shows now in the plainest manner that the core I is attached to different C-atoms before and after the migration. If we, therefore apply this representation to derivatives of benzpinacone, the group or the atom in the core I of benzpinacone then occupies a different position from that in the benzpinacoline obtained from the same.

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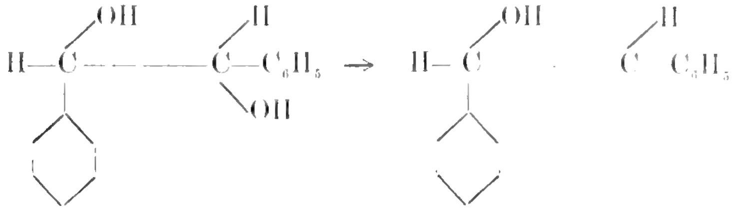
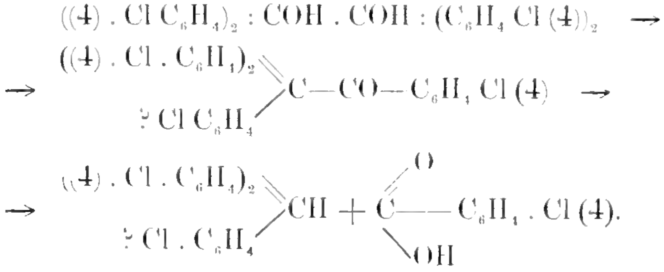
[1] Which H-atom of core I migrates to the group C_6H_4 is not stated by Nef; the ortho-placed H-atom was taken arbitrarely.

Some time ago[1]) I pointed out the possibility of the existence of a similar intermediate product in the transformation of hydrobenzoin into diphenylacetaldehyde



but at the same time I have shown experimentally the incorrectness of that supposition. In an appended note I have already observed that in view of my results obtained, the theory of Nef was not acceptable. It appeared to me therefore, to be of importance to extend my researches also to a derivative of benzpinacone and thus to form a definite opinion as to the correctness or incorrectness of Nef's theoretical explanation.

For this research I took 44′4″4‴ tetrachlorobenzpinacone obtained by reduction of 44′ dichlorobenzophenone. On being heated with acetyl chloride it passes into tetrachlorobenzpinacoline. If this is boiled with alcoholic potassium hydroxide it is resolved into trichlorotriphenylmethane and p. chlorobenzoic acid according to this scheme:



$$((4) . Cl\,C_6H_4)_2 : COH . COH : (C_6H_4\,Cl\,(4))_2 \rightarrow$$

$$\rightarrow \left.\begin{matrix} ((4) . Cl . C_6H_4)_2 \\ ?\,Cl\,C_6H_4 \end{matrix}\right\rangle C—CO—C_6H_4\,Cl\,(4) \rightarrow$$

$$\rightarrow \left.\begin{matrix} ((4) . Cl . C_6H_4)_2 \\ ?\,Cl . C_6H_4 \end{matrix}\right\rangle CH + \overset{O}{\underset{OH}{C}}—C_6H_4 . Cl\,(4).$$

This trichlorotriphenylmethane now appeared to be identical with the 44′4″ trichlorotriphenylmethane obtained from 44′4″ triaminotriphenylmethane (p. leucaniline). This explains the para-position of all chlorine atoms in the first-named trichlorotriphenylmethane. This further shows that the phenyl group is attached to the same C-atom before and after the migration and that therefore the intermediate product as suggested by Nef is an impossibility. The explanation given by Nef for this intramolecular atomic rearrangement is, therefore, incorrect.

The views held as to the transformation of *α*-glycols into aldehydes are two in number:

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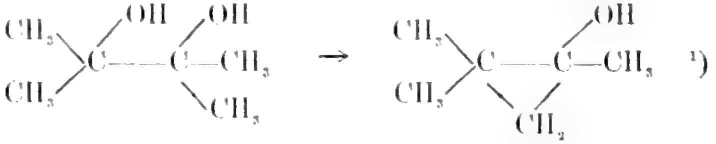
[1]) Rec. 21. p. 30.

1. Splitting off of H_2O, in such a manner that the group OH departs with the H of a C-atom, for example:

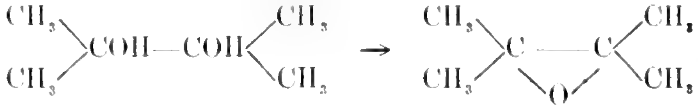


1)

Nef's view of benzpinacone is in accordance with this.

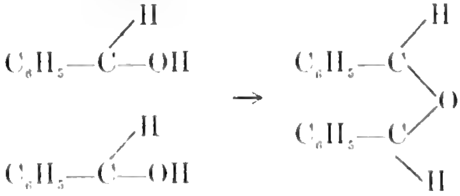
The object of this representation is to abandon the idea of an intramolecular atomic rearrangement and to substitute so-called normally-proceeding reactions.

2. Splitting off of H_2O in such a manner that the group OH departs with an H of the second OH group, for example:



2)

Nef 1): "Es ist jetzt vollkommen klar, dass diese Reaction (Umwandlung der 1.2 Glycolen in Ketonen) bei welcher eine scheinbare Verschiebung der Hydroxyle eintritt, auf eine intermediaire Bildung von Alkylenoxyd zurückzuführen ist."



3)

In this representation we still admit an intramolecular atomic rearrangement; not, however, with the 1.2 glycols but with the oxides.

In the transformation of hydrobenzoïn into diphenylacetaldehyde, and now again in that of benzpinacone into benzpinacoline, I have shown that the first theory is untenable. In view of this I consider the existence of a trimethylene-ring also in the transformation of pinacone into pinacoline too as being less probable. Of course a direct proof, as in the case of the aromatic α-glycols, cannot be produced, but, provisionally, this theory seems to me to lack all foundation. It looks to me as if Nef himself is abandoning this theory, because, whilst formerly 4) he considered the trimethylene-ring as very pro-

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1) Couturier. Ann. chim. phys. [6] 26 p. 434. Erlenmeyer. Ber. 14 p. 322. Note. Zelinsky and Zelikow. Ber. 34 p. 3251.

2) Erlenmeyer. Ann. 316 p. 84.

3) Ann. 335 p. 243.

4) Ann. 318 p. 38,

bable, he now, to judge from the above quotation, definitely adopts the oxide-ring [1]).

The results of my researches, I may draw up in the following rule:

In the transformation of the 1.2 glycols into aldehydes, a real intramolecular atomic rearrangement takes place, which cannot be explained by any normally-proceeding intermediate reaction; it has not, however, been decided as yet whether this atomic migration takes place with the 1.2 glycols themselves or whether the oxides are formed first and then undergo an intramolecular rearrangement.

I am now making experiments in that direction with Dr. MEERBURG.

Chemistry. — Prof. A. P. N. FRANCHIMONT presents to the Library of the Academy a dissertation from Dr. J. MOLL VAN CHARANTE, entitled: *"Sulpho-isobutyric acid and some of its derivatives"* and offers the following explanation.

(Communicated in the meeting of September 24, 1904).

Dr. MOLL VAN CHARANTE has commenced at my instigation to thoroughly investigate sulpho-isobutyric acid. He prepared it according to the process which I had published many years ago for the preparation of those aliphatic sulphocarboxylic acids in which the sulphonic acid group is attached to the same carbon atom as the carboxyl group (namely from the acid anhydrides with sulphuric acid). These acids are not only important from the fact that they are bibasic acids, of which our knowledge leaves generally much to be desired, but also because the two acid functions are of themselves, and not merely on account of their position, of different strength, and are situated together more closely than in the case of the aromatic acids, and can therefore, exert a greater influence on each other. The difficulties experienced in the case of sulphoacetic acid, sulphopropionic acid etc. caused by the mobility of the hydrogen atoms which are placed at the same carbon atom could not present themselves here, because the atom to which the two acid functions are linked, does not carry hydrogen.

The said method of preparing, which had never been fully elucidated, in which two mols. of acid anhydride react with one mol. of sulphuric acid to yield one mol. of sulphonic acid is thus explained by Dr. MOLL VAN CHARANTE: a diacylsulphuric acid is formed which

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[1]) At least if the quotation is meant for *all* the 1.2 glycols.

on being warmed is converted into monacylsulphonic acid, which in contact with water yields sulphonic acid and carboxylic acid:

$C_n H_{2n+1}$ CO.O.SO$_2$.O.CO.$C_n H_{2n+1}$ passing into $C_n H_{2n+1}$ CO.O. SO$_2$.$C_n H_{2n}$ CO.OH and then by H_2O into $C_n H_{2n+1}$ CO.OH and HO.SO$_2$. $C_n H_{2n}$.CO.OH.

Specially undertaken experiments led him to this conclusion and also taught him that when the acid chloride was used instead of the acid anhydride also two mols. of the latter are required to one mol. of sulphuric acid. The action of chlorosulphonic acid on carboxylic acids, which is also given as a method of preparing sulphonic acids, is understood by him to first yield the acid chloride and sulphuric acid, which then react on each other with formation of the sulphonic acid.

Sulpho-isobutyric acid itself is a very hygroscopic substance containing two mols. of water of crystallisation. The barium salt contains three mols. of water, the sodium salt half a mol. The neutral silver salt is anhydrous like the acid salt, which latter can only be obtained in the presence of a large excess of the acid.

When acting on the sodium salt with phosphorus pentachloride Dr. MOLL VAN CHARANTE obtained, according to circumstances, either the dichloride or a chloro-anhydride, which is the chloride of the carboxylic- and the anhydride of the sulphonic acid function. The dichloride is a colourless liquid, which distils at about 55° under a pressure of $1-{}^1/_2$ m.m. mercury, with a sp. gr. $d\frac{20}{4} = 1.4696$ and a refractive power $n_D = 1.4887$; it solidifies at $-10°$. The sulpho-anhydride-carboxy-chloride is solid, crystallises from ligroin and melts at 61°.

With a little water the dichloride yields sulpho-chloride-isobutyric acid, which is crystalline and melts at 134°. With more water, sulpho-isobutyric acid is formed. With methyl alcohol the ester of the carboxylic function is generated whilst the sulpho-chloride function remains. This ester sulpho-chloride is a liquid, which passed over at a pressure of $1^1/_2$ m.m. at about 60° and solidified at 21°.5; the sp. gr. was $d\frac{20}{4} = 1.3436$, the refractive power $n_D = 1.46658$. Treatment with sodium methoxide dissolved in methyl alcohol yielded not the dimethyl ester but the ester sodium salt of the sulphonic acid.

The dimethyl ester prepared from the neutral silver salt with methyl iodide was a liquid which passed over at a pressure of $1-{}^1/_2$ m.m. between 82°—78°, solidified on cooling and then melted at 4°; the sp. gr. was $d\frac{20}{4} = 1.2584$, the index of refraction $n_D = 1.44481$.

The neutral ester is saponified by methyl alcohol and then yields an acid one like all sulphonic esters. With ammonia it yields an ammonium salt of the sulphonic ester function, which is also an ester of the carboxylic acid.

The acid ester, namely the carboxylic ester of the sulphonic acid, was also obtained from the sodium salt of sulpho-isobutyric acid by means of hydrogen chloride and methyl alcohol and is hygroscopic. Its isomer, the carboxylic acid of the sulphonic ester, which was prepared from the acid silver salt with methyl iodide, is not hygroscopic, it crystallises from benzene and melts at 90°. Dr. MOLL VAN CHARANTE's experiences with the esters of sulpho-isobutyric acid agree fairly well with those of WEGSCHEIDER with metasulphobenzoic acid.

The melting points of the compounds obtained behave as might be expected; those of the sulphonic acid chlorides are more elevated than those of the sulphonic esters; those of the carboxylic chlorides are lower than those of the carboxylic esters. The melting points of the esters as well as those of the chlorides of the carboxylic acids are lower than those of the carboxylic acids themselves.

Mathematics. — "*The relation between the radius of curvature of a twisted curve in a point P of the curve and the radius of curvature in P of the section of its developable with its osculating plane in point P.*" By W. A. VERSLUYS. (Communicated by Prof. P. H. SCHOUTE).

(Communicated in the meeting of September 24, 1904.)

§ 1. THEOREM. *For each twisted cubic C^3 the ratio is constant of the radius of curvature in any point P to the radius of curvature of the section of the osculating plane in the point P with the developable O_4 belonging to C^3.*

PROOF. If we take P to be origin of coordinates and the tangent, principal normal and binormal of the curve C^3 in the point P to be the axes of coordinates, then C^3 is the cuspidal curve of the surface O_4 enveloped by the plane

$$A\,t^3 - 3\,B\,t^2 + 3\,C\,t - D = 0,$$

where

$$\begin{aligned} D &= z, \\ C &= c_2\,y, \\ B &= b_1\,x + b_2\,y + b_3\,z, \\ A &= a_1\,x + a_2\,y + a_3\,z + a_4. \end{aligned}$$

The coordinates of the points of the curve C^3 satisfy the conditions:

$$t\,C = z, \qquad t^2\,B = z, \qquad t^3\,A = z,$$

whence

$$z = \frac{a_4\,b_1\,c_2\,t^3}{b_1\,c_2 - a_1\,c_1\,t + (a_1\,b_2 - a_2\,b_1)\,t^2 - a_3\,b_1\,c_2\,t^3} = \frac{a_4\,b_1\,c_2\,t^3}{N}.$$

$$y = \frac{a_4\,b_1\,t^2}{N}, \qquad x = \frac{a_4\,t\,(c_2 - b_2\,t - b_3\,c_2\,t^2)}{N}.$$

Now the radius of curvature R_0 of the twisted curve C^3 in the point P is the same as the radius of curvature of its orthogonal projection on its osculating plane in P, the curve with its projection in P having three consecutive points in common. The parameter expressions for the coordinates of this projection are

$$y = \frac{a_4\,b_1\,t^2}{N} \quad \text{and} \quad x = \frac{a_4\,t\,(c_2 - b_2\,t - b_3\,c_2\,t^2)}{N}$$

From the value of y we find $\frac{dy}{dt} = 0$ for $t = 0$; so for the general formula

$$R = \frac{(dx^2 + dy^2)^{3/2}}{dx\,d^2y - dy\,d^2x},$$

giving the radius of curvature of a plane curve, can be substituted the simpler expression:

$$R_0 = \frac{dx^2}{d^2y_{t=0}} = \frac{\left\{ \frac{b_1\,c_2 \times a_4\,c_2}{(b_1\,c_2)^2} \right\}^2}{\frac{2\,a_4\,b_1}{b_1\,c_2}} = \frac{a_4\,c_2}{2\,b_1^{\,2}}.$$

The equation of the surface O_4 enveloped by the plane

$$A\,t^3 - 3\,B\,t^2 + 3\,C\,t - D = 0$$

is

$$A^2\,D^2 - 6\,A\,B\,C\,D + 4\,A\,C^3 + 4\,B^3\,D - 3\,B^2\,C^2 = 0.$$

The curve of intersection with the osculating plane $D = z = 0$ is:

$$C^2\,(4\,A\,C - 3\,B^2) = 0.$$

So the equation of the conic d_2 lying in the osculating plane is:

$$4\,(a_1\,x + a_2\,y + a_4)\,c_2\,y - 3\,(b_1\,x + b_2\,y)^2 = 0.$$

The equation of the parabola osculating this conic d_2 in the origin is:

$$4\,a_4\,c_2\,y - 3\,b_1^{\,2}\,x^2 = 0.$$

This parabola has in the origin the same radius of curvature r_0 as the conic d_2. The radius of curvature in the vertex of the parabola is the parameter. So the radius of curvature r_0 of the conic d_2 in the origin is $\frac{2 a_1 c_2}{3 b_1^2}$.

From the values:

$$R_0 = \frac{a_1 c_2}{2 b_1^2} \text{ and } r_0 = \frac{2 a_1 c_2}{3 b_1^2}$$

now follows:

$$R_0 : r_0 = 3 : 4. \qquad Q. E. D.$$

§ 2. The theorem can be easily expanded to a general twisted curve C.

Let P be an ordinary point of C, the tangent and the osculating plane in P showing no particularities. Through point P and five consecutive points of C a twisted cubic C^3 can always be laid. The radius of curvature R_0 in the point P is the same for the curves C and C^3, having six consecutive points in common. The osculating planes of the curves C and C^3 in the point P will coincide too. This common osculating plane O intersects the developables belonging to C and C^3 according to the tangent in P counting double and moreover according to two plane curves d and d_2.

If the curves C and C^3 had but a three-point contact in P, the curves d and d_2 would have a common tangent in the common point P, so that the curves d and d_2 would have in P at least two consecutive points in common. If the curves C and C^3 were to have a five-point contact, a common generatrix of the two developables not lying in the common osculating plane O would meet the osculating plane O in a third common point of the curves d and d_2. Now that the curves C and C^3 have a six-point contact in P the curves d and d_2 will have at least four consecutive points in common. These two sections d and d_2 have thus in P the same radius of curvature r_0. Consequently in the ordinary point P of the twisted curve C we have:

$$R_0 : r_0 = 3 : 4.$$

§ 3. When two arbitrary twisted curves have in a point P a three-point contact, they have in that point the same radius of curvature R. If now the common osculating plane O in P of the two curves cuts the two developables belonging to the curves in the plane curves d and d' then the radii of curvature in P of these sections d and d' are both $\frac{4}{3} R$ and therefore equal. The curves d and d' have thus in P also a three-point contact. From this follows the theorem:

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If two twisted curves have in P three consecutive points in common this will be also the case with the plane curves forming part of the sections of the common osculating plane with the developables belonging to the twisted curves.

The radius of curvature of the section d in the point P being four thirds of the radius of curvature of the cuspidal curve C' in this same point, the curves d and C' have in P but two points in common.

From the theorem proved here, follows once again the theorem communicated by me before, concerning the situation of the three points which a twisted curve has in common with its osculating plane. (see These Proc., Febr. 27th, 1904).

§ 4. By expansion of the coordinates of an arbitrary algebraic or transcendent twisted curve in the proximity of an ordinary point P into convergent power series of a parameter t, the theorem of § 1 can be proved also directly for such a twisted curve without using the twisted cubic.

Let P be an ordinary point of the curve C; if the tangent, the principal normal and the binormal in P are taken respectively as X-axis, Y-axis and Z-axis, then the coordinates of the twisted curve C become:

$$x = a_1 t + a_2 t^2 + \ldots \; ,$$
$$y = b_2 t^2 + b_3 t^3 + \ldots \; ,$$
$$z = c_3 t^3 + c_4 t^4 + \ldots \; .$$

The point P corresponds to the value zero of the parameter t. If P is an ordinary point the coefficients a_1, b_2 and c_3 cannot be zero. Let R_0 be the radius of curvature of C in point P, thus the value obtained by the radius of curvature R for $t = 0$. The radius of curvature in P of the projection of C on the osculating plane $z = 0$ is also R_0, this projection having in P three consecutive points in common with C.

The coordinates of the points of this projection are:

$$x = a_1 t + a_2 t^2 + \ldots \; ,$$
$$y = b_2 t^2 + b_3 t^3 + \ldots \; .$$

As $\frac{dy}{dt}$ is equal to 0 for $t = 0$ the general formula for the radius of curvature

$$R = \frac{(dx^2 + dy^2)^{3/2}}{dx\, d^2y - dy\, d^2x} \, ,$$

transforms itself into the simpler one

$$R_0 = \frac{dx^2}{d^2 y_{t=0}} .$$

It is easy to find

$$R_0 = \frac{a_1^2}{2b_1} .$$

The coordinates ξ, η and ζ of an arbitrary point Q on the developable belonging to C' can be expressed in the parameters t and r where r represents the distance from point Q (ξ, η, ζ) to point (x, y, z) of the cuspidal curve measured along the tangent of C' passing through Q. The coordinates of Q are:

$$\xi = x + r \frac{dt}{ds} \frac{dx}{dt} ,$$

$$\eta = y + r \frac{dt}{ds} \frac{dy}{dt} ,$$

$$\zeta = z + r \frac{dt}{ds} \frac{dz}{dt} .$$

For the points Q situated in the osculating plane $\zeta = 0$ the relation

$$0 = z + r \frac{dt}{ds} \frac{dz}{dt}$$

must exist between the parameters r and t. By eliminating r out of this relation and the equations for ξ and η we find expressed in functions of t the coordinates of the points Q situated in the plane $\zeta = 0$. These coordinates of the points of the curve of intersection d are

$$\xi = x - z \frac{dx}{dt} : \frac{dz}{dt} ,$$

$$\eta = y - z \frac{dy}{dt} : \frac{dz}{dt} .$$

or

$$\xi = a_1 t + a_2 t^2 + \dots - \frac{(c_3 t^3 + c_4 t^4 + \dots)(a_1 + 2a_2 t + \dots)}{3c_3 t^2 + 4c_4 t^3 + \dots} = \frac{2}{3} a_1 t + \dots .$$

$$\eta = b_2 t^2 + b_3 t^3 + \dots - \frac{(c_3 t^3 + c_4 t^4 + \dots)(2b_2 t + 3b_3 t^2 + \dots)}{3c_3 t^2 + 4c_4 t^3 + \dots} = \frac{1}{3} b_2 t^2 + \dots .$$

As here too $\frac{d\eta}{dt}$ is equal to 0 for $t = 0$ we find as above that the radius of curvature r_0 in point P of the curve d is:

$$r_0 = \frac{d\xi^2}{d^2 \eta} .$$

This formula gives for r_0 the value:

$$r_0 = \frac{\frac{4}{9}\,a_1^2}{\frac{2}{3}\,b_2} = \frac{2\,a_1^2}{3\,b_2}.$$

From the obtained values $R_0 = \frac{a_1^2}{2\,b_2}$ and $r_0 = \frac{2\,a_1^2}{3\,b_2}$ we get

$$R_0 : r_0 = 3 : 4.$$

Delft, Sept. 1904.

Physiology. — "*Degenerations in the central nervous system after removal of the flocculus cerebelli*". By Dr. L. J. J. Muskens. (Communicated by Prof. C. Winkler).

(Communicated in the meeting of September 24, 1904).

In 6 rabbits the flocculus of the right side was extirpated. This organ lies, as is well known, in these animals in a separate bony hole, so that we here have the possibility to remove a part of the cerebellum without disturbing the nervous structures of the neighbourhood in their conditions of nutrition as well as of pressure. The animals were killed after 8 days to 5 weeks and complete series stained after Marchi, were prepared.

The degenerations of fibres after this lesion in 4 of the 6 cases were found exclusively directed upward i. e. to the superior crus cerebelli and to the pons.

In one case there was a fine degeneration all over the restiform body; in this case however it could not be made out with certainty whether we had to deal with really descending degeneration, because firstly all through the cord fine, black spots were found, and secondly the black spots were of so little dimensions, that there is much doubt about the genuineness of such a fine degeneration. In this animal the staining was insufficient, irregular and not limited to degenerated nerve-fibres, for an unknown reason, so that we do not think much value can be attached to this single case, in which downward degeneration was found.

In another wellstained case in the restiform body a number of degenerate fibres on the operated side was found; also in the longitudinal posterior fascicle and in the field of the tecto-spinal bundle, equally on the operated side. In the superior cervical region also a small field with the base lying towards the margin, the point towards the restiform body was found full of degenerate fibres. Lower down than the upper cervical segments, these degenerate fibres do not reach. In this case not only the flocculus and the floccular peduncle, but also the vestibulary nucleus was severed, so that also this experiment cannot be recognized as a clear experiment.

Although allowance must be made for an eventual different result after extirpation of other parts of the cerebellum of the rabbit, so we think, that these experiments show clearly the absence of descending degeneration after a sharply localised lesion of the floccular cortex. The discussion in the literature between MARCHI, FERRIER and TURNER, THOMAS, BIEDL and RISIEN RUSSELL regards the question, how much of the found degenerations must be ascribed to lesion of the neighbourhood, because, as THOMAS justly remarks, exactly in this region of the cerebro-spinal axis it is characteristic, that also without direct lesion by the severing instrument yet by haemorrhage or an alteration of pressure, extensive degenerations can be caused. As in these experiments certainly no such lesion of the neighbourhood can have arrived and in the completely successful cases the cord was found free of degeneration, we may be sure, that from the ganglioncells of this part axis-cylinders with centrifugal course to the medulla are not found, so that for this part of the cerebellum at least, the original data of MARCHI are not confirmed. Thus these observations as also those of PROBST can be regarded to agree with the English observers, after whom only after lesion of the nucleus-DEITERS descending degeneration of the anterior and lateral tracts is found. In judging this result it is important to observe, that also in another point than by its own bony capsule the rabbit must be regarded as an abnormal form.

The flocculus of the rabbit contains viz. except its part of the cerebellar cortical gray matter and its af- and ef-ferent fibres also a nucleus of large multipolar ganglioncells, such as are found in the nucleus dentatus. The study of the development of kindred animals (squirrel) leave not the least doubt, that indeed a part of the dentate nucleus is dislocated in the flocculus. It appears that it is not always in connection with the principal nucleus.

Now I do not think that for the elucidation of the question, whether there exist descending cerebellar tracts, this circumstance must be regarded an indesirable complication, but rather we may reckon this a useful detail, in so far as it allows to exclude at the same time, that such efferent fibres descending in the cord, should spring from (this part at least of) the dentate nucleus.

Regarding the ascending degeneration in the different operated animals the most complete accordance is found. Two bundles are found in all successful cases, very clearly and in exactly the same place of the cross-sections and both find in the same region of the cerebrum their end, viz. in the regio subthalamica. In the first place the superior cerebellar peduncle being the most voluminous bundle, where we find fibres of heavy caliber. This degeneration shows especially gross fibres, compared with the fine degenerations, found elsewhere in the rabbit. The degeneration is found especially in the middle third part of the superior cerebellar peduncle, whereas the medial and lateral thirds are nearly entirely free from degenerate fibres. Arrived about at the posterior quadrigeminal body, the degenerate fibres curve downward in a nearly rightangle, as this is represented by the authors, building the wellknown peduncular decussation. Only a few sections separate the commencement and the finish of the decussation in the sections. In the substantia reticularis the direction is again purely longitudinal to the long axis of the cerebral stem, where as in the region of the red nucleus it becomes clear, that especially the ventral part of the red nucleus comes in contact with the crossed peduncle. This crossed connection is, as far as the flocculus is concerned complete. Here it may be recalled, that Probst has shown, that after extirpation of more dorsally situated cerebellar parts of the cat also non-crossed fibres run to the subthalamic region.

Besides this most important upward degenerating bundle, there is another tract up to now only described as far as I am aware by PROBST, which is constituted of finer fibres than the first bundle, takes its course by the substantia reticularis, of the contra-lateral side, and joins the first tract about its arrival in the red nucleus. Both together run frontalwards, and end in the ventral part of the nucleus ventralis thalami. The sections leave no doubt, that no fibres from the flocculus arrive in the thalamic region uncrossed, but all decussate either in the decussation of the superior peduncle or as far as the second bundle is concerned in the pontine region, right near its emergence from the flocculus. Also THOMAS has designed this degeneration, but he thinks, that here we have to deal with descending collaterals of the frontal cerebellar peduncle, which leave the principal bundle after the decussation of this peduncle. PROBST on the other hand thinks, that these fibres arise from the dentate nucleus, pass directly through the region of the vestibular nuclei, to the substantia reticularis of the crossed side and ascending frontalwards are found in the same region up to their junction with the superior crus cerebelli.

My own sections suggest very strongly indeed, that these centrifugal (from the cerebellum, or rather from the nucleus dentatus) fibres, take their course by the superficial layers of the middle cerebellar peduncle and then can be followed right through the pyramidal bundles or partly winding around them to the reticular substance.

In different series it becomes clear that proceeding in the series of sections from below upwards there, where are found the first degenerate fibres in the reticular substance, also the first degenerate fibres appear in the middle peduncle. While by THOMAS no sound reasons are given for his conception about the significance of this bundle, it pleads against the opinion of PROBST that in the region of the vestibulary nuclei, no degenerate fibres are found.

Finely the sections show, compared with the sections gained by other experiments, that the ventral thalamic bundle originates for the greater part from the ventral portions of the cerebellum, especially of the flocculus. Sections of cats-brain after similar operations leave no doubt, that after lesion of more dorsal cerebellar portions, there exists a very marked contrast between the very pronounced degeneration of the crus cerebelli ad corpora quadrigemina and the very slight degeneration of the ventral thalamic bundle, whereas as well in the cat as in the rabbit after exclusive lesion of the flocculus, both bundles are affected about equally.

Physics. — *"The validity of the law of corresponding states for mixtures of methyl chloride and carbon dioxide,"* by Prof. H. KAMERLINGH ONNES and Dr. C. ZAKRZEWSKI. Communication N°. 92 from the Physical Laboratory at Leiden by Prof. Dr. H. KAMERLINGH ONNES (continued).

(Communicated in the meeting of June 25, 1904).

§ 1. *Introduction.* In n°. IX of the "Contributions to the knowledge of VAN DER WAALS' ψ-surface" we have expressed the hope of giving an experimental contribution to the investigation of the co-existing mixtures of methyl chloride and carbon dioxide at low temperatures in connection with the test of the law of corresponding states for mixtures, which for many years has formed a subject of experimentation at Leiden. Of the extensive territory of reduced states, which the mixtures of carbon dioxide and methyl chloride afford for measurements on either side of the critical state, (reason why in about 1890 it was chosen for the first investigations of the ψ-surface) a considerable portion round the critical state has been immediately investigated by KUENEN (Comm. N°. 4, April '92). HARTMAN in Comm. N°. 43, June '98 has added to this area that of the coexisting phases at 9°.5 C. We have extended the area investigated in two directions, albeit only by a few preliminary researches.

The results of some of those measurements, though a few are only preliminary and served chiefly as a means for us to decide upon the method of investigation, seem important enough now that still so little is known about the different degrees of approximation to which the law of corresponding states holds for mixtures in different fields of reduced state $\left(v = \frac{v}{v_k},\ t = \frac{T}{T_k}\right)$.

Our measurements refer in the first place to gaseous mixtures under almost normal conditions, in the second place to coexisting phases at low temperatures.

For the normal gaseous phase we found the law of corresponding states to be confirmed to a high degree of approximation. The virial coefficient B, which determines the deviation of mixtures of methyl chloride and carbon dioxide from BOYLE's law at small densities, can be sufficiently derived by means of the law of corresponding states.

Greater deviations were found when we investigated the coexisting phases at low temperature. Here we have determined by means of the dew-point apparatus, described in the first part of this communication, the begin condensation pressure of the mixture $x = {}^1/_2$ at — 25° C.: the temperature for which we have constructed the ψ-surface in Suppl. N°. 8, Sept. '04. The deviations found are rather great, they point to an increase of the deviations from the law of corresponding states in the mixtures at low temperatures in the liquid state. The determination of the end condensation pressure for the same mixture $x = {}^1/_2$ at — 25° C. with the piezometer of the first part of this communication would involve complications (comp. ibid. § 5). In order to obtain an idea of the deviations of the liquid branch of the binodal curve at $x = {}^1/_2$ from that according to the law of corresponding states, we have investigated the condensation pressure for $x = {}^1/_2$ at a lower temperature, viz. — 38°.5 C. This corroborated the result of the investigation of the vapour phase at — 25° C.

I. The compressibility in the neighbourhood of the normal state.

§ 2. *Determination of the second virial coefficient.* The mixtures were prepared and the compressibility determined in the mixing apparatus and volumenometer described in Comm. N°. 84, March '03. The method of observation and calculation has been treated in detail by **Keesom**, Comm. N°. 88, Jan. '04.

The gases were prepared by distillation first in ice, subsequently in solid carbon dioxide. From previous communications it will appear that in this way pure carbon dioxide is obtained. Of methyl chloride the same will be proved in the continuation of this paper (§ 8).

The values found at the temperature t of the pressure p, volume V and molecular composition of methyl chloride x are given in table I.

TABLE I. Compressibility of mixtures of carbon dioxide and methyl chloride.

N⁰.	p in m m	V in c.c.	t
	$x = 1$ (CH_3Cl)		
I.	1137.33	537.67	20.05
II.	593.69	1043.51	20.07
III.	479.23	1296.33	20.07
	$x = 0.6945$		
I.	1200.32	537.49	20.09
II.	624.45	1043.50	20.10
III.	503.49	1297.01	20.08
	x 0.5030		
I.	1173.08	537.73	19.97
II.	608.87	1043.66	19.87
III.	490.88	1296.30	19.87

The values for $x = 0$ may be borrowed from Comm. N°. 88. For the calculation of these observations we shall use the empirical reduced equation of state of Comm. N°. 71, June '01, which is particularly suited for the investigation of the degree of validity of the law of corresponding states, in the form as laid down in § 4, which deviates little from that of Suppl. N°. 8, Sept. '04.

In the first place the observed pressures must be reduced to the same temperature 20° C. For this purpose we have calculated the real coefficients of pressure-variation of carbon dioxide (0,003460) and methyl chloride (0,003586) with the equation of state mentioned and the coefficient of pressure-variation given below for ideal gases, and we have taken linearly interpolated values for the mixtures.

Owing to the small differences in temperature the errors ensuing from this remain below those of the observation.

Let v be the volume expressed in terms of the theoretical normal volume (introduced in Comm. N°. 47 Febr. '99), then we have approximately

$$pv = A + \frac{B}{v}\text{, where } A = 1 + \alpha_\infty t$$

and α_∞ the coefficient of pressure-variation of an ideal gas. One of the advantages of the empirical reduced equation of state is, that it teaches us the degree of approximation to which the higher terms in $\frac{1}{v}$ may be omitted. Then we have for the calculation of the second virial coefficient as a first approximation, if B^2 also is neglected (for further approximations see § 5):

$$\frac{p_1 v_1}{p_2 v_2} - 1 = \frac{B}{A^2}(p_1 - p_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and with $\alpha_\infty = 0{,}00366195$ (instead of 0,0036625 of Comm. N°. 71) we derive from table I:

TABLE II. Second virial coefficient for mixtures of carbon dioxide ($x = 0$) and methyl chloride ($x = 1$) to the first approximation.

composition	$\frac{B}{A^2}$ from I and II	$\frac{B}{A^2}$ from I and III	$\frac{B}{A^2}$ mean	B
$x = 1$	— 0.01797	— 0 01800	— 0.01798	—0.02071
0.6945	— 0.01302	— 0 013[illegible]9	— 0.01310	—0.01509
0 5030	— 0.01034	— 0.01005	— 0.01019	—0.01175
0		KEESOM, Comm. N°. 88.		—0.00654

§ 3. *The virial coefficient B as a quadratic function of the molecular composition x.*

According to VAN DER WAALS' equation of state $B = RTb_{TNW} - a_{TNW}$, if a_{TNW} and b_{TNW} represent VAN DER WAALS' constants with regard to the theoretical normal volume. Hence, to the first approximation, we must have for the mixture with the composition x

$$^{(ClMe.\,CO_2)}_{x}B = {}^{(ClMe)}Bx^2 + 2\,{}^{(ClMe.\,CO_2)}_{(12)}Bx(1-x) + {}^{(CO_2)}B(1-x)^2$$

By means of least squares we found[1]):

$$^{(ClMe)}B_{20^0} = -0.020772$$

$$^{(ClMe.\,CO_2)}_{(12)}B_{20^0} = -0.010067$$

$$^{(CO_2)}B_{20^0} = -0.006515.$$

The agreement appears from the following table:

x	B observed	B computed	Obs.—Comp.
1	— 0.02071	— 0.02077	+ 0.00006
0.6945	— 0.01509	— 0.01490	— 0.00019
0.5030	— 0.01175	— 0.01190	+ 0.00016
0	— 0.00654	— 0.00652	0.00002

The deviations are less than $2\,^0/_0$, hence also less than the deviations of the single values of $\frac{B}{A^2}$ inter se. Thus the agreement with the quadratic form was sufficiently proved, so that for the time being measurements with other mixtures, not exceeding this accuracy, could be left off.

§ 4. *Validity of the law of corresponding states for the virial coefficient B.* According to the law of corresponding states the virial coefficients are derived from the coefficients of the reduced equation of state through multiplication by functions of T_k and p_k (comp. Comm. N°. 71 and also Suppl. N°. 8, Sept. '04, the first four sections).

As the critical data of mixtures of carbon dioxide and methyl chloride have been derived in Comm. N°.59*b* from KUENEN's experiments, we may determine B for a given temperature, for instance B_{20} by

$$B_{20} = \frac{T_k^2}{p_k}\,\mathfrak{B}_\mathfrak{t}.$$

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[1]) The coefficients given here have been derived from values for B which do not differ essentially from those given in table II.

where $\mathfrak{B}_{\mathfrak{t}}$ is the value of the function $\mathfrak{B}$ of the reduced temperature belonging to $\mathfrak{t} = \frac{293{,}01}{T_k}$.

For $\mathfrak{B}$ we have used a function of a form differing slightly from the form VI. 1, given in Suppl. N°. 8, which did not only agree with hydrogen, oxygen and nitrogen but also with ether, viz. a form VI. 2, which instead of agreeing with ether in the same way as VI. 1, agrees with the average of ether and isopentane:

$$10^{5}\,.\,\mathfrak{B} = +\,179{,}883\,\mathfrak{t} - 374{,}487 - 181{,}324\,\frac{1}{\mathfrak{t}} - 110.267\,\frac{1}{\mathfrak{t}^{3}}$$

The agreement appears from the following table, where we find in the first column the values calculated according to the last formula, and in the second column those of the quadratic formula of § 3:

	according to corresponding states	according to quadratic formula	difference
1	— 0.021920	— 0.020772	— 0.001148
1/2	— 0.016502	— 0.015866	— 0.000636
3/4	— 0.012179	— 0.011855	— 0.000324
0	— 0.006485	— 0.006515	+ 0.000030

The deviations on the side of the methyl chloride are larger than those of the errors of observation and those of the quadratic formula. Methyl chloride, therefore, does not agree so well with ether and isopentane as carbon dioxide. This same result is also arrived at in another way. It appears, however, that the mixtures do not deviate more than the methyl chloride itself.

(To be continued).

Physics. — "*On the measurement of very low temperatures. VII. Comparison of the platinum thermometer with the hydrogen thermometer*". (Continuation of Comm. N°. 77, Febr. 1902). By B. Meilink. Communication N°. 93 from the Physical Laboratory at Leiden by Prof. H. Kamerlingh Onnes.

(Communicated in the meeting of June 25, 1904).

§ 5. *The measurements at low temperatures.* The thermometers were mounted as described by Kamerlingh Onnes in Comm. N°. 83 Febr. 1903 § 5. During the first preliminary measurements, the hydrogen thermometer and the resistance thermometer (cf. Comm. N°. 77 § 2) were placed in the cryostat (described in Comm. N°. 51, Sept. 1899), which was modified as described in § 2 Comm. N°. 83. In this cryostat a vacuum vessel was placed inside of B_1 Pl. I, Comm. N°. 51), which vacuum vessel by means of cork was pressed against the walls of B_1 (cf. end of § 2 and also Pls. I and II of Comm. N°. 83). The inner wall took the place of ξ_0 in Pl. II, Comm. N°. 83 (the same parts of Comms. N°. 83 and N°. 77 are marked with the same letters).

These preliminary experiments had shown, that, after repeated measurements at the lowest temperatures, the original value was again found for the resistance at 0° C., hence that the platinum wire, though its expansion differed from that of glass, was not lengthened and that it also remained properly in the notches. Further it had become clear that an accurate comparison of the two thermometers was only possible when the temperature of the bath was kept constant with the utmost care, and there we met with the difficulties treated in § 2 of Comm. N°. 83. It was attained by arranging the cryostat as described in § 5 of Comm. N°. 83. It may moreover be remarked that the liquid gas was always kept higher than ξ_2' (Comm. N°. 83, Pl. II); else, notwithstanding the level in and outside the protecting cylinder would go up and down through the motion of the stirrer, no circulation would be produced.

The course of a measurement was as follows. As soon as the circumstances under which we desired to make a measurement were established, the resistances of the leads were determined, then the resistance of the platinum wire was adjusted and, by giving signs to the assistant charged with the regulation of the pressure, care was taken that this resistance, and hence the same temperature, were maintained. After about ten minutes we began, while constantly reading the galvanometer, the measurements with the hydrogen thermometer and continued them until the liquid was evaporated or until we deemed that sufficient data were obtained. At the end the measurement of the resistance of the leads was repeated.

The observer at the galvanometer had, therefore, only to look after the continual closing and breaking of the currents and the noting down of the values of the galvanometer readings and of the time belonging to them. Afterwards the deflections were derived from this (see Pl. III Comm. N°. 83) and the mean deflection during the time of observation was found by means of a planimeter.

§ 6. *Zero after the measurements.* By a too rapid decantation of liquid oxygen, numerous bursts had unfortunately come in the cylinder of the resistance. To repeat with it the above described operations for the determination of the zero seemed rather dangerous, especially as the refastening in the cryostat would have involved many difficult operations.

Therefore in order to bring the resistance thermometer to a constant temperature near 0° C., the case V of the cryostat (Pl. I, Comm. N°. 83) was screwed off from the cover N_2 (Pl. I, Comm. N°. 51), while the other parts of the cryostat remained fastened to the cover, and it was replaced by a zinc cylindrical vessel, which could be managed more easily. This vessel was provided with a rim fitting on to N_1 and was placed in another larger zinc vessel, so that a jacketing space of 5 c.m. remained which was entirely filled with ice. Then isopentane was distilled into B_{a2} (Pl. II, Comm. N°. 83) and the apparatus was left to itself during one night. The next day the temperature (near 0°) had become constant and we determined it (while stirring) by means of a thermoelement (Θ Pl. II, Comm. N°. 83).

§ 7. *Corrections.* A survey of the mounting of the WHEATSTONE's bridge (cf. § 3 Comm. N°. 77) is given in fig. 5. R indicates the resistance to be measured, R_1 and R_2 the two coils of manganin wire, R_3' and R_3'' the resistance boxes of HARTMANN and BRAUN and of SIEMENS and HALSKE giving together the resistance $R_3 = R_3' - \frac{R_3'^2}{R_3' + R_3''}$ which with r_{23} forms the fourth arm of the bridge; C_1 and C_2 are the commutators with mercury contact (Comm. N°. 27, May and June 1896), C_3 is the copper commutator treated in § 3 Comm. N°. 77 and represented there in fig. 2.

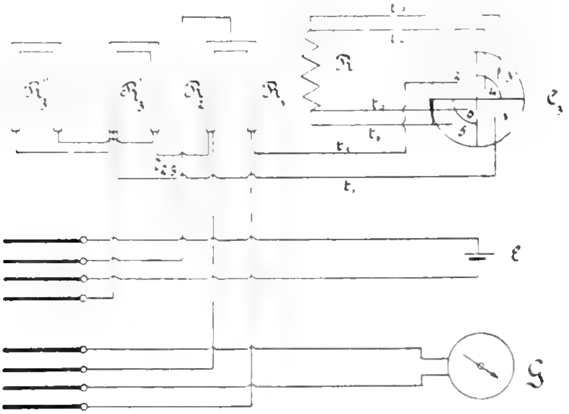

Fig. 5.

Putting for the factor for the inequality of the branches of the bridge $\frac{R_1}{R_2} = 1 + \alpha$, we found $\alpha = 0.00216$ (as mean value of twenty values ranging from 0.00219 to 0.00214). As according to § 3 Comm. N°. 77 the resistance of the platinum wire R is equal to the difference between two measured resistances, one l (the resistance of the leads), another $R + l$, and as the branches of the bridge are so nearly equal, r_{23} is eliminated, and hence we need not know the value of r_{23}.

To the resistances read on the box R_3', the corrections found by calibration must be applied. We may easily convince ourselves that the arrangement of box R_3'' parallel to box R_3' has no perceptible influence on the value of the corrections at R_3'. The corrections of the errors in the nominal box values could be neglected for all coils below 1 Ohm.

For the measurements at low temperature a correction had to be applied, because during the regulation of the temperature the mean deflection was not zero.

In order to express that deflection in terms of the resistance, the platinum thermometer in the bridge, after the measurements were made, was replaced by an equally large box resistance and for a known modification of this resistance the deflection was observed. The regulation of the temperature was in most cases so successful that it was hardly necessary to take the correction into consideration.

The resistance, measured near 0°, was reduced to 0° C. with the approximate formula $W = 110.041\,(1 + 0.0038644\,t - 0.000001031\,t^2)$, derived from preliminary observations.

§ 8. *Survey of a measurement.* The course of a measurement is described in § 5.

The quantities which are derived directly from observation are given in table I (p. 294). Under the head "Connection" I have recorded between which blocks of the commutator C'_3 a conducting connection existed.

Therefore commutator C'_2 was not used while the measurement lasted. This had become possible because the platinum wire was wound free from induction, so that no induced current was observed when the principal current was closed.

From these data we now derive for each connection the value of R_3, i.e. the resistance of the branch of the bridge in which the resistance boxes are placed (apart from r_{23}).

If the value of R_3 which is found when we measure the platinum wire with the leads, is diminished by the value of R_3 which is found with the leads alone, we obtain the resistance of the platinum wire, in the supposition 1°. that the arms of the bridge are equal, 2°. that during the measurement the mean deflection was zero and 3°. that the resistance box requires no correction. For each of these suppositions

TABLE I. Calibration Platinum Thermometer in Oxygen Boiling under Reduced Pressure (May 22, 1902).

Resistance Measurements.

Time.	Connection.	R'_3	R''_3	Position commutator C_1	Position of equilibrium of galvanometer.	Deflection galvanometer.
	1–5 2–6	0.4	1.5		58.5	
	Leads.			Left.		74.5
				Right.		41.7
			1.6	Left.		43.4
					58.2	
	1–3 2–4	0.4	1.6	Left.		43.8
					58.0	
	1–5 2–4 platinum wire.	20 + 2 + 0.3	3200			
					45.2	
$3^h.49'$				Left.		44.0
						45.0
						46.0
						46.7
						47.0
						45.0
$50'$						44.2
					45.4	
to $4^h.25'$				Right.		and so on for all minutes to $4^h 25'$.
$4^h.27'$	Leads.					
	1–3 2–4	0.4	1.5	Left.	46.0	
						55.7
	1–5 2–6	0.4	1.5	Left.		53.8
					46.0	

we must apply the correction mentioned in § 7 in order to find the true resistance. The mean deflection during the measurement is found, according to Comm. N°. 83 § 5, by means of a planimeter.

(See for the graphical representation Pl. III, Comm. N°. 83, which does not, however, bear upon our case).

In the following table the corrections are combined.

TABLE II. Calibration Platinum Thermometer in Oxygen Boiling under Reduced Pressure (May 22, 1902).

Resistance measurement, Corrections.

Ratio arms.	+0.00216	
Correction to R for box values	20 and 2	+0.0005
Mean deflection	+0.1 cM.	

After what has been said above about the method of calculation the further calculation will be sufficiently clear from the following table.

TABLE III. Calibration Platinum Thermometer in Oxygen Boiling under Reduced Pressure.

Resistance at — 197°.08 C.

Time	Connection	R'_3	R''_3	R''_3 mean	R_3	Resistance Pt wire
	1—5 2—6	0.4	1.54	1.55	0.3182	
	1—3 2—4	0.4	1.57			
$3^h.49$—	1—5 2—4	20 + 2	3200		22.1457	
$4^h.25$		+0.3				
	1—3 2—4	0.4	1.53	1.53	0.3171	
	1—5 2—6	0.4	1.53			21.8281

Correction arms of the bridge	+0.0485
Correction resistance box	+0.0005
Correction to mean deflection 0	+0.0002
Resistance	21.8773

Determinations made at other temperatures did not yield anything particular. Only for the zero determination the corrections are somewhat different, as that for the reduction to the mean deflection 0 is no longer necessary. A new one, however, is added because the determination has not been made exactly at 0° C. but at a little higher temperature. After what has been remarked about this in § 7, it seems superfluous to illustrate this small variation by an instance.

§ 9. *Determinations of the resistance at* 0° C. They are made in three series. For the first we still used leads of 0.5 m.m. (Comm. No. 77 § 2 and fig. 3), the insulating liquid was petroleum ether or amylene; for the second the leads were 5 m.m. thick (l.c. fig. 4), the insulating liquid was isopentane; and the third (insulating liquid isopentane) was that treated in § 6.

TABLE IV. Calibration of Platinum Thermometer.

Zero.

	Number of determinations.	Resistance. Smallest	Largest	Mean value.
Series 1. June '01	4	110.031	110.048	110.040
2. Nov.Dec.'01	7	033	57	43
3. Nov. '02.	3	043	51	48
Mean resistance at 0° C.				110.045

§ 10. *Determinations at low temperatures.* The measurements were made at fairly gradually decreasing temperatures; at the lowest temperatures the intervals are smaller.

The measurements with the hydrogen thermometer (see Comm. N°. 77 § 2) are made by Dr. W. Heuse to whom my best thanks are due for the trouble he has taken.

The determinations are made up of two series.

The first series was made between May 13 and July 10, the second series between Dec. 10 and Dec. 22, 1902.

It seems desirable to consider the two series separately.

The first series has yielded results that may be derived from the following table.

In order to judge how the values given here agree inter se, I have first calculated the formula of the form

$$w = w_0 (1 + at + bt^2),$$

TABLE V. Calibration of Platinum Thermometer.

First Series.

Date.	Temperature determined with the hydrogen thermometer.	Resistances measured.	Bath in which the measurements were made.
	0° C.	110.045	comp. § 9.
May 24, '02	— 51°.43 C.	87.760	methyl chloride boiling under reduced pressure.
May 13, '02	— 104°.66	64.256	ethylene.
„	— 104°.38	64.371	id.
„	— 127°.71	53.910	ethylene boiling under reduced pressure.
„	— 128°.88	53.372	
May 16, '02	— 161°.15	38.676	methane.
„	— 161°.15	38.672	id.
„	— 161°.47	38.515	id.
May 22, '02	— 182°.63	28.692	oxygen.
July 10, '02	(— 195°.75) [1]	(22.600)	nitrogen.
May 22, '02	— 197°.08	21.877	oxygen boiling under reduced pressure.
„	— 197°.58	21.673	
July 10, '02	— 209°.93	16.025	nitrogen boiling under reduced pressure.

which agrees with the observations at 0°, at —104°.66 C. and at —182°.63 C., the temperatures which best correspond with those which as a rule are also used by other observers.

The formula becomes

$$w = 110.045\,(1 + 0.0038788\,t - 0.000\,000\,9257\,t^2).$$

The deviations of the observed resistances from the formula are given in the column Obs.—Comp.$_I$ of table VI, and are quite appreciable. In the case of methyl chloride the deviation amounts to 65 on 87760 or a difference in temperature of 0°.15 C. For methane these deviations are 63 on 38674 or a difference in temperature of also 0°.15 C. In oxygen, boiling under reduced pressure, the deviation is 90 on 21637 or about 0°.2 C.

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[1] This observation is less reliable because an uncertain correction to the hydrogen thermometer attained a rather high value.

To find out whether these deviations are perhaps due to irregular errors in the measurement, it will be useful to investigate whether, by addition of another term, the differences between these observations and the calculation might be reduced to within the limits of the errors of observation. It succeeded indeed fairly well as may be seen in column Obs.—Comp.$_{II}$ of table VI. The calculated values are derived by means of the formula

$$w = 110.045\,(1 + 0.0039167\,t - 0.000\,000\,3432\,t^2 + \\ + 0.000\,000\,002069\,t^3).$$

TABLE VI. Test of a Parabolical and of a Third Degree Formula.

First series.

Temperatures determined with the hydrogen thermometer.	Measured resistances	Obs.—Comp.$_I$	Obs.-Comp.$_{II}$
0°	110.045	0	0
— 51°.43	87.760	— 0.065	+ 0.012
— 104°.38	64.371	— 0.011	— 0.017
— 104°.66	64.256	0	— 0.005
— 127°.71	53.910	+ 0.039	0.—
— 128°.88	53.372	+ 0.030	— 0.011
— 161°.15	38.674	+ 0.063	+ 0.019
— 161°.47	38.515	+ 0.051	+ 0.008
— 182°.63	28.692	0	+ 0.008
(— 195°.75)	(22.600)	(+ 0.014)	(+ 0.078)
— 197°.08	21.877	— 0.083	— 0.014
— 197°.58	21.637	— 0.090	— 0.017
— 209°.93	16.025	+ 0.077	+ 0.229

The deviations from formula II, with the exception of the last, although they are not entirely within the limits of the errors of observation which were expected, are only little in excess.

In the case of methane, where the deviation is 19 on 38674, an error in the temperature of 0°.04 C. is sufficient to explain this amount.

In the case of nitrogen boiling under reduced pressure, however, the deviation has become very large, so large even that it cannot be explained by errors of observation. Hence the circumstance that the formula is not fit to represent the resistance so near to the absolute zero must account for this deviation. All the same it is remarkable that this turn appears so suddenly. At —197° C. the formula still holds, at —210° C. there is a deviation of 229 on 16025, i. e. a deviation of 0°.49 in temperature. But if we take into consideration that, according to the formula, the resistance at —243° C. would become zero and that we are only about thirty degrees from this point, we need not wonder at this result.

In order to gain certainty that there was indeed a fairly rapidly increasing variation in the shape of the curve that represents the resistance as a function of the temperature, I resolved to repeat especially these measurements at very low temperature in nitrogen. These constitute what I have called at the beginning the 2nd series. Unfortunately the result was unsatisfactory.

Though the observations indeed point in the same sense, yet one error or another seems to have crept into them and it could no more be detected at the time when the calculations revealed it. We shall omit them here.

Therefore the results as to the amount of the deviations remain more or less uncertain; yet it is very probable that even in nitrogen boiling under reduced pressure, a beginning may be observed of the variation in the course of the temperature function which, as follows from DEWAR's experiments, appears so strongly at the temperature of liquid hydrogen.

The conclusions to which the measurements lead may be summarized as follows.

A representation of the resistance by a quadratic formula, according to the temperature, even if we do not go below — 180° C., is only permitted when no higher degree of accuracy than 0°.2 C. is aimed at. When a greater precision is desired we require for the calibration of a platinum thermometer a greater number of points of comparison. For a comparison to within $\frac{1}{20}$ ° C. a number of at least 6 temperatures of comparison is considered very desirable.

Below — 197° C. the deviations of the platinum thermometer become so large that before using it for this range an investigation must be made of the course of the resistance as a function of the temperature.

Physics. — *"On the measurement of very low temperatures. VIII. Comparison of the resistance of gold wire with that of platinum wire."* By B. Meilink. (Communication N°. 93 (continued) from the Physical Laboratory at Leiden by Prof. H. Kamerlingh Onnes).

(Communicated in the meeting of June 25, 1904.)

§ 1. The investigation described in this paper forms part of the subject mentioned sub 2 in § 1 of Comm. N°. 77, Febr. 1902 and had for its chief object the establishment of the method of observation.

The gold wire was made of the material kindly given us by Dr. C. Hoitsema, inspector and assay-master general of the Mint, according to whom no impurities could be detected in it by means of chemical processes, which, with regard to the accuracy of the gold analysis, excludes an impurity of more than $^1/_{200}$ %. The piece was drawn out to a wire of $^1/_{10}$ mm. in diameter. The great length of the wire used, however, had rendered a soldered joint in the middle necessary.

§ 2. *Arrangement of the wires.* The same advantages which made us prefer a naked platinum wire to one enclosed in a glass tube (cf. Comm. N°. 77) exist also when the wire is made of an other metal, though the difficulties, especially with regard to the action on the metal, are greater.

The difficulties of the arrangement increased, however, considerably with metals of such high conductivity as gold, because then the wire must be so much longer in order to produce a sufficient resistance. With the first forms that were tried, the metal wire lay in a screw-thread etched on a glass cylinder. But with the longer wire the latitude for the expansion became so great that it could slip too easily from the screw grooves and thus cause short-circuiting. In order to obtain deeper grooves the glass cylinder was coated with a paste of oil and carborundum and slowly spirally moved with a speed of $^1/_2$ or $^3/_4$ mm. The cylinder grinds against an iron or copper disk, which is kept in rapid rotation and thus by means of the carborundum a groove is ground in the glass. This groove proved to be much deeper than that formed by etching[1]); the wires of 0.1 mm. in diameter were entirely enclosed in it. On a cylinder of 37 mm. diameter and 55 mm. height we could wind more than 12 meters of wire.

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[1]) Later we have again succeeded in making still deeper grooves by etching.

The investigated wire covered two of these cylinders c_1 and c_2 (see fig. 1, Pl. I), the one fitting into the other and leaving a jacket of about 2 mm. for the circulation of the liquids. A third cylinder c_3 round these two served to protect the wire.

The cylinders rest on a copper star with 3 teeth d in which concentrical grooves are made to hold the glass cylinders. At the other end each of the cylinders, by means of copper ridges e_1, e_2 and e_3, lying on the glass rim, is pressed against the star by means of a tightening rod f and nuts g_1, g_2 and g_3, thus forming one tightly connected whole. As the ridges e_1 and e_2 and also the lower star d served at the same time as connective places for the wire, they were insulated from the tightening rod and the nuts by glass cylinders h_1 and h_2 and plates of mica i_1, i_2 and i_3.

The winding and the mounting was done in the following way. We began by fixing the inner cylinder c_1 between the star and the ridge e_1, the wire was soldered on to the ridge e_1 and led downwards along the groove of the screw-thread on the cylinder. At the bottom it was soldered on to the star. Then the second cylinder was placed round it, the wire was turned upwards along it and fastened to e_2. If the two screws in the glass are wound in the same sense, the wire is almost free from induction. (Cf. the platinum thermometer of the previous paper where this was attained in a different manner).

As in the case of the platinum wire which was treated in the previous paper, there were 4 leads. For the method with the differential galvanometer (cf. § 4) it does not matter that they have little resistance, hence wires of 1 mm. were taken, flattened over the last 5 cms. The entire apparatus was suspended by a copper tube k, which was screwed on to the tightening rod f, and which, in order to prevent too much conduction of heat along it, had a piece of ebonite inserted in it (not shown in the drawing).

§ 3. *Determination of the zero.* The zero was determined in the same way as described in Comm. N°. 77, when thin leads were used. Besides with the gold wire, determinations were also made with a copper and a silver wire. A single determination never offered any difficulties. With copper, however, the values determined at different times did not agree. They showed a regular increase of the resistance at 0° C. This must probably be ascribed to a chemical process. Copper oxydises so easily that the greatest precautions must be taken to avoid moisture during the storage. If in distilling the insulating liquid into the zero-vessel the vapour was passed over phosphorous pentoxide and if care was taken that while the wire was kept, the air could only enter over phosporous pentoxide, we succeeded in stopping that process. Yet at any rate this experience obliged us to perform measurements at low temperatures, like those treated here for the gold wire, in a very short time in the case of copper wire. With gold and silver this phenomenon did not appear.

§ 4. *Comparison of the resistances.* In order to investigate the variation of the resistance of the wire, wound as described in § 2, the ratio of this resistance to that of platinum had to be determined in different baths. To this end previous investigators have always measured the resistance of the two wires alternately and hence derived the mean ratio. The first experiments made by me were also arranged in that way.

In order to attain a higher degree of accuracy I have followed the advice of Prof. KAMERLINGH ONNES and arranged the measurements so that at a definite moment the ratio itself can be read.

If we use the WHEATSTONE's bridge, it seems that this may be attained by arranging the wire to be compared in parallel to the box of HARTMANN and BRAUN (R'_s) instead of arranging it in parallel to the platinum resistance.

An insuperable obstacle for this simultaneous determination is, that at any rate a connection is required between the two wires, which connection may be made by two of the leads from the bath, in which we measure, to one of the angles of the bridge. Elimination of all the resistances of the connections except that of the stops used in the measurement, as it was obtained in the previous paper, is impossible. Errors may then creep in of which the amount may only be estimated. Resistances of the connections may occur to a considerable amount and be brought about by minor causes. If we cannot constantly test their amount the results remain uncertain.

Moreover in the WHEATSTONE's bridge the unavoidable resistances of the connections are so large that we cannot reach the accuracy proposed in the outset with wires of so little specific resistance as gold. For in that case, even though we succeeded in winding a wire of more than 20 meters in the necessarily small compass of the bath, a resistance of no more than 35 Ohms at 0° C. was obtained, which in liquid oxygen or nitrogen fell to below about 6 Ohms.

All these reasons led us to choose the method of the differential galvanometer for the comparison of the metals inter se. It enables us to determine at once the ratio of two resistances, while resistances of the connections have no appreciable influence. It is true that a measurement cannot be made in such a short time as with the WHEATSTONE's bridge but this inconvenience is sufficiently balanced by the advantages mentioned.

§ 5. *The mounting with the differential galvanometer.* The mounting as it finally was made is represented in Pl. I, fig. 3. The commutator C' serves for the element. The commutator C'_2 enables the observer to compare either the platinum wire with the resistance R'_3 (complete lines), or the gold wire with the platinum wire (dotted lines). It is convenient that by a single commutation we should be able to interchange these two mountings, because for the comparison of gold with platinum wires it will be always desirable to know the approximate value of the platinum resistance for the determination of temperature (cf. § 8). C'_3 is a commutator to interchange the two conducts of the differential galvanometer. This is necessary for the determination of the ratio between the currents in the two not perfectly equivalent conducts when the deflection is zero and moreover it seemed desirable to me to test continually whether this ratio remained unchanged.

The galvanometer was first a thin wire THOMSON with two pairs of coils each with a single wire. To attain the required symmetry, the four coils were replaced by new ones, in each of which two wires were wound together. This was done in the workshops of the laboratory. The sensibility was a deflection of 1 mm. on the scale with a difference in intensity of current of 10^{-10} Ampère, period of oscillation 20″. Then the galvanometer was aperiodic. Like the galvanometer of the WHEATSTONE's bridge in the previous paper, this was protected against disturbances arising from terrestrial magnetism by a soft iron ring.

The resistance boxes R'_3, R_5 and R_6, are all of manganin wire, having therefore an almost negligible temperature coefficient; R'_3 is the carefully investigated resistance box of HARTMANN and BRAUN, also used in the measurements with the WHEATSTONE's bridge; R_5 is the box wound in our own laboratory, which produced two branches in the WHEATSTONE's bridge (cf. previous paper), of which I also determined the absolute values. R_6 is a resistance box of SIEMENS and HALSKE tested by the Reichsanstalt. I have determined a few times the ratio between the units R'_3 and R_6 and found 1.00255 (11 determinations, greatest ... 264, smallest ... 242).

§ 6. *The measurements at low temperatures.* After the zero of the wire that was to be compared, had been determined a few times, and sufficiently harmonizing results were obtained, the wire was placed into the cryostat inside the platinum thermometer at the place occupied by the hydrogen thermometer when the former was calibrated (cf. Comm. N°. 77, § 4 and N°. 83, Pl. II).

When enough liquefied gas was poured off, the ratio between the resistances of the two wires was determined while we stirred. Before and after this determination, we measured the ratio between the platinum resistance and one of the resistances in R_5. As a rule that resistance in R_5 was taken of which the value corresponded best with that of the platinum wire. Thence the temperature could be derived. In later measurements a thermoelement was sometimes placed inside the cylinder C_1 of the wire, and after the temperature had been determined once by the measurement of the ratio to R_5, an assistant at the thermoelement took care that the temperature remained constant in the way described in Comm. N°. 83. Consequently the measurements could be made in a still shorter time.

§ 7. *Calculation and corrections.* The mounting is drawn schematically in Pl. I, fig. 2, where r_{pt} and r_x are the resistances to be compared, W_1 and W_2 the resistances of the galvanometer conducts provided with the resistance boxes R''_2 and R_6. Suppose that with certain values in the boxes there is equilibrium and that we can then represent the ratio between the two currents in the two galvanometer conducts by $1+\beta$, where β may be considered as a small number; then we have the relation

$$\frac{1}{1+\beta}\frac{r_x}{r_{pt}} = \frac{W_1}{W_2} + \frac{\beta}{1+\beta}\frac{r_x}{W_2}.$$

W_1 and W_2, however, are as regards the galvanometer coils copper resistances, and if a rather high degree of accuracy is required, W_1 and W_2 must be determined before each determination of the ratio between r_x and r_{pt}. If the galvanometer could be placed in a space of constant temperature the greatest difficulty of this would be removed and one adjustment would show us the ratio.

W_1 and W_2 being unknown, we can proceed as follows. We add to W_1 and W_2, a_1 and a_2 units of resistance so that again equilibrium is attained, then we also have:

$$\frac{1}{1+\beta}\frac{r_x}{r_{pt}} = \frac{W_1+a_1}{W_2+a_2} + \frac{\beta}{1+\beta}\frac{r_x}{W_2+a_2}.$$

Hence

$$\frac{1}{1+\beta}\frac{r_x}{r_{pt}} = \frac{a_1}{a_2}.$$

or

$$\frac{r_x}{r_{pt}} = (1+\beta)\frac{a_1}{a_2}.$$

How large we shall choose a depends on circumstances. The variations in W_1 and W_2 with regard to the leads during the course of one experiment, as appeared in the measurements with the **Wheatstone**'s bridge in the previous paper, certainly never exceeded 0.01

Ohm. If the galvanometer is carefully packed in cotton wool it appeared that during the time required for one measurement the temperature was sufficiently constant and hence the total variation in W'_1 and W'_2 did not exceed 0.1 Ohm. If then we take for the smallest of the a_1 and a_2 1000 Ohms, the inaccuracy due to this uncertainty need not therefore be larger than $^1/_{10000}$. It is likely, moreover, that the first adjustment after the measurement where a_1 and a_2 were added to W'_1 and W'_2 will be repeated in most cases so that we then can more or less judge of those variations in W'_1 and W'_2.

In the relation $\frac{r_x}{r_{pt}} = (1+\beta)\frac{a_1}{a_2}$, β is still to be determined. To this end by means of commutator C_1 (Pl. I, fig. 3), the conducts of the galvanometer are interchanged, so that the turns which first were parallel to r_x are now arranged in parallel to r_{pt} and reversely.

A new determination yields $\frac{r_x}{r_{pt}} = (1-\beta)\frac{a'_1}{a'_2}$ (β is considered small).

If β is unknown we find $\frac{r_x}{r_{pt}} = \frac{1}{2}\left(\frac{a_1}{a_2} + \frac{a'_1}{a'_2}\right)$.

Besides we can determine β, and find for it

$$\beta = \frac{\frac{a_1}{a_2} - \frac{a'_1}{a'_2}}{\frac{a_1}{a_2} + \frac{a'_1}{a'_2}}$$

If a rapid determination of the ratio is desirable, as it was naturally always the case with the measurements at low temperatures, it is better to determine β beforehand. We must then have convinced ourselves by preliminary experiments that β remains sufficiently constant. This was the case for observations made at not too long intervals. Thus 11 determinations from June 14 to July 12 yielded as smallest value 0.000764, as mean value 0.000780 and as largest value 0.00083 (?).

Thus supposing the value of β to be known we can derive the ratio $\frac{r_x}{r_{pt}}$ from a single determination of a_1 and a_2; a_1 and a_2 were read on the resistance boxes R'_3 and R_6.

§ 8. *The determination of the temperature.* The determination of the temperature, now that we do not measure the resistances separately but determine the ratio at once, need not be made with the accuracy which was required for the test of the platinum thermometer. It was obtained by measuring the resistance of the platinum wire after each complete determination of the ratio. If in the arrangement of Pl. I, fig. 3, the commutator C_2 is placed differently, we can, instead of comparing the gold with the platinum resistance, compare the latter at once with the resistance in the box R_5.

In determining the ratio between the resistances of the platinum wire and the values in box R_5 we have not, however, repeated the whole measurement as described above for the determination of the ratio between the platinum and the gold resistances, but one measurement sufficed.

For with R_5 instead of r_x as in § 7 we find:

$$\frac{1}{1+\beta}\frac{R_5}{r_{pt}}=\frac{W_1}{W_2}+\frac{\beta}{\beta+1}\frac{R_5}{W_2}$$

where W_1 and W_2 are the resistances of the circuits where the galvanometer turns and the resistances occur.

If we know the resistance of the turns, $\frac{R_5}{r_{pt}}$ may be derived from one determination of a resistance in the boxes.

The resistances of the turns can be derived from the two determinations of the ratio between the platinum and the gold resistances. Let A and B be the resistances of the turns round the galvanometer, and r_1 and r_2 the resistances in the boxes, then they give with

$$W_1=A+r_1,\quad W_2=B+r_2,$$

$$\frac{1}{1+\beta}\frac{r_x}{r_{pt}}=\frac{A+r_1}{B+r_2}+\frac{\beta}{1+\beta}\frac{r_x}{B+r_2}$$

$$\frac{1}{1-\beta}\frac{r_x}{r_{pt}}=\frac{B+r'_1}{A+r'_2}-\frac{\beta}{1-\beta}\frac{r_x}{A+r'_2}.$$

whence A and B may be derived and consequently W_1 and W_2 may be found. Inaccuracies occur, that is to say we neglect the resistance of the connecting wires between the commutator holes; but as the value of A and B was about 940 Ohms, an inaccuracy of 1 Ohm was allowed and this resistance certainly remained below this amount.

For the calculation it is important to remark that $\frac{1}{1+\beta}\frac{r_x}{r_{pt}}$ is equal to $\frac{a_1}{a_2}$ and $\frac{1}{1-\beta}\frac{r_x}{r_{pt}}$ is equal to $\frac{a'_1}{a'_2}$, while $\frac{a_1}{a_2}$ and $\frac{a'_1}{a'_2}$ may be derived directly from observation. Besides $\frac{\beta}{1+\beta}$ is small, so that in the last term of the equations an approximate value for A and B is sufficient.

§ 9. *Survey of an observation.* The way in which the observations were made will be seen best from an instance which at the same

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Fig. 2.

Fig. 1

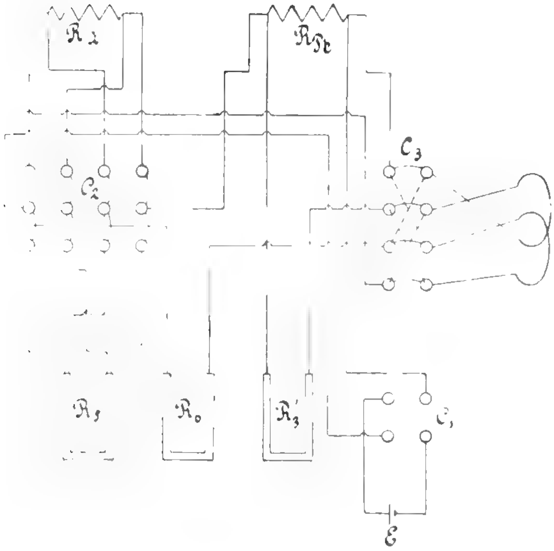

Fig. 3.

time will be developed as an instance for the calculation. It refers to a measurement with the gold wire in oxygen boiling under reduced pressure.

The values of the following table (p. 308) were read directly.

In this measurement the temperature was kept constant by means of the thermoelement so that the determination of temperature need not be repeated.

For the derivation of the results from the observations see table II, which does not require further explanation.

§ 10. *Results.* The determinations of the zero yielded the following results.

Date.	Resistance gold wire.	Method of the measurement of resistance.
April 23, 1902	31.5506	WHEATSTONE's bridge.
May 23, ,,	31.556	,, ,,
,, ,, ,,	31.565	Differential galvanometer.
May 26, ,,	31.555	WHEATSTONE's bridge.

Our chief object of the determination with the differential galvanometer was to ascertain that the two methods gave the same results, so that the latter could also be employed for a determination of temperature. During this measurement we did not stir and so it is possible that the temperature has increased a little. In connection with the following results the agreement is sufficient.

After the measurements at low temperatures, which are made between June 17 and July 12, the zero was redetermined in October and then a deviating value was found, viz. 31.043. I have searched in vain for the reason of this deviation. It does not probably lie in the measurement of resistance. A known resistance determined in the same way gave the true value. While I searched for possible causes the gold wire broke so that I have not attained any certainty on this subject. It may be that during the interval between the two determinations a short circuit has been formed between the two ends of the gold wire, in consequence of which the resistance is apparently so much diminished. A change in the gold wire itself would probably always have produced an increase of resistance.

The values for the further determinations of the ratio between the platinum resistance and the gold resistance will be sufficiently clear from the following table (p. 310).

The measurements show that this method to determine the ratio between the resistances is certainly a good one and preferable to that of measuring the resistance of each wire separately. It will

TABLE I. Comparison between Gold and Platinum Resistances in Oxygen boiling under Reduced Pressure.

Observations.

Position Commutator C_p.	Resistance in SIEMENS & HALSKE.	Resistance in HARTMANN & BRAUN.	Position Commutator C_p.	Equilibrium Galvanometer.	Deflection Galvanometer.	Time.
Temperature determination.						2 h. 30′
—	500	140 436		27.00	33.00 23.00	
Determination of the ratio.						
=	0	1000+400+ 300+20+10	‖ = ‖	27.50	31.50 23.90 31.50	
		+ 2	‖ = ‖		28.05 27.00 28.30	2 h. 45′
	1000	3+1 . 1000 4+3 . 100	‖ = ‖		26.50 27.70 26.60	
		+ 3	‖ = ‖		25.40 29.20 25.55	
×	1000	3+1 . 1000 4+2 . 100	‖ = ‖		30.30 28.30 30.30	
		+4+3	‖ =		29.12 29.62	
	0	1000+ 4+3 . 100 2+1 . 10	= ‖		21.00 38.20	
		2 . 10 4+ 3	= ‖		31.99 27.75 31.85	
=	0	1000 4+3 . 100 2+1 . 10			26.70 31.65 26.80	
	1000	3+1 . 1000 4+2 . 100	|		29.40 27.50 29.25	
		+ 2	—		30.40 26.80 30.05	3 h. 8′

TABLE II. Comparison between Gold and Platinum Resistances in Oxygen boiling under Reduced Pressure.

Calculation of the Ratio.

Commutator C_3	Resistance SIEMENS & HALSKE.	Resistance HARTM. & BRAUN.	Deflection of the galvan.	Value at which equilibrium would exist HARTM. & BRAUN.	Differences in the two branches.		Corrections			Differences corrected a. SIEM. & H. b. HARTM. & BR.	Ratio. $\frac{a}{b}$	$\frac{r_x}{r_F}$
							Box of S. & H.	Reduction S. & H. to H. & BR.	Box of H. & BR.			
=	0	1000 + 400 + 300 + 20 + 10	− 7.6	1731.73	1000	3866.92	−0.05	+2.55	+0.48	a. 1002.50 b. 3867.40	0.34962	0.34934
		+ 2	+ 1.2									
	1000	3000 + 1000 + 400 + 200	+ 1.15	4598.65								
		+ 3	+ 3.73									
×	1000	3000 + 1000 + 400 + 200	− 2.00	4597.60	1000	3871.66	−0.05	+2.55	+0.48	a. 1002.50 b. 3872.14	0.34904	0.34932
		3000 + 1000 + 400 + 100 + 40 + 30 + 20 + 7	+ 0.50									
	0	1000 + 400 + 300 + 20 + 10	− 17.20	1726.06								
		1000 + 400 + 300 + 20 + 7	− 4.10									
	0	1000 + 400 + 300 + 20 + 10	− 4.80	1731.10	1000	3866.80	−0.05	+2.55	+0.48	a. 1002.50 b. 3867.28	0.34963	0.34935
	1000	3000 + 1000 + 400 + 200	+ 1.82	4597.90								
		+ 2	+ 3.30									

Resistance for temperature calculation $R_5 = 28.62$ Ohms.

TABLE III. Comparison between Gold and Platinum Resistances.

Resistance platinum wire.	Resistance gold wire.	Ratio $\frac{\text{gold resistance}}{\text{platinum resistance}}$	Ratio between the resistances of a gold wire and a platinum wire which at 0° C. have the same resistance.	Dates.
110.045 (at 0° C.)	31.550 31.556 31.565 31.555	0.28672 0.28675 0.28684 0.28674	1	April 23, 1902. May 23 id. May 26.
64.78 64.85		0.295677 0.295736 0.295569 9.295564 0.295531 0.295562	$\frac{0.29554}{0.28674} =$ $= 1.0307$	June 17, in ethylene.
52.34 52.68		0.301954 0.301952 0.301949 0.301946	$\frac{0.301950}{0.28674} =$ $= 1.0530$	June 17, in ethylene boiling under reduced pressure.
28.71 28.71		0.330287 0.330314 0.330285 0.330304 0.330256 0.330289	$\frac{0.330295}{0.28674} =$ $= 1.1519$	June 23, in oxygen.
22.79 22.81 22.74 22.79		0.34490 0.34497 0.34490 0.34498 0.34464? 0.34495	$\frac{0.34497}{0.28674} =$ $= 1.2029$	July 12, in nitrogen.
21.39 21.47		0.34934 0.34932 0.34935	$\frac{0.34933}{0.28674} =$ 1.2173	June 23, in oxygen boiling under reduced pressure.

be necessary, however, at least for low temperatures, to take great care that the temperature is kept constant during the time required for a measurement. In these measurements the determination of the temperature was less accurate than seemed desirable with a view to the accuracy of the determination of the ratio during the measurements on one day.

In the results there is a striking difference between the gold and the platinum. Though the values found do not help us to fix the temperature function for gold for want of certainty about the zero to which they belong, yet they show that the curvature of the line which for gold represents that temperature function is much smaller than in the case of platinum and that the curve is bent more towards the absolute zero. Hence a gold wire would be more suited for extrapolation than a platinum wire, because here the deviations which we cannot but expect, are much smaller.

Mathematics. — "*A congruence of order two and class two formed by conics*". By Prof. J. de Vries.

For a twofold infinite system of conics (congruence) *order* is called the number of conics through an arbitrary point, *class* the number of conics with an arbitrary right line for bisecant.

The congruences of order one and class one arise from the projective coordination of a net of planes to a net of quadrics[1]). Under investigation were furthermore the congruences of order one and class two and those, the conics of which cut a fixed conic twice [2]).

In this communication the characteristic numbers are deduced of the congruence determined by the tangent planes of a quadric Q^2 on the planes of a net $[Q^2]$ of quadrics to which they are projectively conjugate.

2. To obtain this conjugation we project the points P of Q^2 out of a fixed point P_0 of Q^2 on a plane Φ. A projectivity between the points P' of Φ and the surfaces of $[Q^2]$ furnishes then immediately a projectivity between $[Q^2]$ and the system $[\pi]_2$ of the tangent planes π of Q^2.

To a pencil (Q^2) in $[Q^2]$ corresponds a range of points (P') in

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[1]) D. Montesano, Su di un sistema lineare di coniche nello spazio, Atti di Torino, 1891—1892, t. XXVII, p. 660.

[2]) M. Pieri, Sopra alcune congruenze di coniche, Atti di Torino, 1892—1893, t. XXVIII, p. 135.

Φ, thus a conic on Q^2, thus the system of the tangent planes π passing through a fixed point T. Through T and a point X of the base-curve of (Q^2) two planes π pass; wherefore X bears two conics of the congruence, which is thus of *order two* ($P = 2$).

3. To the tangent planes π through an arbitrary point T correspond the points P of a conic not passing through P_0, having thus for image a conic in Φ. So to this system $(\pi)_2$, of index two, is conjugate a system $(Q^2)_2$ possessing likewise index two, having two surfaces in common with each pencil (Q^2). When considering the ranges of points determined by the projective systems $(\pi)_2$ and $((Q^2)_2$ on an arbitrary right line we find that they generate a surface T^6 of degree six, which is the locus of the conics of the congruence the planes of which pass through a fixed point T. Hence we get $\mu\nu = 6$.

4. Through two arbitrary points pass two tangent planes π, hence the planes of two conics; so an arbitrary right line is bisecant of two conics, and the congruence is of *class two* ($\mu^2 = 2$).

The numbers $P = 2$, $\mu\nu = 6$ and $\mu^2 = 2$ satisfy the well known formula $P = \mu\nu - 2\mu^2$.

Through a right line of Q^2 pass an infinite number of planes π; the conics they bear form a cubic surface.

As each ray through T meets two conics, T^6 has in T a double point. If A^2 is one of the conics on which T is situated, T^6 is touched in T by each bisecant of A^2 out of T. So T is a biplanar point.

If T is one of the eight base points of the net $[Q^2]$ then T^6 has in T a fourfold point; for on every ray through T lie but two points besides T.

5. Let us take for Q^2 the paraboloid $xy = z$, then the substitution $x = \alpha\varrho$, $y = \beta\varrho$, $z = \gamma\varrho$ furnishes first $\varrho = \gamma : \alpha\beta$ and then

$$x = \gamma : \beta \quad , \quad y = \gamma : \alpha \quad , \quad z = \gamma^2 : \alpha\beta.$$

So the tangent planes π are represented by

$$\beta\gamma x + \alpha\gamma y - \alpha\beta z - \gamma^2 = 0.$$

The above-indicated conjugation is arrived at by putting

$$\alpha A + \beta B + \gamma C = 0,$$

where A, B, C are quadratic functions of x, y, z. We represent their coefficients by a_{kl}, b_{kl}, c_{kl} and we write briefly

$$d_{kl} = \alpha a_{ik} + \beta b_{ik} + \gamma c_{ik}.$$

If a Q^2 of the net is to be touched by the conjugate plane π, then

$$\begin{vmatrix} d_{11} & d_{12} & d_{13} & d_{14} & \beta\gamma \\ d_{12} & d_{22} & d_{23} & d_{24} & \alpha\gamma \\ d_{13} & d_{23} & d_{33} & d_{34} & -\alpha\beta \\ d_{14} & d_{24} & d_{34} & d_{44} & -\gamma^2 \\ \beta\gamma & \alpha\gamma & -\alpha\beta & -\gamma^2 & 0 \end{vmatrix} = 0,$$

must be satisfied.

We find here a relation

$$D_7(\alpha, \beta, \gamma) = 0,$$

which is homogeneous and of degree 7 in α, β, γ. If we regard these parameters as homogeneous coordinates, this relation represents a curve of degree 7 possessing nodes in the points A ($\beta = 0$, $\gamma = 0$) and B ($\alpha = 0$, $\gamma = 0$).

6. For the conics passing through point $T(x_1, y_1, z_1)$ we have the relation

$$M_2(\alpha, \beta, \gamma) \equiv x_1\beta\gamma + y_1\alpha\gamma - z_1\alpha\beta - \gamma^2 = 0.$$

It is represented by a conic passing through A and B.

Besides A and B the auxiliar curves D^7 and M^2 have ten points in common. So through T pass the planes of ten conics each degenerated into two right lines ($\delta\mu = 10$).

That the points A and B must not be taken into consideration is shown as follows: For $\alpha = 0$, $\gamma = 0$ we find B $= 0$ and $y = 0 : 0$, thus the pencil of planes around OX; of these tangent planes of course only one is conjugate to B $= 0$ and the conic determined by it does not form a pair of lines generally.

Out of the relation [1])

$$3\mu\nu = 2\eta\mu + \delta\mu + 4\mu^2$$

ensues, as $\mu\nu = 6$, $\delta\mu = 10$ and $\mu^2 = 2$,

$$\eta\mu = 0.$$

This could be foreseen, for the cones of $[Q^2]$ form a system ∞^1; the number of those cones touched by the homologous planes π is thus finite and all twofold symbols in which η appears have therefore the value zero.

7. The right line $x = 0$, $y = 0$ is cut by the conics for which we have

$$\alpha\beta z + \gamma^2 = 0 \quad \text{and} \quad d_{33}z^2 + 2d_{34}z + d_{44} = 0.$$

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[1]) Compare my communication in these Proceedings, p. 264.

thus

$$N_5\,(\alpha, \beta, \gamma) \equiv d_{33}\,\gamma^4 - 2d_{34}\,\alpha\beta\gamma^2 + d_{44}\,\alpha^2\,\beta^2 = 0.$$

The curve N^5 representing this relation has evidently nodes in A and B.

By connecting N^5 with M^2 and D^7 we find anew $\mu \mathbf{r} = 6$ and farther

$$\delta \mathbf{r} = 27.$$

The pairs of lines of the congruence form a skew surface of degree 27.

8. To find the characteristic numbers containing the symbol ϱ we consider the pairs of points which the conics of the congruence have in common with the plane $z = 1$. They are indicated by

$$\beta\gamma x + \alpha\gamma y = \alpha\beta + \gamma^2,$$

$$d_{11}x^2 + 2d_{12}xy + d_{22}y^2 + 2(d_{13} + d_{14})x + 2(d_{23} + d_{24})y + (d_{33} + 2d_{34} + d_{44}) = 0.$$

So for the conics touching $z = 1$

$$\begin{vmatrix} d_{11} & d_{12} & d_{13} + d_{14} & \beta\gamma \\ d_{12} & d_{22} & d_{23} + d_{24} & \alpha\gamma \\ d_{13} + d_{14} & d_{23} + d_{24} & d_{33} + 2d_{34} + d_{44} & -\alpha\beta - \gamma^2 \\ \beta\gamma & \alpha\gamma & -\alpha\beta - \gamma^2 & 0 \end{vmatrix} = 0.$$

This is a relation

$$R_6\,(\alpha, \beta, \gamma) = 0.$$

which is represented by a curve R^6 having A and B for nodes.

By combining R^6 and D^7, M^2 and N^5 we find successively

$$\delta\varrho = 34. \qquad \mu\varrho = 8. \qquad \mathbf{r}\varrho = 22.$$

From this ensues that the skew surface of the pairs of lines has a double curve of degree 17 and that the conics touching a given plane (in particular thus the parabolae of the congruence) form a surface of degree 22.

Out of the relations

$$3\mathbf{r}^2 = \delta\mathbf{r} + 4\mu\mathbf{r} \quad \text{and} \quad 3\varrho^2 = 2\delta\varrho + 2\mu\varrho$$

we finally find for the missing characteristic numbers

$$\mathbf{r}^2 = 17 \quad \text{and} \quad \varrho^2 = 28.$$

So the conics cutting a fixed right line form a surface of order 17.

Physiology. — *"On a new method of damping oscillatory deflections of a galvanometer"*. By Prof. W. Einthoven.

(Communicated in the meeting of September 24, 1904).

In a number of investigations, requiring the use of a galvanometer or electrometer, it is desirable to damp the oscillatory deflections shown by most of these instruments under many circumstances. Either mechanical damping is applied or electromagnetic damping or both are combined in order to obtain a stronger effect.

In some instruments, e.g. the Deprez-d'Arsonval galvanometer, in which the coil is movable in a stationary magnetic field, the electromagnetic damping may without any special arrangement be so great that the deflections have lost their oscillatory character and have become quite dead-beat. The movements are thereby retarded. This retardation may be very considerable and so become troublesome, even to such an extent that the instrument becomes impracticable. Means of diminishing the damping are then applied, e.g. by increasing the resistance in the galvanometer.

In order to apply electromagnetic damping in a needle-galvanometer the rotating magnetic system is to a greater or less extent enveloped by a mass of pure copper in which during the motion of the needles damping vortex currents are raised.

Mechanical damping is applied as liquid or air damping, thin plates of aluminium or mica or insect wings being often used.

The method of damping to be described in this paper is entirely different from the methods just mentioned. It consists in inserting a condenser between the ends of the galvanometer wire as is indicated in fig. 1. In the figure E represents a source of current by means of which an arbitrary potential difference can be established between P and P_1. G is the galvanometer and C the condenser.

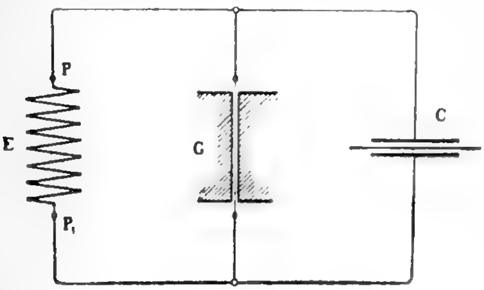

Fig. 1.

The action of the condenser is most easily understood by assuming the mass of the moving parts of the galvanometer to be zero and the eventual causes by which the motion is damped to tend to zero. If under these conditions the capacity of the condenser is zero, when a potential difference between P and P_1 is suddenly established, the galvanometer will also at once assume the corresponding position of equilibrium. If on the other hand there is a certain capacity, the deflection will require some time.

The way in which the image of the mirror or in the string-galvanometer the quartz thread then moves, is entirely determined by the way in which a condenser is charged or discharged. Calling a the deflection of the galvanometer at the time t after the potential difference is established and A the permanent deflection, we have

$$a = A\left(1 - e^{-\frac{t}{w'c}}\right)$$

where e is the base of natural logarithms, c the capacity of the condenser and w' a resistance of which it is easy to give a nearer definition.

In the closed circuit containing the source and the galvanometer the external resistance be W_e, the resistance of the galvanometer be W_i, then, if we neglect the resistance of the wires joining the condenser and the galvanometer, we have

$$w' = \frac{W_i\, W_e}{W_i + W_e} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The value $w'c$ is the time constant of the deflection

$$w'c = T.$$

Expressing w' in Ohms and c in Farads, T is given in seconds.

When the deflection of the galvanometer is recorded on a uniformly moving plane, a curve will be obtained which is the expression of an exponential function and which agrees entirely with the wellknown normal or standardising curves of the capillary electrometer[1]).

The constants of the curve, besides being determined by the rate of motion of the recording plane and the amplitude of the deflection, will depend only on the value of T. By changing w' and c we can regulate the value of T at will. This means that we are able to retard or damp the deflection of the galvanometer to any extent.

The reasoning given is confirmed by the observations. As an example we reproduce three curves, figs. 1—3 of the plate, recorded by the string-galvanometer[2]). The connections are schematically

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[1]) See e. g. W. Einthoven. Pflüger's Arch. f. d. gesammte Physiol. Bd. 56, p. 528. 1894. And „Onderzoekingen" Physiol. laborat. Leyden, 2nd series I.

[2]) See W. Einthoven, Ann. der Phys. 12. p. 1059. 1903 and 14. p. 182. 1904. Also in Kon. Akad. v. Wetensch. te Amsterdam, Report of the meeting of June 27, 1903 and March 30, 1904.

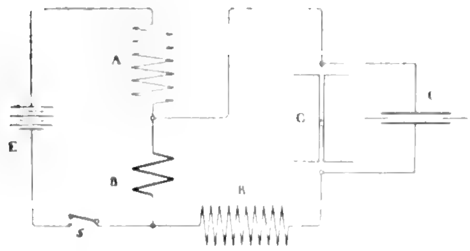

Fig. 2.

represented in fig. 2. Here E is a battery, S a key, G the string-galvanometer and C the condenser, A, B and R representing resistances. The sensitiveness of the galvanometer has been kept about equal in the three cases so that a deflection of 1 mm. corresponds to a current of 2×10^{-7} Amp., the electromotive force E of the battery and the resistances A, B and R being so chosen that when the current is passed a permanent deflection of 20 mm. is obtained. The rate of motion of the recording plane is 500 mm. per second. Hence in the net of square millimetres on the plates [1]) 1 mm. of absciss $= 0.002$ sec. and 1 mm. ordinate $= 2 \times 10^{-7}$ Amp. The circuit was automatically made and broken at S by an arrangement attached to the recording plane.

For R a carbon resistance was taken with large resistance and B was small compared with R. W_e could be put equal to R without an appreciable error. In figs. 1 and 2 of the plate W_e was 1.11 megohm, whereas W_e in fig. 3 amounted to 117000 ohms. The resistance of the galvanometer W_i was 8600 ohms.

In fig. 1 of the plate the capacity of the condenser is 0. The string is seen to make oscillatory movements with a period of about 1,3 mm. $= 2.6\,\sigma$ [2]).

These movements are damped by inserting a certain capacity in the condenser. In fig. 2 of the plate that capacity is 0.94 microfarad, in fig. 3 of the plate 0.2 microfarad.

Calculating the value of w' from W_i and W_e by formula (1) and then the time constant $T = w'c$, the time constant of fig. 2 is found to be $8.0\,\sigma$, and that of fig. 3 $1.6\,\sigma$ and it is clear that the amount of retardation or of damping is determined by the value of the time constant.

For clearness' sake we started in the above reasoning from the simplest case and assumed that the mass m of the string and the forces which independently of the condenser damp its motion and which we will collectively indicate by r, may be neglected. This hypothetical case will the more closely agree with reality, the larger, other conditions being equal, T is taken. Hence in this respect fig. 2

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[1]) On the way of recording and the net of square millimetres see Annalen der Phys. l. c.

[2]) $1\,\sigma = 0.001$ sec.

of the plate answers better the conditions required than fig. 3, but the great practical importance of the method is exactly that it is possible to damp the oscillations and at the same time to retard the deflection as little as possible. When measurements are made one will always try to choose T such that exactly the limit between oscillatory and aperiodical motion is attained. In this case T is relatively small and m and r may no longer be neglected.

The question now arises how for known values of m and r the value of T must be calculated in order to obtain the limiting case mentioned.

In passing it be remembered that with the capillary electrometer the damping of the motion of the mercury meniscus is also composed of mechanical friction and of retardation by capacity.[1] And from the combination of these two results a motion which can be expressed by a simple exponential function either quite accurately or with only small deviations. The resistance of air or liquid damping as well as electromagnetic damping influence the motion of a body having mass, in exactly the same way as conductive resistance influences the motion of electricity when a condenser is charged or discharged.

A simple reasoning will show, however, that adding a condenser to the galvanometer has not always an influence on the movements of the string of the same nature as an increase of the damping forces which we called r.

For the addition of the condenser has the effect of a temporary change of the active force. And the way in which the force is increased or decreased from moment to moment is not determined by the motion of the string, as the mechanical and electromagnetic damping, but by the product of the conductive resistance and the capacity $w' c = T$.

When applying the condenser method, the character of the motion of the string near the limiting case of aperiodicity can only be represented by a more or less complicated formula. I have therefore for this limiting case preferred direct experimental determination of the value of T to calculation.

Some curves have been reproduced which exemplify the motion

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[1] Some investigators have been of opinion that the motion in the capillary electrometer is dependent on the charge of the mercury meniscus only. But in reality damping by mechanical friction is much more active here. See **Pflüger's** Arch. f. d. ges. Physiol. Bd. 79, p. 1. 1900; and „Onderzoekingen" Physiol. laborat. Leyden, 2nd series, 4.

of the string in the limiting case in question[1]). Figs 4, 5 and 6 of the plate were taken with the same string as the former figures. For the connections we refer to figure 2 in the text. The deviation is now 30 mm. Again 1 mm. of abscissis 0,002 sec. and 1 mm. of ordinate $= 2 \times 10^{-7}$ Amp.

$R\ = 1300$ Ohms.
$B\ =\ \ 27$ „
$W_i = 8600$ „ , from which we calculate
$W_e = 1327$ and $w' = 1148$ Ohms.

In fig, 4 the capacity of the condenser $= 0$, hence $T = 0$.
„ „ 5 „ „ „ „ „ $= 0{,}6\mu f.$, „ $T = 0{,}69\ \sigma$.
„ „ 6 „ „ „ „ „ $= 0{,}7\mu f.$, „ $T = 0{,}80\ \sigma$.

One sees that the oscillatory motion, the period of which is about 2,7 σ, is damped by the application of the condenser method and that the time constants T of 0.69 and 0,80 σ, obtained by means of capacities of 0.6 and 0.7 microfarad, are required in order to reach the desired limit of aperiodicity.

In fig. 5, where a capacity of 0,6 $\mu f.$ is used, the limit has not yet fully been reached, in fig. 6 the limiting value has already been passed with a capacity of 0.7 $\mu f.$

The two last-mentioned plates show that the motion of the string in the neighbourhood of this limit is not very simple. In the small oscillation which has remained in fig. 5 the string, after having deflected through 30 mm., passes the new position of equilibrium by 0.5 mm. and then returns to a point which is still 0.3 mm. lower than the position of equilibrium, The ratio of the values of these deflections does not agree with the laws which damped motions generally obey. Moreover the first turning-point is reached after 2 σ, the second after 1 σ, whereas with damped vibrations, such as generally occur, these times are equal.

In fig. 6 the string comes to rest after about 0.002 sec. at a distance of 0.3 mm. from the new position of equilibrium and reaches its equilibrium after a small movement in the opposite direction. If in the measurement of a current one is contented with an accuracy of 2°/₀ the result is known in about 1,5 σ.

Another example is found in figs. 7 and 8 of the plate. These photograms were taken in the same way as those immediately

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[1] The process by which the photograms of the plate have been reproduced does not reveal the minor details of the curves. I shall be pleased to send direct photographic copies of the original negatives to those who are interested in them.

preceding, but the string is lighter here, has a greater conductive resistance and is slightly more stretched.

1 mm. abscis = 0,002 sec., 1 mm. ordinate = 3×10^{-7} Amp. $W_i = 17800$, $W_e = 20000$, hence $w' = 9420$ Ohms.

In fig. 7 the capacity is 0; in fig. 8 it is 0,05 μf, hence $T = 0,47\ \sigma$. In this latter photogram the string shows a turning-point after about 1,1 σ exactly on the new position of equilibrium. It moves back through 0.9 mm. and then reaches its equilibrium again and finally.

If in the measurement of a current one is contented with an accuracy of 3 %, the result is obtained in 0.8 σ. If an accuracy of 0.3 % is wanted, the result is only obtained in 2.2 σ.

These examples may suffice to see what can be expected of the method. It is obvious that when seeking the exact value of T for reaching the limit, we were led by theoretical considerations although we could not use a rigorous formula. One of these considerations was that for a given string and constant resistances, the capacity required for the limit must be the smaller the more strongly the string is stretched. For with greater tension of the string the period t of its oscillations becomes smaller and we may expect the wanted value of the time constant T to change in the same sense as the period t.

This consideration leads to some paradoxically sounding predictions. So, for example, it is to be expected that the motion of a strongly stretched string that has been made dead-beat by applying the condenser method, will become oscillatory again as soon as the tension is diminished and thereby the motion is retarded. Such an expectation seems at variance with the experience gained with other galvanometers, we might say, gained without exception with all instruments in which vibratory motions are observed.

The result, which was expected with some anxiety, completely confirmed the prediction. A quartz-thread of such a tension that a permanent deflection of 1 mm. corresponded to a current of 2×10^{-7} Amp., showed, when a current was suddenly passed or interrupted, (see figure 2 in the text) a number of oscillations. By inserting a capacity $c = 0.135\ \mu f$ the motion was damped to such an extent that the limit of aperiodicity was reached. Next the tension of the string was exactly 4 times relaxed so that a deflection of 1 mm. was caused by 5×10^{-8} Amp. The oscillations then re-appeared, and could not be checked again until the capacity was increased to 0.40 μf. With a 4 times smaller tension, i.e. with a 4 times greater sensitiveness the capacity and at the same time the value of T had to be increased 2.96 times in order to reach the limit of aperiodicity.

Observations with other quartz-threads, the tension of which was varied, always gave corresponding results: with strong tension a small value, with a more feebly stretched string a larger value of $w'c$ is required in order to check oscillations.

If w' is kept unchanged, one has an easy means of accurately regulating the desired degree of damping in a commercial condenser, in which capacities are shunted in by means of plugs in the same way as the resistances of a resistance-box. And it is remarkable that less of the means of damping is sufficient as the oscillations pass the zero-point farther and last longer and consequently the need of damping is greater. The phenomenon that, leaving the other circumstances unchanged, diminution of the tension only, i.e. — with the same deflection —, diminution of the moving force, changes an aperiodic motion into an oscillatory one, stands quite isolated and has, as far as is known to me, no mechanical or electrical analogon, no more in scientific instruments than in industry.

We shall now give some results of measurements which although they cannot compensate the lack of a simple formula, may yet be helpful to form an idea of the method in practical work.

1. When the damping influences already existing are increased, for example when the electromagnetic damping is strengthened by diminishing the resistance in the galvanometer circuit, a smaller value of T will suffice in order to reach the limit of aperiodicity when the quartz-thread is the same and the tension is not changed.

2. If the change in the electromagnetic damping which is caused by varying the value of W_e is taken into account, it makes no difference how the single factors w' and c are chosen. If only their product $w'c = T$ retains the same value, also the damping influence will remain the same. This latter is only determined by the product T.

3. If the motion of the quartz-thread is oscillatory it will be observed when the condenser method is applied, beginning with small values of T and gradually rising until the limit of aperiodicity is reached, that increasing T does not always cause a regular increase of the damping. Especially with feeble tension of the quartz-thread, when only a few small oscillations are normally produced, one sees an irregularity appear. The addition of a very small capacity can then even slightly enlarge the existing vibrations.

When such a value of T has once been taken that the limit of aperiodicity is reached, T has only little to be raised in order to obtain a regularly shaped curve. With further raising of T the motion is more and more retarded, the regular form of the curve being retained.

4. That we may form some opinion about the value of the time constant T that is required in various circumstances in order to reach the limit of aperiodicity, we give the following table, containing the results of measurements, part of which have already been mentioned above.

W_i in Ohms.	W_e in Ohms.	w' in Ohms.	c in micro-farads.	$T = w'c$ in thousandths of a second.	t in thousandths of a second.	k Damping-ratio.
8600	117000	8000	0.40	3.2	7.7	7.6
8600	117000	8000	0.135	1.08	2.7	3.1
8600	1.11×10^6	8520	0.12	1.02	2.64	3.1
8600	1327	1148	0.65	0.75	2.7	4.5
17800	20000	9420	0.05	0.47	1.41	3.16

The first five columns of this table need no nearer explanation; they give the conductive resistances, the capacities and the values of the time constant T. For the values of T mentioned the limit of aperiodicity was just reached.

The two last columns indicate how the string vibrates when the capacity of the condenser and together with it T is zero. In the last column but one we find the period t expressed in thousandths of a second, while the last column gives the damping ratio k. The observations have been arranged according to the values of T.

Finally some remarks may find a place here on the circumstances under which the condenser method will be useful in practice. For the present the applications will presumably be restricted to such measuring instruments as possess a great internal resistance and a short period of oscillation. A galvanometer for thermo-electric currents with a small internal resistance and a great period of oscillation would for damping by the condenser method require an enormous capacity. The mica or paper condensers, which admit of easy regulation, would be out of the question here, since even the largest sizes of the trade would turn out to be still a hundred thousand times too small. So one would have to have recourse to another kind of condensers, e.g. electrolytic ones, and it would require a separate investigation how far these can indeed be rendered practicable for the purpose in view.

The conditions of a short period of oscillation combined with a relatively high internal resistance are fulfilled by only one instrument besides the string galvanometer, as far as is known to me, namely by the oscillograph. Here the damping is effected by means of oil which is heated [1]).

The temperature of the oil determines its viscosity and the regulation of the degree of damping is consequently obtained in the oscillograph by regulating the temperature of the oil. It is doubtful whether the instrument would greatly gain in practical usefulness if the oil with the heating arrangement were done away with and replaced by a condenser.

In the string galvanometer the condenser method will be successfully applied in cases where it is desired to measure variations of current of very short duration. Taking a very short and strongly stretched quartz-thread, it will be possible to obtain deflections whose quickness leaves little to be desired. Without a condenser these would be useless for many purposes on account of the oscillations, whereas now they may become useful for a number of physical and electrotechnical investigations by a judicious damping. In these cases the string galvanometer will for equal quickness of deflection appear to be a much more sensitive apparatus than the oscillograph.

Also in a number of electrophysiological investigations we can avail ourselves of the condenser method, while the study of sounds will be particularly facilitated by it. I hope to make a nearer communication on this subject in a following paper.

Physics. — "*Dispersion bands in the spectra of δ Orionis and Nova Persei*". By Prof. W. H. JULIUS.

When light, giving a continuous spectrum, passes through a selectively absorbing, non-homogeneous mass of gas, the spectrum of the transmitted light contains places which, according to circumstances, may contrast as bright or as dark regions with their surroundings [2]). Though resembling emission and absorption lines, these bands have a wholly different origin. They are due to anomalous dispersion and, therefore, the name *dispersion bands* has been suggested for them [3]).

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[1]) Also a mixture of two liquids is used, of which one has a great, the other a small viscosity. The mixture is so chosen that the desired viscosity is just obtained.

[2]) Proc. Roy. Acad. Amst. II, p. 580 (1900).

[3]) Proc. Roy. Acad. Amst. VII, p. 134—140 (1904).

Dispersion bands always appear in the proximity of absorption lines, covering them more or less symmetrically; they show great variety in width and strength, and the distribution of the light in them may be irregular, so as to give the impression that one is witnessing cases of shifting or doubling or complicate reversal phenomena of widened absorption lines. All these cases can be produced almost at pleasure in the absorption spectrum of sodium vapour by merely varying the structure of the non-homogeneous medium through which the light is made to travel.

In the spectrum of the various parts of the solar image dispersion bands play an important part[1]). We can scarcely doubt that they are also present in stellar spectra: for the light coming from the stars must, as a rule, have travelled through immense gaseous envelopes and suffered ray-curving and anomalous dispersion, just as well as the light from the Sun.

Taking for granted that most of the visible stars are *rotating* gaseous bodies, with or without a solid core, we must suppose them to have a structure, describable by surfaces of discontinuity with waves and vortices, and resembling the peculiar structure of the Sun, by which it has proved possible to explain solar phenomena[2]). Consequently, the stars too give existence to "irregular fields of radiation" rotating with them. Our line of sight continually cuts other parts of the refracting mass; it may pass closely along surfaces of discontinuity, now on the one, now on the other side of them; so the light reaching us must vary in strength and in composition.

The variability of many stars is very likely to result from this cause; and from the same principle it necessarily follows that their spectral lines should be liable to every kind of change in place and in appearance.

In many cases where the application of DOPPLER's principle leads to very unsatisfactory conclusions, the dispersion bands afford a plain solution. Let us consider, for instance, the spectrum of δ Orionis.

In this spectrum rapid changes in the position of the lines had been observed by DESLANDRES (1900), who concluded from them that δ Orionis was a spectroscopic binary having a revolving period of 1.92 days. Some observations made by J. HARTMANN[3]) did not agree with this period. Professor HARTMANN, therefore, submitted the

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[1]) Proc. Roy. Acad. VII, p. 140—147 (1904).

[2]) Proc. Roy. Acad. Amst. V, p. 162—171; 589—602; VI, p. 270—302 (1903).

[3]) J. HARTMANN. Untersuchungen über das Spectrum und die Bahn von δ Orionis. Sitzungsber. der Kön. Preuss. Akad. d. Wissenschaften, XIV, S. 527—542, März 1904.

star to an extensive spectographic investigation in the winter months of 1901—2 and 1902—3, and, from the 42 plates obtained, drew the following conclusions.

The spectrum contains chiefly the lines of hydrogen and helium; besides a few belonging to silicium, magnesium, calcium.

The calcium line at λ 3934 (corresponding to *K* of the solar spectrum) is extraordinarily weak, but almost perfectly sharp; all the other lines (nineteen in number) are very diffuse and dim, often appear crooked and unsymmetrical, sometimes indeed double. While every prepossession of the observer was most strictly avoided during the measurements, it was found, that the centres of the diffuse lines really oscillate, the period being 5,7333 days; but, owing to the unsymmetrical appearance of many of the lines, no evidence could be obtained that the values of the displacements were in mutual agreement for all the lines on one and the same plate. From the average displacements HARTMANN calculated the "variable velocity in the line of sight", and finally the elements of the orbit.

An utterly surprising result, yielded by the measurements, was that the calcium line at λ 3934, does not share in the periodic displacements of the other lines, but shows a constant shift corresponding to a velocity in the line of sight of + 16 km. (reduced to the Sun).

HARTMANN rejects the idea that this line should have originated in the Earth's atmosphere; also the assumption that it belongs to the second component of the binary system. He is thus led to the hypothesis that at some point in space in the line of sight between the Sun and *δ* Orionis there is a cloud of calcium vapour which recedes with a velocity of 16 k.m. By examining the spectra of neighbouring stars no further information as to the existence of such a cloud was obtained.

A quite similar phenomenon, however, had been exhibited by the spectrum of Nova Persei in 1901: the lines of hydrogen and other elements were enormously broadened and displaced and continually changing their appearance, but during all the time the two calcium lines at λ 3934 and λ 3969, as well as the *D*-lines, were observed as perfectly sharp absorption lines, yielding the constant velocity of + 7 km. HARTMANN therefore assumes that also in the line of sight between the Sun and Nova Persei there exists a nebulous mass consisting, in this case, of calcium and sodium vapour, and moving from the Sun at the rate of 7 km. a second.

It must be admitted that these hypothetical clouds do not form a satisfactory solution to the problem.

A much simpler explanation of the phenomena may be derived from our conception of the irregular fields of radiation caused by the stars.

We need only suppose that the outer parts of δ Orionis and of Nova Persei, like those of so many other stars, contain much hydrogen and helium, little calcium and sodium. The currents and vortices in the gaseous mass, which produce the irregularities of the field of the star's radiation, bring about very broad dispersion bands in the vicinity of the lines of hydrogen, helium, etc. The darkest parts of these bands will be displaced when, by the star's rotation, masses in which the density is variously distributed, pass our line of sight. The dispersion bands of calcium and sodium, on the other hand, are so narrow, that the varying position of their darkest parts cannot be distinguished from the fixed position of the corresponding absorption lines. The constant displacement of the latter indicates that δ Orionis recedes from the Sun with a velocity of 16 km., Nova Persei of 7 km. a second.

According to our opinion δ Orionis, therefore, is *no* spectroscopic binary.

In the spectra of a great many stars oscillations and duplications have only been observed with diffuse lines. In those cases too the displacements are, as usual, expressed in so many kilometers a second, because no other interpretation than motion in the line of sight is thought of. From the above considerations it follows, however, that the observed oscillations are very likely to be executed by dispersion bands and not by the absorption lines; then no sufficient ground remains for classing such stars among spectroscopic binaries and for calculating orbital elements.

Several difficulties to which the conclusions derived from DOPPLER's principle lead us, will then disappear at the same time. How, for instance, are we to realize the physical conditions of the orbital motion in such so-called binaries as ι Orionis, 57 Cygni, θ Orionis and many others, all of which are involved in nebulous matter, but whose motion in the line of sight is nevertheless — according to FROST and ADAMS — subject to periodical variations of 70, 90, 140 km. a second, in spite of our physical notions concerning resistant media? When, on the other hand, the observed displacements of spectral lines, as well as the oscillations of the brightness of similar stars, are supposed not to result from motion in orbits, but from irregularities in their fields of radiation, there remains nothing astonishing in the fact that such variations often occur with stars involved in nebulosity.

In order to explain certain peculiarities in the spectra of Novae the principle of anomalous dispersion has already been applied by H. EBERT [1]). A characteristic of those spectra, viz. the presence of double lines consisting of a bright and a dark component, the bright one being displaced towards the red, the dark one towards the violet, is very suggestively explained by this author in connection with the theory of SEELIGER. According to this theory the appearance of a Nova results from a dark or faintly luminous celestial body entering at a great velocity into a cosmic nebula. During this process the front part of the star's surface will become excessively heated and luminous, and a dense gaseous atmosphere will be formed, in which, as EBERT shows, the incurvation of the rays must necessarily be such as to cause the dispersion bands appearing in the spectrum to be *bright* on the red-facing and *dark* on the violet-facing side of the absorption lines.

EBERT expresses the opinion that displacements and duplications of lines in the spectra of many variables of short period might be explained in a similar way, i.e. by admitting that the radiating power of such bodies is very unequal in different parts of their surface, and that they are surrounded by dense atmospheres. Their rotation will then cause us to see, as it were, the phenomena of the Novae periodically repeated.

In certain cases this interpretation may undoubtedly account for the peculiarities observed in the spectra of variables; nevertheless we cannot generalize the idea without meeting with some serious difficulties. First, it is not easy to form a clear conception of the physical conditions prevailing in a star, the incandescent surface of which is supposed to contain permanently large regions radiating very much less than the rest. The Sun with its spots may certainly not be adduced as an analogous case. Moreover, there are plenty of instances that in the spectrum of a variable, bright bands appear at the *violet* side, dark bands at the *red* side of the absorption lines, i.e. just the reverse of the phenomenon presented by the Novae; and it happens that with one and the same star bright and dark dispersion bands change places in course of time with respect to the average position of the absorption lines. This occurs e.g. in the spectrum of Mira Ceti, as will appear when comparing the observations made by VOGEL and WILSING in 1896 (Sitzungsber. der Berl. Akad. XVII) with those made by CAMPBELL in 1898 (Astroph. Journ. IX, p. 31) and by STEBBINS in 1903 (Astroph. Journ. XVIII, p. 341;

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[1]) H. EBERT, Ueber die Spektren der neuen Sterne. Astron. Nachr. Nr. 3917. Bd. 164, p. 65, 1903.

also in the spectrum of θ Orionis observed by HUGGINS in 1894 and 1897 (An Atlas of representative Stellar Spectra, p. 140), etc. In those cases the explanation suggested by EBERT would require the addition of special hypotheses.

Our fundamental hypothesis that the structure of most stars is similar to that of the Sun (it being admitted, of course, that the stars may greatly differ as to the extent of their respective gaseous envelopes, the average steepness of the density gradients in them, their chemical composition, temperature, etc.) seems to admit of the interpretation of a greater variety of facts. It makes displacements of the dispersion bands towards the long and the short waves almost equally probable — if we leave the asymmetry in the form of the dispersion curves out of question and provisionally assume the directions of the axes of the stars to be distributed at random through space.

The direction in which we see a star may be regarded as a steady line in space, allowance being made for aberration and parallax. If, now, the distribution of the matter constituting that celestial body remains nearly unchanged for a long time, then after each rotation of the star our line of sight will again pass through the same points of the "optical system", and we shall observe an accurately periodical course in the star's brightness and in the appearance of its spectral lines. In most cases, however, currents and vortices will cause more or less considerable alterations to arise in the distribution of the density of the gaseous mass, and, consequently, in the composition of the beam of light reaching the Earth at a given phase of the star's rotary motion. Thus the strictly periodical succession of phenomena is open to any degree of disturbance. The very irregular and sometimes rapid changes in the brightness of objects like *o* Ceti, SS Cygni, μ Cephei, etc. are much more intelligible from this point of view, than from interpretations based on the assumption of violent eruptions, large spots, or eclipses caused by dark companions. And it is so difficult to make a sharp distinction between variables of long period and Novae, that we should not resent the idea of comparing even the appearance of a new star to the sudden gleam of a revolving coast-light when the optical system, giving to the beam a considerable decrease in divergence, passes our line of sight.

Chemistry. — Prof. C. A. LOBRY DE BRUYN presents a paper of J. OLIE JR.: *"The transformation of the phenylpotassium sulphate into p-phenolsulphonate of potassium"*.

(Communicated in the meeting of June 25, 1904).

(This paper will not be published in these Proceedings).

Chemistry. — Prof. C. A. Lobry de Bruyn presents a paper of J. F. Suyver: *"The intramolecular transformation in the stereoisomeric α- and β-trithioacet and α- and β-trithiobenzaldehydes"*. (N°. 11 and 12 on intramolecular rearrangements).

(Communicated in the meeting of June 25, 1904).

(This paper will not be published in these Proceedings).

Chemistry. - Prof. C. A. Lobry de Bruyn presents a paper of J. W. Dito: *"The viscosity of the system hydrazine and water"*.

(Communicated in the meeting of June 25, 1904).

(This paper will not be published in these Proceedings).

Chemistry. - Prof. J. M. van Bemmelen read a paper: *"On the composition of the silicates in the soil which have been formed from the disintegration of the minerals in the rocks."*.

(This paper will not be published in these Proceedings).

ERRATUM.

p. 238, l. 5 from the bottom, for "increases" read "decreases".

(November 23, 1904).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday November 26, 1904.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 26 November 1904, Dl. XIII).

CONTENTS.

The following papers were read:

Zoology. — "*On the development of the brain in Tarsius spectrum.*" By Prof. Th. Ziehen of Berlin (Communicated by Prof. A. A. W. Hubrecht).

(Communicated in the Meeting of September 24, 1904).

Owing to the kindness of Prof. Hubrecht seven series of embryos of Tarsius spectrum were at my disposal, among them a sagittal series. With regard to the central nervous system of the adult animal I refer to two short papers published by myself, Anat. Anz. Bd. 22, N°. 24, p. 505 seq. and Mon. Schr. f. Psychiatrie u. Neurol. Bd. 14, p. 54 seq.

The first stages of development are only known to me from Hubrecht's paper. In the youngest embryo the segregation of the two hemispheres has only just commenced. The next youngest embryo shows the hemispheres already developed, namely at the lower posterior periphery of the anterior vesicle. They are separated from this latter by a sulcus hemisphaericus which anteriorly forms a pretty deep and sharp groove but occipitally terminates in a shallow groove. The segmentation of the posterior brain (5 segments) is clearly shown especially by the youngest embryo.

The following stages are very similar to those of other mammalian orders. In frontal sections through the hind-brain the uncommon depth of the sulcus limitans in the distal parts is especially striking. Frontally it soon becomes smooth. A sulcus intermedius (Groenberg) is indicated. The inner and outer labial grooves ("Lippenfurchen") are present. The cerebellum consists of two symmetrical lamellae, one to the right and one to the left, joined by a thin and narrow medial part. On the outer surface of each lamella a broad medial longitudinal groove in the immediate proximity of the median part and a narrower but relatively deeper lateral groove are to be seen. Corresponding to these two grooves we find on the ventricular surface of each lamella two longitudinal ridges and three grooves (an unpaired sulcus medianus dorsalis, a sulcus medialis dorsalis and a sulcus lateralis dorsalis on each side). The roof of the mesencephalon is rather pointed and edged like a keel. The pharyngeal part of the hypophysis shows an almost compact appendix, extending backwards and downwards. Also two lateral continuations in a backward and downward direction of the ventricle of the mid-brain deserve notice. The chorioid fissure is already developed and shows some bulgings. The sulcus hemisphaericus has also become much more marked occipitally. The sickle-fold ("Sichelfalte") forms a sharp but shallow groove and is enclosed by the bifurcating ventricle of the fore-brain. The sulcus hemisphaericus lies at the right and left in close proximity of it. The Ammon fold (Hippocampal furrow) is still entirely absent. At a stage which for the rest has only little advanced, the shape of the fore-brain has already materially progressed in development. The sickle-fold is a deep groove. In its wall the Ammon fold is noticed to which corresponds on the surface of the ventricle a distinct Ammon ridge. In an occipito-parietal direction the sickle-fold reaches as far as the anterior limit of the mid-brain, basally it finally terminates smoothly in the lamina terminalis. The sulcus Monroi is very sharply marked. On one side it terminates smoothly in the neighbourhood of the stalk-fold of the optic vesicle and on the other side in the neighbourhood of the floor fold of the primary foramen Monroi (not in the foramen itself).

The above-mentioned appendices of the lumen of the midbrain have already become rudimentary. The characteristic enclosure of the cerebral part of the hypophysis by the pharyngeal part is met with here in a similar way as in other orders of mammals. The lamella of the cerebellum has grown thicker. Of the longitudinal grooves, it is only the sulcus dorsalis medialis and the sulcus medianus dorsalis that are well marked on the inner surface. On the outer surface the ridges and grooves have been almost entirely flattened out. The posterior longitudinal bundle, the spinal root of the trigeminus and the lower olive form already distinct prominences. The chorioid plexus of the fourth ventricle has already invaginated itself considerably. The differences in level of the fossa rhomboidea have already a little more flattened out. The sulcus intermedius is lacking, the sulcus limitans is distinct. The labial grooves have become flatter.

The next-following changements may be briefly summarised as follows :

a. The hemispheres show a deep groove corresponding to the thalamencephalon, vallis diencephalica. The medial wall of each hemisphere shows on horizontal section three ridges projecting towards the lumen of the ventricle, which we will denote by *R*, *S* and *T* in their order from before backwards. Between *S* and *T* we find, following up the series in a basal direction, a great diminution in the thickness of the ventricular wall (part *d*). In this thinner part and much nearer to *S* than to *T* the formation of the chorioid fissure occurs and the invagination of the plexus chorioideus ventriculi lateralis. *S* and *R* coalesce more and more. Meanwhile from the lower posterior part of the wall of the hemispherical ventricle the broad ridge of the caudate nucleus arises. The lateral ventricular wall shows only a very slight thickening, resp. elevation *X* in its posterior part, which at higher (i. e. more parietally situated) levels, together with the caudate nucleus marks a narrow slit and coalesces with the caudate nucleus at lower levels. Between the caudate nucleus and the ridge *T* there is a fold, which may be denoted by *r*. A very shallow prominence *P* is also shown by the lateral wall in its most anterior part. The further the series is followed in a basal direction the more conspicuously a short anterior portion is marked off on the medial hemispherical surface of the vallis diencephalica, which portion is not contiguous with the thalamencephalon, but is separated from the corresponding part of the other hemisphere by the primitive sickle fold only. Within reach of this portion we find now also a slight ridge projecting into the ventricle, which we shall here designate by *Q* for briefness' sake. To all these just mentioned prominences of the interior wall-surface correspond only very slight grooves of the exterior surface or none at all. Only the ridge *S* corresponds in future pretty accurately to a shallow groove *S'*, which must be interpreted as the fissura hippocampi. This groove belongs to that part of *S* which is nearest the chorioid fissure and finally has an almost hook-shaped bend near the neighbouring lip of the chorioid fissure. The more in the following sections *S* is arched, the more also the fissura hippocampi is deepened, while at the same time all other ridges are levelled. Only the caudate nucleus remains entirely unchanged. On its surface a very slight groove is temporarily seen. The grooves **r** and **τ** become gradually obliterated for the greater part, so that the caudate nucleus coalesces with *P* and *T*. The thinner part *d* of the medial wall does not coalesce with the caudate nucleus. So the bottom of the groove **τ** finally corresponds exactly to the border of *d* and *T*. When we progress still further in a basal direction, the first connection between the thalamencephalon and the hemispheres appears immediately below the bottom of the groove **τ**, i.e. in the former region *T* and rapidly increases first in an occipito-basal direction. At the same time the lamella *d* now seems to originate in the bend between the caudate nucleus and the optic thalamus.

In the following sections we find *d* more and more connected with the lateral wall of the thalamencephalon, i. e. with the optic thalamus itself.

The insertion of the lamella *d* seems to shift more and more towards the roof of the thalamencephalon and the lamella itself seems to become shorter. It is one of the most difficult questions of cerebral development whether this shifting and shortening of the lamella *d* and also the coalescence of the caudate nucleus with *T* and the lateral wall of the thalamencephalon must be interpreted as a secondary coalescence of originally separated parts. My histological investigations of TARSIUS do not allow me to give a definite answer to this question. Still more basal sections show the disappearance of the chorioid fissure. Since *d* has in the meantime also disappeared, *S* passes immediately into the epithelial roof of the thalamencephalon or primary fore-brain. The groove-shaped longitudinal depression on the surface of the corpus striatum becomes a little more distinct. The fissura hippocampi resp. the fissura prima is pointed so that in the cross-sections the well-known picture appears, resembling a lance point. Also the roof of the median-mantle-slit which was at first formed by the folded roof of the thalamencephalon, now becomes sharply pointed. The fissura hippocampi or rather its lower lip marks pretty sharply, even after the separation of the hemispheres from each other, the point reached by the formation of the pallium. It is also very remarkable that *S* and *S'* no longer exactly correspond to each other topographically, but that *S'* becomes situated somewhat ventrally of *S*. Below *S* the medial wall of the frontal brain shows a second feeble prominence *U*. *U* and the caudate nucleus terminate in the medial respectively lateral wall of the ventriculus lobi olfactorii and in doing so grow smoother. After the disappearance of the fissura hippocampi the medial wall first remains quite undivided in many sections, but then (almost exactly in the corresponding place) the medial terminal part of the rhinal lateral fissure appears as a shallow groove.

β. The cavity of the thalamencephalon shows in its posterior parts two grooves, an upper one $\varkappa$, which is continued in the lateral groove of the midbrain ventricle (aqueduct) and frontally very soon smoothes out, and a lower one λ, which can be traced as far as the region of the foramen Monroi. The latter one is accompanied during the anterior part of its course by a parallel groove μ of a slightly more basal situation. Further folds of the surface are temporarily observed within reach of the optic stalks and of the corpora mammillaria. I regret not to be able to decide whether λ or μ has to be interpreted as the sulcus Monroi: to me it seems more likely that μ deserves this designation.

The picture is materially completed by studying a sagittal series belonging to about the same stage of development (length of the embryo 11 mm).

In a section situated somewhat laterally of the medial plane, we find as follows:

The fossa mesodiencephalica is sharply marked. Before it and for a smaller part also in it, lies the long-stretched cross-section of the posterior commissure. A very shallow groove which I designate by *E* corresponds approximately to the frontal plane of the epiphysis. There is no objection to designating with v. KUPFFER (cf. v. KUPFFER in HERTWIG's Vergl. Entw. geschichte p. 95) as synencephalon the roof part between the fossa mesodiencephalica and *E*. The fossa praediencephalica is not sharply marked. It might be sought at the place where the invagination of the plexus chorioideus ventriculi tertii occurs. It must be emphasised that it remains doubtful whether this spot corresponds to the velum transversum of lower vertebrates.

The region above the invagination of the plexus is the posterior roof portion of the primary fore brain. Below the invagination of the plexus lies the lamina reuniens, the lower part of which corresponds to the lamina terminalis of the adult animal. Before the praeoptic recess we find on the basal inner surface a shallow transverse prominence, which is laterally prolonged into the central mass of the striated body.

This transverse ridge of which even in the median plane we can recognise indications, corresponds to the crus metarhinicum corporis striati of the human embryo, described by His [1]). Consequently it passes medially into the lamina terminalis. Only in somewhat more laterally situated sagittal planes we meet before the crus metarhinicum with a second transverse prominence, which sinks away into the olfactory lobe. I designate it as crus rhinicum corporis striati. It corresponds to the crus mesorhinicum of the human embryo. A crus epirhinicum is scarcely indicated. In my opinion it is only counterfeited by the fold of the lateral rhinal fissure. On the outer contour we find corresponding to the border of the crus metarhinicum and rhinicum a shallow groove, corresponding approximately to the posterior edge of the cappa olfactoria and also approximately to the anterior edge of the olfactory tubercle. It by no means corresponds exclusively, as His seems to assume, during its whole course to the crus rhinicum or mesorhinicum. I believe that its formation is essentially independent of the morphological condition of the striated corpus and has rather to be explained by thickening of the wall of the olfactory lobe by superposition of the olfactory ganglion (cappa olfactoria) on one hand and of the olfactory tubercle [2]) on the other. To this is added a sharp bend in the brain tube in a basal direction when it passes from the hemisphere to the olfactory lobe. Moreover we must bear in mind that the lumen of the ventricle, when passing from the hemisphere to the olfactory lobe, at first tapers very rapidly, but then again very slowly [3]). Especially at the base this behaviour is very conspicuous. Obviously this must result, quite independently of a thickening of the wall by the striated corpus, in a basal transverse groove. The designation "fissura mesorhinica" which His has given to this latter, does not seem to me appropriate under these conditions. I propose to speak of a *vallis* mesorhinica. A second transverse groove is found caudally of the

[1]) His, Die Entwickelung des menschlichen Gehirns während der ersten Monate. Leipzig, S. Hirzel, 1904. S. 61 (cf. also fig. 34, p. 56).

[2]) The two borders only coincide by chance and not accurately.

[3]) Die Entwickelung des menschl. Gehirns etc. Leipzig 1904, p. 54 and p. 60.

vallis mesorhinica behind the origin of the olfactory tubercle and before the region of the praeoptic (= optic) recess. I propose to denote it as vallis praeoptica, whereas His seems to look upon it as a continuation of his stalk-fold (my sulcus hemisphaericus)[1]. It also is brought about independently of the striated corpus by the bulging of the olfactory tubercle on one hand and of the region of the chiasma on the other. The niche in the ventricle corresponding to the olfactory tubercle is designated by His (at least in man) as the posterior olfactory brain in opposition to the olfactory lobe s. str., which he calls the anterior olfactory brain. To the posterior olfactory brain he reckons particularly also the substantia perforata anterior. Against the designation "posterior olfactory brain" I only object that it favours confusion with the lobus piriformis, i. e. with the posterior part of the rhinencephalon[2].

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[1] Cf. on this point also His, die Formentwickelung der menschl. Vorderhirns, etc. Abh. d. math. phys. Cl. d. Kgl. Sächs. Ges. d. Wiss. Bd. 15, fig. 32, p. 725.

[2] Concerning the nomenclature in this region I would make the following remarks. All cerebral parts that lie basally of the fissura rhinalis (=ectorhinalis=rhinalis lateralis of many authors) I denote as rhinencephalon. As lobus olfactorius (=lobus olfactorius anterior of many authors) I designate in a purely topographical sense the anterior part of the rhinencephalon as far as it is quite separated from the lower surface of the pallium. For the posterior part of the rhinencephalon the designation "lobus piriformis" might be reserved, but it is more advisable to give up this name entirely. Part of the lobus olfactorius is covered with a microscopically sharply characterised formation, the so-called formatio bulbaris. This cover I designate as cappa olfactoria. From the developmental point of view it corresponds to the ganglion olfactorium of His. The separation of the lobus olfactorius and the pallium is exclusively brought about by the fissura rhinalis (lateralis). Hence we must also regard as a part of the fissura rhinalis the separating groove of olfactory lobe and frontal lobe which is visible in the median plane, i. e. I assume that the fissura rhinalis incises at the front as far as the median plane. The cappa olfactoria is marked off from the free surface, i. e. from the surface of the olfactory lobe that is not covered by the formatio bulbaris, by a limiting groove, the margo cappae olfactoriae. Laterally it is much more clearly marked than medially. In many animals (hedgehog, Echidna) the cappa olfactoria covers almost the whole olfactory lobe. The olfactory tubercle is also marked off against its surroundings by a shallow

Finally we mention as self-evident that in exactly medial sections all the just mentioned borders, grooves and prominences are almost entirely lacking.

Sagittal sections further prove concerning the mid-brain that at this stage it covers the isthmus to a relatively small extent, less e. g. than in a human embryo of 2 to 3 months. The cerebellum shows in sagittal sections still a horn-shaped form. Of the occipitally directed ridge, which is so characteristic for man, nothing is to be found yet.

The oldest of the embryos at my disposal had been dissected into a somewhat slanting frontal series. Here also nothing can be detected of a crus epirhinicum corporis striati. Notable is the considerable thickening of the wall in the basal portion of the medial ventricular wall. It only becomes distinct after the lateral ventricle and the ventricle of the olfactory lobe have already coalesced for some time[1]). The thickened lower portion and the not-thickened upper portion of the wall are separated on the inner surface of the ventricle by a very distinct groove which can be followed almost as far as the frontal plane of the terminal lamina. It has nothing to do with the marking off of the olfactory lobe, as it appears considerably later and also lies somewhat higher than the fissura rhinalis lateralis. In the same way it is entirely independent of the ammon fold, since it lies considerably lower than this latter. Microscopically it forms a pretty sharp basal limit for the pallium formation. Therefore I designate it as margo pallii medialis internus (v. also below). In the section where the third ventricle is visible for the first time, it appears as a paired structure; between the two terminal points of the ventricle a median groove incises into the ventricular roof (cf. above).

Special notice deserves the floor of the third ventricle. Its median groove forms a very sharp incision. The lateral parts of the floor rise, so to say, in three gradations. The most lateral prominence

groove, the margo tuberculi olfactorii. This groove also is generally not so distinctly perceptible at the medial edge, on the other hand at the lateral and anterior edges it is well developed and hence has here often been designated as fissura rhinalis medialis s. entorhinalis. At the posterior edge, towards the substantia perforata anterior, it is generally rather shallow. When the cappa olf. reaches far backward, the anterior margo tub. olf. coincides entirely or partly with the margo cappae olf.

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[1]) In what follows the series is supposed to be examined from before backward.

which at the same time is the broadest, proceeds from the crus rhinicum of the corpus striatum and forms in future the principal mass of this ganglion. The middle elevation corresponds to the crus metarhinicum of the corpus striatum. It disappears with the separation of the hemispheres. In the lamina terminalis it meets the homologous opposite prominence. It is interrupted by the anterior commissure. The most medial and smallest elevation only becomes visible before the lamina terminalis and is at first very flat; then it rises pretty steeply frontally but remains narrow. From the homologous opposite elevation it remains separated by the shallow median floor groove. Following the series farther in a frontal direction, the two hemispheres split finally within reach of the median groove of the floor and the most medial elevation coalesces before the foramen Monroi with the upper portion of the medial wall, corresponding pretty accurately to the margo pallii medialis internus.

From this description we must conclude that also this most medial elevation can by no means be interpreted as the crus epirhinicum in His' sense.

The optic thalamus projects in the following sections between the middle and lateral ridge just mentioned. More sharply developed than in preceding stages a longitudinal groove on the outer surface of the thalamencephalon (sulcus fastigialis thalami) is now visible dividing the pointed crest of the optic thalamus from the broad basal mass of this ganglion.

It is situated somewhat higher than the above mentioned groove $\varkappa$, which for the rest is now much less distinct. λ and μ are no longer clearly divided. Instead of them we find a broader groove, which doubtless must be designated as sulcus Monroi.

The hind brain presents no peculiarities.

Reviewing the whole of the peculiarities in the development of the brain of Tarsius that have been noted in the preceding pages, a far-reaching agreement with the development of the brain of the primates is obvious. The essential differences are sufficiently explained by the rather pronounced macrosmatic character of the brain of Tarsius. It is much more difficult tô determine the relations of the Tarsius brain in the descending direction. Carnivores and Ungulates are out of the question. The development of the brain of Chiroptera is unfortunately too little known as yet but certain analogies are certain. Very great is also the agreement with the development of the brain of Rodents, only one must not consider the brain of the rabbit as the typical representative of the brain of Rodents, as is often done. As the rodent brain in its turn is not far distant in its development from the brain of the Insectivores, it is clear that the Tarsius brain shows unmistakable genetic relations with this latter also.

A more detailed account with figures will be published in the Handbuch d. Entwicklungsgeschichte edited by HERTWIG

Mathematics. — *"On the equation determining the angles of two polydimensional spaces".* By Prof. P. H. SCHOUTE.

The problem which we wish to solve is the following:

"In a space S_n with n dimensions a rectangular system of coordinates $O\,(X_1\,X_2\,.\,.\,.\,X_n)$ has been taken and with respect to this system a space S_p passing through O has been given by the equations

$$x_{p+i} = a_{1,i}\,x_1 + a_{2,i}\,x_2 + \,.\,.\,.\, + a_{p,i}\,x_p\,;$$
$$(i = 1, 2, \ldots, n - p)$$

supposing this space S_p to have with the space of coordinates $O\,(X_1\,X_2\,.\,.\,.\,X_p)$ but one point O in common, the p angles $\alpha_1, \alpha_2, \ldots \alpha_p$ are to be determined between these two p-dimensional spaces."

By means of geometry we should set to work as follows. Suppose in the given space S_p a spherical space having O as centre and unity as radius and thus forming in S_p the locus of the points at distance unity from O; if this spherical space projects itself on the space of coordinate $O\,(X_1\,X_2\,.\,.\,.\,X_p)$ as a quadratic space with the half axes $a_1, a_2, \ldots a_p$, we get

$$a_1 = \cos \alpha_1,\ a_2 = \cos \alpha_2,\ \ldots,\ a_p = \cos \alpha_p.$$

In an almost equally simple way the tangents of the demanded angles are connected analytically with the central radii-vectores of an other quadratic space. If P is an arbitrary point of S_p and Q its projection on the space of coordinate $O\,(X_1\,X_2\,.\,.\,.\,X_p)$, then the angle $P\,O\,Q = \alpha$ is also determined by the relation

$$tg^2\,\alpha = \frac{OP^2 - OQ^2}{OQ^2} = \frac{\sum\limits_{i=1}^{n-p} (a_{1,i}\,x_1 + a_{2,i}\,x_2\ .\,.\,.\ + a_{p,i}\,x_p)^2}{\sum\limits_{i=1}^{p} x_i^2}\,.$$

If we consider in S_p the points P the coordinates of which are bound to the condition

$$\sum_{i=1}^{n-p} (a_{1,i}\,x_1 + a_{2,i}\,x_2 + \ldots + a_{p,i}\,x_p)^2 = 1 \,.\,.\,.\,.\,.\,.\,.\, (1),$$

containing only $x_1, x_2, \ldots x_p$ and thus expressing that the projection Q of P on $O(X_1 X_2 \ldots X_p)$ remains in this latter space on the quadratic space represented by (1), then the relation holds good

$$tg\,\alpha = \frac{1}{OR}.$$

If $b_1, b_2, \ldots b_p$ are the half axes of this new quadratic space, we shall find

$$tg\,\alpha_1 = \frac{1}{b}, tg\,\alpha_2 = \frac{1}{b_2} \ldots, tg\alpha_p = \frac{1}{b_p}.$$

Now (1) passes into the symbolic form

$$(A_1 x_1 + A_2 x_2 + \ldots + A_p x_p)^{(2)} = 1$$

by the substitutions

$$\sum_{i=1}^{n-p} a^2_{k,i} = A_{k,k} \quad . \quad \sum_{i=1}^{n-p} a_{k,i}\, a_{l,i} = A_{l,k};$$

so the well know secular equation

$$\begin{vmatrix} A_{11} - \lambda & A_{21} & \ldots & A_{p,1} \\ A_{12} & A_{22} - \lambda & \ldots & A_{p,2} \\ \ldots & \ldots & \ldots & \ldots \\ A_{1,p} & A_{2,p} & & A_{p,p} - \lambda \end{vmatrix} = 0$$

furnishes by its roots $\lambda_1, \lambda_2, \ldots \lambda_p$ the coefficients of the equation of that quadratic space reduced on the axes.

From the relations

$$\lambda_1 = \frac{1}{b_1^2}, \lambda_2 = \frac{1}{b_2^2}, \ldots \lambda_p = \frac{1}{b_p^2}$$

ensues immediately that the demanded equation is arrived at by replacing in the above mentioned determinant λ by $tg^2\,\alpha$.

Mathematics. — *"The locus of the principal axes of a pencil of quadratic surfaces"*. By Prof. J. CARDINAAL.

1. The envelope of the axes of a pencil of conics was investigated among others by M. TREBITSCHER[1]). He found that the axes of the above mentioned conics envelop a curve of class three touching the right line at infinity of the plane in two points conjugate to the directions of the axes of the two parabolae of the pencil with respect to the

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[1]) Ueber Beziehungen zwischen Kegelschnittbüscheln und rationalen Curven dritter Classe, Sitzungsber. der Kaiserl. Akademie der Wissenschaften, Bnd. LXXXI, p. 1080.

isotropic points I and J. So the curve is of order four, i.e. rational. This result is mentioned, in the "Encyklopädie der Mathematischen Wissenschaften" III, p. 101. However, if we consult in the same work the theory of the quadratic surfaces we find no evidence of an attempt to determine the locus of the principal axes of the surfaces of a pencil. The present writer makes it his aim in the following to publish some investigations on this locus.

2. We presuppose a simpler special case of the pencil and we take a pencil of concentric quadratic cones, of which the locus of the principal axes is a cone the order of which can be determined. Let us suppose to this end the section of one of the cones with the plane at infinity; the conic formed in this way determines with the isotropic circle a common autopolar triangle and the vertices of that triangle determine the directions of the principal axes of the cone. From this follows:

The principal axes of all the cones of the pencil cut the plane at infinity in the vertices of the common autopolar triangles of the conics situated in this plane and the isotropic circle. These triplets of points form the Jacobian curve of the net of conics determined by two of the conics and the isotropic circle.

So the cone of the axes is a cone of order three cutting the plane at infinity in the just mentioned Jacobian curve.

To realize the position of the principal axes of this cubic cone we choose a generatrix a_1. If we assume a plane through the vertex normal to a_1 this will cut the cone according to three rays a_2, a_3, b_1: a_2 and a_3 are normal to each other, b_1 belongs to an other trieder of axes, obtained by assuming through the vertex a plane normal to b_1; this plane passes through a_1 and cuts the cone moreover in the two principal axes b_2 and b_3 normal to each other.

As a rule this cone will not have a nodal generatrix, so it will not be rational.

3. Suppose a pencil of quadratic surfaces be given. Out of a point O in space as vertex we construct the parallel cones of the asymptotic cones of the various surfaces; in this manner a pencil of cones is formed, with respect to which we can construct the cone of the axes. The trieders of axes of this cone are parallel to the trieders of axes of the surfaces of the pencil.

Let further a skew cubic q_3 be constructed, which is the locus of the centres of the surfaces of the pencil; if then out of each centre a trieder is constructed parallel to the corresponding trieder of axes of the cone, the surface is formed which is the locus of the principal axes. From this ensues:

The locus of the principal axes of quadratic surfaces belonging to a pencil is a skew surface of which one of the directrix curves is a skew cubic φ_3 possessing a director cone: each point of the skew cubic is homologous to a trieder of rays of the cone.

4. The order of the surface can be determined by investigating by how many principal axes an arbitrary right line l is cut, or how many planes possessing a principal axis can be made to pass through l, which comes to the same thing.

Let A be a point of φ_3, to which three points A'_1, A'_2, A'_3 correspond on the Jacobian curve C'_3 in the plane at infinity P_∞. Let moreover P be a plane through l; then this cuts φ_3 in three points A, B, C, to which correspond again in P_∞ the points $A'_1\ A'_2 \ldots C'_3$, so to the plane P correspond through l nine planes $P'_1\ P'_2 \ldots P'_9$.

If reversely we assume a point A' on C'_3 only *one* point A on φ_3 corresponds to it. If we now make a plane P' pass through l, it cuts C'_3 in three points A', B', C', to which correspond three points A, B, C; so to a plane P' correspond three planes P. From this ensues:

The two coaxial pencils of planes P and P' have a (3,9)-correspondence. So the number of elements of coincidence amounts to 12. From this reasoning, however, we may not conclude that the order of the skew surface is to be 12; this number must be diminished by the number of points common to φ_3 and C'_3. The three points of intersection of φ_3 and P_∞ are namely situated on C'_3; if we call one of these points S, then S_1 coincides with S quite independently of the position of the assumed right line l. So of the 12 planes of coincidence 3 pass through the points of intersection of φ_3 and C'_3; so 9 remains for the order of the skew surface.

5. A full investigation of this surface O_9 is a very extensive one; however, we can consider some properties and trace some particularities. From the plan of the problem ensues that from each point of φ_3 three generatrices can be drawn meeting P_∞ in the three corresponding points; so φ_3 is a threefold curve of O_9.

The section of P_∞ and O_9 possesses some particularities which we shall look into. In the very first place lie on it the three centres S_1, S_2, S_3 of the paraboloids of the pencil supposed to be real for the present. Out of each of those points two principal axes can be drawn having therefore twelve common points of intersection. Moreover each of these axes cuts C'_3 in two more points, which can thus be regarded as double points. One of these points belongs however to a triplet of points corresponding to a point of intersection of φ_3 and C'_3; so it can be regarded as a point of contact of the plane

P_∞ and O_9. If we combine these results, we arrive at the following theorem:

The section of O_9 and P_∞ is a degenerated curve of order nine broken up into a plane cubic and six right lines. On this section are situated twelve nodes, points of intersection of the principal axes two by two; moreover six nodes are situated on it, formed each time by one of the points of intersection of a principal axis with C_3, and six points of contact, which are the remaining points of intersection. So P_∞ is a sixfold tangent plane of O_9.

So we come to the conclusion that O_9 possesses besides the threefold curve φ_3 still a nodal curve of which for the present we cannot make out how it is composed, but of which the total order is 18.

The number of points of intersection of this curve with one of the generatrices of O_9 can be determined. Let a be one of the right lines connecting a point A of φ_3 with one of the corresponding points A'_1 on C_3. An arbitrary plane Q through a cuts φ_3 in two more points B and C to which correspond on C_3 two triplets of points B'_1, B'_2, B'_3 and C''_1, C''_2, C''_3. In like manner a plane Q' through a cuts the curve C_3 in two more points to which correspond two points on φ_3: so there exists between the pencils of planes Q and Q' a (6,2)-correspondence and the number of planes of coincidence amounts to 8. So all together a is cut by 8 principal axes. As in the general case this number must be diminished by 3, for now too the three points of intersection of φ_3 and C_3 must be taken into account; so a is cut by five principal axes. Each generatrix of O_9 has thus five points in common with the nodal curve.

From the preceding is apparent that the general section of the surface possesses 18 nodes and 3 triple points; if we have in mind that the latter are equivalent to 9 nodes we see that the general section is not rational, as a curve of order nine can have 28 nodes and the curve under investigation possesses only 27 nodes.

6. We shall consider a single case, where the surface O_9 is simplified. We have already noticed that the cone of axes is of order three without nodal generatrix; there would be one if the net of conics possessed in P_∞ a point, common to all conics. As however to this pencil belongs the isotropic circle this case is excluded; it may however happen that the cone of axes breaks up into a quadratic cone and a plane, or into three planes.

7. We choose an example of the first case. When the cone of axes breaks up into a quadratic cone and a plane, then the Jacobian curve in P_∞ must degenerate into a right line C_1 and a conic C_2. This happens:

a. When the conics of the net pass through two fixed points.

b. When the net possesses a double right line.

We restrict ourselves in this communication to the first of these cases; then the base curve of the pencil of surfaces is circular.

It is in the first place necessary now that the cone is degenerated into two parts to consider the distribution of the axes on cone and plane. If the base curve of the pencil of surfaces is circular, there is a system of parallel planes so that each plane is cut according to a pencil of circles. Of each surface of the pencil *one* principal axis runs parallel to these planes. From this ensues:

When in consequence of the existence of a circular base curve the cone of axes degenerates into a quadratic cone and a plane, then of the three points A'_1, A'_2, A'_3, homologous to a point A on φ_3 one lies on the right line C'_1 in P_∞ and two on the conic C'_2. So the skew surface O_9 degenerates into two other skew surfaces intersecting each other in their common directrix φ_3. For one skew surface φ_3 is a nodal curve, for the other it is single. This already suggests that the former of the two skew surfaces is of order six, the latter of order three. This can be reasoned more minutely in the following manner:

Let l be once more a right line; a plane P through l has three points A, B, C in common with φ_3 to which six points $A'_1, A'_2 \ldots C'_1, C''_2$ on C'_2 correspond; so six planes P'' correspond to P; if reversely we make a plane P'' to lie through l, it cuts C'_2 in two points to which on φ_3 two points correspond, so that between the planes P and P'' a (2, 6)-correspondence exists. However φ_3 has a point in common with C'_1, as C'_1 contains the point of contact of a hyperbolic paraboloid of the pencil with P_∞; so there remain for φ_3 two points of contact with C'_2 and the order 8, which would arise on account of the (2, 6)-correspondence, must be diminished by 2; so we get a skew surface O_6 of order six. The second skew surface is of order three.

In the general case the section of P_∞ and O_9 consisted, besides of C'_3, of three pairs of right lines, to be called a_1a_2, b_1b_2, c_1c_2. If O_9 degenerates in the manner described above these right lines will also be distributed themselves on O_6 and O_3. Let A' again be the point where φ_3 cuts the right line C'_1, thus the point of contact of a hyperbolic paraboloid of the pencil; through A' pass the two principal axes a_1a_2 and these belong to O_6, whilst the principal axis not lying in P_∞ through A' belongs to O_3. To O_3 belongs thus one principal axis of each of the pairs b_1b_2 and c_1c_2, so P_∞ is a double tangent plane of O_3 and the section of O_6 and P_∞ consists of the conic C'_2, the pair of axes a_1a_2 and the principal axes b_1 and c_1. Of a_1 and a_2 the point of intersection a_1a_2 is the node in the curve of intersection of P_x and O_6, one of each of the points of intersection of a_1 and a_2 with C'_2 is point of contact; so on a_1 as well as on a_2 another node is situated. Of each of the points of intersection of b_1 and c_1 with C'_2 *one* is point of contact, the other is also point of intersection of φ_3 and C'_2. So the points of intersection b_1, c_1, a_1, a_2 mutually are left as nodes; these are five in number besides the point of intersection counted already $a_1 a_2$ belonging to φ_3. So the entire number of the nodes of the section of O_6 and P_x not lying on φ_3 amounts to 7. From this ensues that O_6 has besides φ_3, another double curve of order seven. If we make a plane to pass through a generatrix O_1 and if we investigate how many right lines are situated in it, we shall find the number to be 3 corresponding to former results.

The nodal curve of order seven is thus intersected three times by the right lines of O_6.

8. The closer investigation of the surface O_9 as well as that of O_6 and the other possible forms appearing by variously assuming the pencil of surfaces, gives rise to very extensive considerations, which are not to be included in this communication, as for the present its aim was but to show the general properties of the discussed locus.

Physics. — "*Simplified Deduction of the Field and the Forces of an Electron, moving in any given way.*" By Prof. A. SOMMERFELD. (Communicated by Prof. H. A. LORENTZ).

§ 1. *Summary.*

In the "Göttinger Nachrichten" [1] I communicated a general representation of the field of an electron, moving in any given way, which seems to be simpler than the formulae, hitherto known, which are based on the work of H. A. LORENTZ. This is the difference: My formulae express the potentials by a *simple integral, extending over the past time* and containing only the varying distances of the point in question *from the centre of the electron,* supposed to be spherical, whereas the formulae hitherto known are *double or triple integrals,* extending over the *space,* charged with electricity, and containing the distance of the point in question *from the position of the charge at a certain former time.* It may be remarked, that

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[1] Nachrichten d. K. Gesellschaft d. Wissenschaften 1904 Heft 2; in the following to be cited as "first paper".

P. Hertz[1]) has published a method, though only for special cases, equivalent to my general representation of the field, for which he very happily uses the figure of a sphere contracting itself with the velocity of light.

In the "Göttinger Nachrichten" I start from rather a toilsome Fourier's integral, whereas I shall now choose a very simple way, using only the theorem of Green. In this way I represent the potential in the first place by a quadruple integral, (§ 2), one integration extending over the time, the others over the space occupied by the charge.

Here the road divides: *Either you can calculate the integration over the time*; this leads to Lorentz's representation; then the integration over the charge gets rather a complicated form, relating no more to simultaneous positions of the elements of the charge, but to positions occupied by each element at a certain former time, or, as you may say, relating no more to the real shape of the electron, but to a deformed one.

Or you can calculate the integration over the charge; this leads to my formulae; it is then no longer the integration over the time, in general cases of motion, that you have to evaluate (§ 3).

§ 4 applies our formulae to problems, essentially known, viz. to the determination of the field in a great distance from the electron, and to the case of stationary motion, especially with a velocity exceeding that of light, in order to complete the statements of my first note and to study in detail the behaviour of the field in the neighbourhood of the "shadow of motion".

In the last § I pass on to the representation of force, exerted by the electron's own field. This force is computed exactly for any motion, excluding rotations, according to the principles of H. A. Lorentz. At first sight the general formulae I am using here, seem to be more complicated, than the more explicit formulae, I have published in the "Göttinger Nachrichten" [2]) but in reality they are very easy of application to the case of stationary motion. For you may derive immediately from them the known result, that the stationary motion with a velocity less than that of light is in every case a possible free motion of an electron. Moreover you deduct easily the value of the force, necessary to maintain a motion of a bodily charge with a velocity exceeding that of light. This force is distinctly finite, even

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[1]) Untersuchungen über unstetige Bewegungen eines Elektrons. Dissertation Göttingen 1904, § 3.

[2]) Nachrichten d. K. Gesellschaft d. Wissenschaften 1904, Heft 5, in the following to be cited as "second paper".

in case of infinite velocity; its value has been calculated, for the first time, as far as I know, in my second paper. Further you derive from the same formulae the surprising result, stated in my second paper not only for the case of stationary, rectilineal motion, but for any motion you like: The motion of a surface-charge with a velocity exceeding that of light, is actually impossible, requiring continually an infinite supply of force. In order to make this more evident, let me point out: the more the charge is concentrated, the more the force will increase; in case the charge is concentrated at one point, the force is infinite even in the case of a velocity less than that of light.

It may seem unsatisfactory, to be restricted to the special shape of a sphere. Only a few of the following results are independent of this restriction, that is those, which do not contain the radius of the electron, e.g. the approximate formulae for the field of a charge, stationarily moved, in the case of a velocity less than that of light, and those in case of a velocity exceeding that of light, in the regions I and III (§ 4), whereas the formulae relating to the limit of the shadow of motion, that is to the region II, depend on the special spherical shape. Yet it is evident, that on more general suppositions, you could probably not proceed so far.

It is kown, that H. A. LORENTZ[1]) has lately supported the hypothesis, that the shape of the electron is variable, conforming itself to a "HEAVISIDE-ellipsoid", according to its momentary velocity. As for velocity exceeding that of light this hypothesis fails, because in this case you can hardly speak of a "HEAVISIDE-hyperboloid". So I have not been able, to use this hypothesis.

§ 2. GREEN'S *Theorem.*

All natural philosophy proves the wonderful power of GREEN'S theorem. We shall use it here very much like KIRCHHOFF[2]) in his enunciation of HUYGENS' principle.

Let φ be the scalar potential, satisfying the differential equation:

$$\angle \varphi = \frac{1}{c^2}\frac{\partial^2 \varphi}{\partial t^2} - \varrho \ , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c means the velocity of light, and ϱ the density of charge of the electron; as regards the choice of units see H. A. LORENTZ, Encyklopädie der Mathem. Wissenschaften Bd. V. Art. 13, N°. 7.

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[1]) K. Akademie van Wetenschappen te Amsterdam Mei 1904. Proceedings p. 809.

[2]) Vorlesungen über Mathematische Optik, 2te Vorlesung, § 1. Leipzig 1891.

Let v be an auxiliary function

$$v = \frac{1}{r} F\,(r - c\,(t - t'))\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

r the distance of a certain point in question A from any point P, t the moment, for which the value of φ at the point A is required, t' a variable moment of time. Our auxiliary function v then satisfies the differential equation:

$$\Delta\, v = \frac{1}{c^2} \frac{\partial^2 v}{\partial t^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Like KIRCHHOFF we shall suppose, that the function $F\,x$ is represented by a narrow prong, enclosing the area 1, viz. that $F\,x$, vanishes for all abscissae different from $x = 0$, but in the point $x = 0$ increases so strongly and so suddenly, that notwithstanding

$$\int\limits_{-\infty}^{+\infty} F\,(x)\, dx = 1\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If we apply GREEN's theorem in its most common form to the functions φ and v, we have:

$$\int (\varphi\, \Delta\, v - v\, \Delta\, \varphi)\, dS = \int \left(\varphi \frac{\partial v}{\partial n} - v \frac{\partial \varphi}{\partial n} \right) d\sigma. \quad . \quad . \quad . \quad (5)$$

The surface integral on the right hand side is to be extended over the border of the space S and over an infinitely small surface, enclosing the point A, in as much as this point is contained in S. This holds good, because we shall let S finally expand into infinity. The part of the surface integral, relating to the surface enclosing A, is known to give:

$$4\,\pi\,\varphi_A\, F\,(-\,c\,(t - t')).$$

If we use on the left side of (5) the differential equations (1 and (3), substituting in φ as variable time t' and noticing, that $\frac{\partial^2 v}{\partial t^2} = \frac{\partial^2 v}{\partial t'^2}$, it follows:

$$\frac{1}{c^2} \frac{\partial}{\partial t'} \int \left(\varphi \frac{\partial v}{\partial t'} - v \frac{\partial \varphi}{\partial t'} \right) dS + \int \varrho\, v\, dS = \int \left(\varphi \frac{\partial v}{\partial n} - v \frac{\partial \varphi}{\partial n} \right) d\sigma +$$
$$+\, 4\,\pi\,\varphi_A\, F\,(-c\,(t - t'))\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The second integral on the left is extended over the charge of the electron, the first on the right no more than over the surface of S.

Multiply the last equation with $c\,dt'$ and integrate with respect to t' from $-\infty$ to $+\infty$. Thereby the first term on the left vanishes on account of the nature of the function F. In fact this member relates, after the integration is performed, only to the moments

$t' = \pm \infty$, and certainly $v = 0$ stands for $t' = \pm \infty$ according to the definition of F. Further we suppose, that the first integral on the right vanishes also, on account of the nature of the potential φ. In order to understand this, we may perform the integration with respect to t', as follows:

$$\int_{\infty}^{+\infty} v \frac{\partial \varphi}{\partial n} c\, dt' = \frac{\partial \varphi_0}{\partial n} \int_{-\infty}^{+\infty} v\, c\, dt' = \frac{1}{r} \frac{\partial \varphi_0}{\partial n}$$

where φ_0 means the value of φ for that t', for which the argument of F vanishes viz. $t' = t - \frac{r}{c}$. Similarly we show:

$$\int_{-\infty}^{+\infty} \frac{\partial v}{\partial n} \varphi\, c\, dt' = \varphi_0 \frac{\partial}{\partial n} \frac{1}{r} - \frac{1}{r} \frac{\partial r}{\partial n} \frac{1}{c} \frac{\partial \varphi_0}{\partial t'},$$

If the electron was at rest originally, for instance until the moment t_0, we can in any case expand the bordering surface σ so far, that the value t' just now defined gets less than t_0. In this case φ_0 becomes the electrostatical potential of the electron and $\frac{\partial \varphi_0}{\partial t'} = 0$. The surface integral in question is then reduced to the following expression

$$\int \left(\varphi_0 \frac{\partial}{\partial n} \frac{1}{r} - \frac{1}{r} \frac{\partial \varphi_0}{\partial n} \right) d\sigma,$$

which we know by the potential theory to vanish, if it is calculated for a surface sufficiently distant.

So you keep in equation (6) only the second member on the left and on the right, and you have:

$$\int_{-\infty}^{+\infty} c\, dt' \int \varrho v\, dS = 4\pi \int_{-\infty}^{+\infty} \varphi_A\, F(-c\,(t-t'))\, c\, dt'.$$

Perform the integration on the right in the way used repeatedly and denote for short with φ the value at the point A at the time t. We get conclusively:

$$4\pi\varphi = \int_{\infty}^{+\infty} c\, dt' \int \frac{\varrho}{r} F(r - c\,(t-t'))\, dS. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The scalar potential is represented here by a quadruple integral, viz. a time-integral and a space-integral.

§ 3. *Transition to* LORENTZ's *potential-formulae on the one hand, and to those given by myself on the other.*

It is tempting, to perform in (7) the integration with respect to t'. As F is different from 0 only for the moment $t' = t - \frac{r}{c}$, we get immediately

$$4 \pi \varphi = \int \frac{\{\varrho\}}{r} d S, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $\{\varrho\}$ means the density, contained in the element dS at the time $t' = t - \frac{r}{c}$.

As for the proof of formula (8), H. A. LORENTZ [1]) refers to the expression (8) satisfying the differential equation (1).

WIECHERT [2]) and others do not start from GREEN's theorem, but from BELTRAMI's, which naturally is only a transformation of GREEN's theorem and, it strikes me, not a very transparent one.

Instead of performing the integration in (7) with respect to time, it is better, to evaluate that in respect to space. Now for this purpose it is necessary to add a certain supposition as to the shape of the electron. In the first instance we suppose the electron to be an *infinitely thin spherical shell* of the radius a, on which the charge ε is uniformly distributed. So we take:

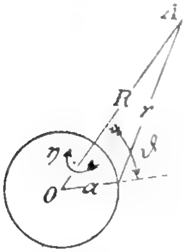

Fig. 1.

$$\frac{\varepsilon}{4 \pi a^2} d \sigma \text{ instead of } \varrho \, dS$$

and get from (7)

$$4 \pi \varphi = \frac{\varepsilon}{4 \pi a^2} \int_{-\infty}^{+\infty} c \, dt' \int \frac{1}{r} F(r - c(t - t')) \, d \sigma.$$

Let O be the centre of the spherical shell. Round OA we count the azimuth η and from OA the angle ϑ, so that η, ϑ mean the geographical longitude and the complement of the latitude on the surface of the electron. Let R be the distance OA from the centre to the point in question, it follows:

$$r^2 = R^2 + a^2 - 2 Ra \cos \vartheta, \qquad r dr = Ra \sin \vartheta \, d\vartheta.$$

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[1]) La théorie électromagnétique de MAXWELL, Leiden, 1892, pag. 119.

[2]) Elektrodynamische Elementargesetze. LORENTZ—JUBELBAND, pag. 560, Haag 1900.

$$\int \dots d\sigma = a^2 \int_0^{2\pi}\int_0^{\pi} \dots d\eta \sin\vartheta\, d\vartheta = 2\pi a^2 \int_0^{\pi} \dots \sin\vartheta\, d\vartheta =$$

$$2\pi a \int_{|R-a|}^{R+a} \dots \frac{r\,dr}{R}.$$

so :

$$4\pi\varphi = \frac{\varepsilon}{2a}\int_{-\infty}^{+\infty} \frac{c\,dt'}{R} \int_{|R-a|}^{R+a} F(r - c(t - t'))\,dr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

The lower limit $|R-a|$ equals $R-a$, if $R > a$, but equals $a-R$, if $R < a$. Now as follows from the definition of F, the integral with respect to r is equal to 1 or 0, according as the argument $r-c(t-t')$ vanishes for one of the values of r, contained between $|R-a|$ and $R+a$, or not. Write for abbreviation :

$$\tau = t - t',$$

then our integral becomes equal to 1, if

$$R + a > c\tau \text{ and } |R - a| < c\tau$$

that is, if we can form a triangle with the sides R, a and $c\tau$; it becomes equal to 0 in the contrary case. If λ means the number 1 or 0, according as that triangle is possible or not, we may also write

$$4\pi\varphi = -\frac{\varepsilon c}{2a}\int_{+\infty}^{-\infty} \frac{\lambda\,d\tau}{R}.$$

instead of (9) ; reversing the limits and noting that the condition $|R-a| < c\tau$ is never satisfied for $\tau < 0$, we may finally put :

$$4\pi\varphi = \frac{\varepsilon c}{2a}\int_0^{\infty} \frac{\lambda\,d\tau}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This is exactly the formula (17) of my first paper. There is no question of imagining a deformed shape of electron. The formula (10) holds good for the exterior as well as for the interior of the electron. The only difference between the two cases is this : The limits τ_1, τ_2, between which λ does not vanish, are determined at a point of the exterior by

$$R_1 - a = c\tau_1 \qquad\qquad R_2 + a = c\tau_2 \,. \quad . \quad . \quad . \quad (11)$$

R_1, R_2 meaning the distances of the point in question from the position of the centre occupied at the time $t-\tau_1$ and $t-\tau_2$; on the other hand for a point of the interior by

$$a - R_1 = c\tau_1 \qquad\qquad a + R_2 = c\tau_2 \, . \quad . \quad . \quad . \quad (11')$$

It may happen, that several pairs of values τ_1 τ_2 exist; it may also happen, that the point in question is situated so as to be an interior point for a certain time, an exterior point for another.

It is easy to pass from the potential for a spherical shell to that of a solid sphere, uniformly charged, which is to be divided into spherical shells. If ε is the whole charge of the solid sphere, the charge $3\,\varepsilon\, r'^2 \frac{dr'}{a^3}$ is contained in a shell of radius r' and the thickness dr'. Now it is only required to substitute r' for a and $\frac{3\varepsilon}{a^3} r'^2\, dr'$ for ε and to add an integration with respect to r' from 0 to a; then we have:

$$4\,\pi\,\varphi = \frac{3\,\varepsilon\, c}{2\,a^3}\int_0^\infty \frac{d\tau}{R}\int_0^a \lambda\, r'\, dr' \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

To begin with we take an *exterior* point, for which $R > a$, and a certain value τ. Equations (11), in which r' is to be substituted for a, show, that $\lambda = 1$, if $c\,\tau$ lies between $R - r'$ and $R + r'$, or, what comes to the same thing, if $r' > |\, R - c\,\tau \,|$. Now two cases are possible: $|\, R - c\,\tau \,|$ may either be smaller than a or larger. In the first case a triangle with the sides $(a, R, c\,\tau)$ is possible, not in the second case. In the first case we have:

$$\int_0^a \lambda\, r'\, dr' = \int_{|R-c\tau|}^a r'\, dr' = \frac{1}{2}\left(a^2 - (R - c\tau)^2\right),$$

in the second:

$$\int_0^a \lambda\, r'\, dr' = 0 \, .$$

If we define a quantity $\varkappa$ by

$$\varkappa = \frac{3}{2}\left(1 - \left(\frac{R - c\tau}{a}\right)^2\right) \text{ or by } \varkappa = 0 \, , \, . \quad . \quad . \quad (13)$$

according as the triangle $(a,\ R,\ c\tau)$ is possible or not, we can write for an exterior point instead of (12)

$$4\,\pi\,\varphi = \frac{\varepsilon c}{2a}\int_0^\infty \frac{\varkappa\, d\tau}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14).$$

In the case of an *interior* point, for which $R < a$, the equations

(11') require, that $c\tau$ must be smaller than $r' + R$ and larger than $r' - R$, so as not to let λ vanish. Accordingly r' must be $> c\tau - R$ and $< c\tau + R$. Now three cases are possible:

a). $c\tau - R < a$, $c\tau + R > a$, triangle $(a, R, c\tau)$ possible.

b). $c\tau + R < a$, consequently $c\tau - R < a$, triangle $(a, R, c\tau)$ impossible, a the largest of the three sides $a, R, c\tau$.

c). $c\tau - R > a$, consequently $c\tau + R > a$, triangle $(a, R, c\tau)$ impossible, a not the largest of the three sides $a, R, c\tau$.

In these three cases we evidently have:

$$\int_0^a \lambda r' dr' = \int_{c\tau - R}^a r' dr' = \frac{1}{2}\left(a^2 - (c\tau - R)^2\right) \, . \; . \; . \; . \; . \; . \qquad (a)$$

$$\int_0^a \lambda r' dr' = \int_{c\tau - R}^{c\tau + R} r' dr' = 2\, c\tau R \, . \; . \; . \; . \; . \; . \; . \; . \qquad (b)$$

$$\int_0^a \lambda r' dr' = 0 \, . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (c)$$

Now if we define the quantity $\varkappa$ by (13) in the cases *a*) and *c*), but by

$$\varkappa = 6\,\frac{c\tau R}{a^2} \, . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (13')$$

in the case *b*), the potential is given by (14) for interior points as well, according to equation (20) of my former paper.

Notwithstanding the simplicity of our quantities λ and $\varkappa$, it is easier for further purposes, to replace them by an analytical expression, holding good for all values of τ.

As for an expression of λ, we know, that

$$\int_0^\infty \sin sx \frac{ds}{s} = +\frac{\pi}{2} \quad \text{or} \quad -\frac{\pi}{2} \; . \; . \; . \; . \; . \; . \qquad (15)$$

according as x is positive or negative. Now:

$$\sin sa \sin sR \sin sc\tau = \frac{1}{4}\Big\{\sin s\,(a + R - c\tau) + \sin s\,(a - R + c\tau) -$$

$$- \sin s\,(a + R + c\tau) - \sin s\,(a - R - c\tau)\Big\} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (15')$$

As for the four quantities

$$a + R - c\tau \;,\; a - R + c\tau \;,\; -a - R - c\tau \;,\; -a + R + c\tau$$

three are positive and one negative if the triangle $(a, R, c\tau)$ is possible, two positive and two negative, if the triangle is impossible. After having multiplied equation (15') by $\frac{ds}{s}$ and having integrated with respect to s from $s = 0$ to $s = \infty$, you get in the first case $\frac{\pi}{4}$, in the second case 0; i. e. you have in both cases:

$$\int_0^\infty \sin sa \sin sR \sin sc\tau \frac{ds}{s} = \frac{\pi}{4}\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad , \qquad (16)$$

That is the required expression for λ; substituting it in equation (10), we have in the case of *surface-charge*:

$$\varphi = \frac{\varepsilon c}{2\pi^2 a}\int_0^\infty \frac{d\tau}{R}\int_0^\infty \sin sa \sin sR \sin sc\tau \frac{ds}{s} \quad . \quad . \quad . \quad . \qquad (17)$$

Replacing further a by r' in equation (16), we get simultaneously for the integral, contained in (12):

$$\int_0^a \lambda\, r'\, dr' = \frac{4}{\pi}\int_0^\infty \frac{ds}{s}\int_0^a \sin sr'\, r'\, dr' \sin sR \cdot \sin sc\tau =$$

$$= \frac{4}{\pi}\int_0^\infty \frac{\sin sa - sa\cos sa}{s^2} \sin sR \sin sc\tau \frac{ds}{s}$$

Therefore we can write instead of (12) in the case of *bodily-charge*:

$$\varphi = \frac{3\varepsilon c}{2\pi^2 a}\int_0^\infty \frac{d\tau}{R}\int_0^\infty \frac{\sin sa - sa\cos sa}{(sa)^2} \sin sR \sin sc\tau \frac{ds}{s} . \quad . \quad . \qquad (18)$$

It may be remarked, that in my first paper the foregoing equations (17) and (18) appear as primary and the equations (10) and (14) are deducted from them by performing the integration with respect to s.

Moreover it is probable, that the quantities λ and $\varkappa$ may be replaced in several other ways by a uniform analytical expression.

Almost the same formulae stand for the vectorpotential, if the motion is free from rotations. Our deduction proves immediately, that it is only necessary, to multiply the integrand by $\frac{\mathfrak{v}_{t-\tau}}{c}$, $\mathfrak{v}_{t-\tau}$ meaning the value of the velocity $\mathfrak{v}$ at the time $t-\tau$. If on the contrary the motion is accompanied by rotations, you must add to the part due to translation another part due to rotation, where the quantities λ, $\varkappa$ are to be replaced by some quantities λ', $\varkappa'$ rather more complicated. The expressions for this are derived in my first paper and may be derived more easily by the present method.

§ 4. *The field of stationary motion especially with a velocity exceeding that of light.*

In my first paper I have applied the foregoing representation of the field in order to derive the well known approximate formulae of LIÉNARD and WIECHERT for the field at a great distance of an electron moved anyhow. It strikes us in these formulae, that the cases of velocities smaller or greater than that of light seem to differ from each other only by the sign, whereas in reality a fundamental physical difference must exist between the two cases: If the velocity is less than that of light, the whole surroundings of the electron is seized by the effects of the moving electron, if the velocity exceeds that of light, only those points are seized which lie in the "shadow of motion" of the electron so to speak. This incongruency is cleared, if the roots of equation (11) are discussed, what was not sufficiently pointed out in my first paper.

In general we note this (details depend on the special character of the motion). If veiocity is less than that of light, each of the equations (11) always has a positive root; if the velocity exceeds that of light, imaginary and negative roots are possible as well; they appear in all those points which are situated so to speak in the front of the electron; positive roots exist only for those points that lie in the shadow of motion; and here for each of the equations (11) even a pair of positive roots exist. Only for a narrow region bordering on the shadow of motion and about equal to the diameter of the electron we have not two but only one pair of positive roots. It follows: The approximate formulae mentioned before, which I have derived formerly supposing two roots τ_1 τ_2 to exist, hold good absolutely if the velocity is less than that of light; in the opposite case they are to be replaced by 0 out of the shadow of motion, and they are to be completed by a member similarly formed within the shadow of motion.

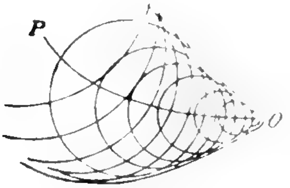

Fig. 2.

Fig. 2 explains, what shadow of motion means. Here the momentary position O of the electron and its preceding path OP is marked. Round every point P of the path the sphere may be constructed with the radius $c\tau$, where τ denotes the time, in which the electron gets from that point to O. The envelope of these spheres defines the shadow of motion. Evidently it is the smaller, the more the velocity of the electron exceeds that of light. The region bordering on the shadow of motion, which was mentioned before, is also sketched in the figure as a narrow strip.

The foregoing general remarks are corroborated by closer discussion of *stationary motion* with constant velocity v. The field of stationary motion can be found exactly by a singular process of reciprocation [1] if $v < c$. What happens if $v > c$, has been explained by DES COUDRES following the steps of HEAVISIDE. Compared to DES COUDRES' treatment the following is hardly new. It may merely be pointed out, that the infiniteness of the HEAVISIDE-DES COUDRES [2] solution near the borders of the shadow of motion is not real, the formula no longer holding good in this region. The infiniteness mentioned just now results from DES COUDRES treating the case of a charge concentrated in one point, which is passing to the limit of vanishing dimensions of the electron. We shall adopt in general this simplification and thereby dispense with a rigorous solution, but at the same time we shall point out, that this simplification is not legitimate near the border of the shadow. We suppose bodily charge, as it will be shown later, that in case of surface charge any motion with $v > c$ is actually impossible.

Let the stationary motion be directed towards the positive axis of x. The system of coordinates has its origin O at the position of the centre of the electron at the time t. Let the coordinates of the point in question be x, y, z, let its distance from O be $r = \sqrt{x^2 + y^2 + z^2}$, so that r now has a different meaning from that in § 2 and § 3. At the time $t - \tau$ the centre of the electron was in the point $- v\tau$ of the axis of x; the distance of the point in question from this point is

$$R = \sqrt{(x + v\tau)^2 + y^2 + z^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The conditions, under which the triangle $(R, a, c\tau)$ is just possible, are given by the equations (11)

$$R_1 - a = c\tau_1 \quad , \quad R_2 + a = c\tau_2 , \quad . \quad . \quad . \quad . \quad (11)$$

in the case of an exterior point (more correctly $R > a$); we can combine (11) into

$$(x + v\tau)^2 + y^2 + z^2 = (c\tau \pm a)^2$$

or

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[1] V. the summary of H. A. LORENTZ in "Encyklopädie der mathematischen Wissenschaften". Bd. V. Art. 14. Nr. 11.

[2] Zur Theorie des Kraftfeldes electrischer Ladungen. LORENTZ-Jubelband, p. 652. Haag 1900.

$$(c^2 - v^2)\,\tau^2 - 2\,(v\,x \mp a\,c)\,\tau + a^2 - r^2 = 0 \quad . \quad . \quad . \quad (20)$$

the upper sign relating to the roots τ_1, the lower one to the roots τ_2. The product of the two roots τ_1 or the two roots τ_2 is:

$$\frac{a^2 - r^2}{c^2 - v^2}.$$

As $r > a$ in a point of the exterior, this product is *negative*, if $c > v$, it is positive, if $c < v$. We conclude:

If the velocity is less than that of light, the two roots of our quadratic are real and have opposite signs. Each of the two equations therefore has *one available positive root.*

If the velocity exceeds that of light, the two roots may be conjugate-imaginaries; if they are real, they have equal signs, and therefore they may both be either positive or negative. *Each of the two equations has therefore either no roots or two available positive roots.*

We distinguish between real and imaginary roots by consulting the discriminant of our equation (20). The roots are imaginary if

$$(v\,x \mp ac)^2 < (r^2 - a^2)\,(v^2 - c^2),$$

for which we may also put

$$(c\,x \mp av)^2 < (y^2 + z^2)\,(v^2 - c^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

We introduce the abbreviations:

$$\beta = \frac{v}{c}\ , \qquad \xi = x \mp a\,\beta\ , \qquad \varrho^2 = y^2 + z^2$$

so that ϱ means the distance of the point in question from the direction of motion, ξ the distance of the same point, measured in the direction of motion, from two points P_1 P_2 (see fig. 3) of which the coordinates are $x = \pm\, a\,\beta$.

Replacing in (21) the sign $<$ by $=$, we get

$$\xi^2 = \varrho^2\,(\beta^2 - 1)\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

This defines a cone of revolution about the direction of motion, of which the apex lies in the point P_1 or P_2 according to the meaning of ξ and of which the generatrices are inclined towards the direction of motion in the angle $arctg\,(\beta^2 - 1)^{-\frac{1}{2}}$. For points in the interior of these cones, i. e. between the conical surface and the conical axis, the roots of (20) are real, for points in the exterior they are imaginary.

In case of the reality of roots the distinction between positive and negative values results from the sign of the coefficient of τ in equation (20).

Both the roots are positive if

$$\frac{vx \mp ac}{c^2 - v^2} > 0, \quad \text{i. e.} \quad x < \pm \frac{a}{\beta};$$

they are negative, if

$$\frac{vx \mp ac}{c^2 - v^2} < 0, \quad \text{i. e.} \quad x > \pm \frac{a}{\beta}.$$

Evidently the planes $x = \pm \frac{a}{\beta}$ are polar planes of the points P_1 P_2 with respect to the surface of the electron. We distinguish a back and a front of these planes judging from the direction of motion.

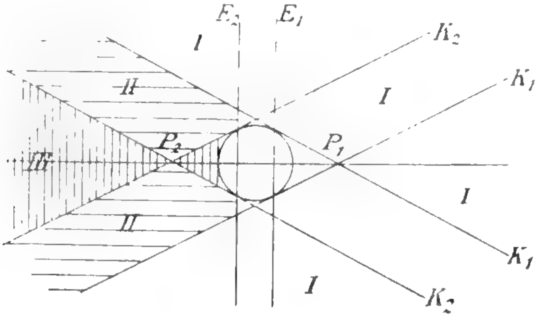

Fig. 3.

Fig. 3 gives the result of our discussion. Here the points P_1, P_2 and their polar planes are constructed. From P_1, P_2 the cones K_1, K_2 diverge, which touch the surface of the electron at its intersection with E_1 E_2; they appear in the figure as two pairs of straight lines. We call such points *region I*, for which *both* pairs of roots are either *imaginary* or *negative*. *Region II* consists of such points, for which only *one* pair of roots (τ_1) is *positive*. Finally *region III* is that, in which *both* pairs of roots are positive. The regions I, II and III are distinguished in the figure by different shading. We need not concern ourselves with the interior, where the field acts differently.

We now proceed to the computation of the scalar potential.

If $v < c$, we get on account of the existence of a positive root τ_1 and τ_2 (see (13) and (14)):

$$4\pi\varphi = \frac{3\varepsilon c}{4a} \int_{\tau_1}^{\tau_2} \left(1 - \left(\frac{R - c\tau}{a}\right)^2\right) \frac{d\tau}{R} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Here we introduce the variable

$$u = \frac{c\tau - R}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

From (11) we have

for $\tau = \tau_1 \ldots u = -1$, for $\tau = \tau_2 \ldots u = +1$;

Further according to (19) and (24)

$$a\,du = \left(c - \frac{\partial R}{\partial \tau}\right) d\tau = \left(c - v\,\frac{x + v\tau}{R}\right) d\tau\,,$$

$$\frac{c\,d\tau}{aR} = \frac{du}{R - \beta(x + v\tau)}\,.$$

or, if we put in the value of R from (24)

$$\frac{c\,d\tau}{aR} = \frac{du}{c\tau(1-\beta^2) - au - \beta x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

On the right hand we must here express τ by u. According to (24) we have between τ and u the quadratic:

$$(a\,u - c\,\tau)^2 = R^2 = (x + v\,\tau)^2 + y^2 + z^2\,.$$

If we solve it with respect to $c\,\tau$, we get

$$(1 - \beta^2)\,(c\,\tau)^2 - 2\,(a\,u + \beta\,x)\,c\,\tau = r^2 - a^2\,u^2,$$

$$c\,\tau = \frac{a\,u + \beta\,x \pm \sqrt{(a\,u + \beta\,x)^2 + (1 - \beta^2)\,(r^2 - a^2\,u^2)}}{1 - \beta^2}\,. \quad (26)$$

What was proved before for the limits $\tau_1\,\tau_2$ of the interval of integration viz. that only one of the two possible values is positive, holds as well for the values of τ in the interior of the interval.

The one positive value is obviously given by the positive sign of the root in (26). Omitting therefore the negative sign we conclude from (26):

$$c\,\tau\,(1 - \beta^2) - a\,u - \beta\,x = +\sqrt{(a\,u + \beta\,x)^2 + (1 - \beta^2)\,(r^2 - a^2u^2)} =$$
$$+\sqrt{(x + a\,u\,\beta)^2 + (1 - \beta^2)\,(y^2 + z^2)} \quad (27)$$

This happens to be the denominator occurring on the right of (25). Instead of (25) and (21) we therefore write:

$$\frac{c\,d\,\tau}{a\,R} = \frac{d\,u}{\sqrt{(x + a\,u\,\beta)^2 + (1 - \beta^2)\,(y^2 + z^2)}} \quad . \quad . \quad . \quad (28)$$

$$4\,\pi\,\varphi = \frac{3\,\varepsilon}{4} \int_{-1}^{+1} \frac{(1 - u^2)\;d\,u}{\sqrt{(x + a\,u\,\beta)^2 + (1 - \beta^2)\,(y^2 + z^2)}}\,. \quad . \quad (29)$$

This is the rigorous expression of the potential. The integration leads to elementary functions, but becomes rather troublesome. So we content ourselves with an approximation putting $a = 0$. Then the root in (29) becomes independent of u and we get:

$$4\pi\varphi = \frac{\varepsilon}{\sqrt{x^2+(1-\beta^2)(y^2+z^2)}}\,\frac{3}{4}\int\limits_{-1}^{+1}(1-u^2)\,du = \frac{\varepsilon}{\sqrt{x^2+(1-\beta^2)(y^2+z^2)}} \qquad (30)$$

So the equipotential surfaces are *oblate ellipsoids of revolution* about the direction of motion.

If $v > c$, we have to distinguish, whether the point in question lies in region I, II or III.

III). In this case there are two positive roots τ_1 and two positive roots τ_2. We distinguish them as τ_1', τ_1'', τ_2', τ_2'' and easily see that they arrange themselves according to their magnitude as follows:

$$\tau_1', \ \tau_2', \ \tau_2'', \ \tau_1''.$$

Indeed if we imagine a diagram in which for the abscissa $c\tau$ the curves $y = R - a$, $y = R + a$ and the straight line $y = c\tau$ are drawn, the latter intersects the former curves in four points, viz. firstly, beginning from O, the curve $y = R - a$, then the curve $y = R + a$, then the curve $y = R + a$ for a second time, lastly the curve $y = R - a$ for a second time. These four points belong to the values τ_1', τ_2', τ_2'', τ_1'', before mentioned. Moreover the diagram shows immediately, that the triangle $(R, a, c\tau)$ is possible only for those values of τ, for which either $\tau_1' < \tau < \tau_2'$ or $\tau_2'' < \tau < \tau_1''$. On this account we obtain from (13) and (14):

$$4\pi\varphi = \frac{3\varepsilon c}{4a}\int\limits_{\tau_1'}^{\tau_2'}\left(1-\left(\frac{R-c\tau}{a}\right)^2\right)\frac{d\tau}{R} + \frac{3\varepsilon c}{4a}\int\limits_{\tau_2''}^{\tau_1''}\left(1-\left(\frac{R-c\tau}{a}\right)^2\right)\frac{d\tau}{R}\ . \qquad (31)$$

We introduce by (24) the variable u.

It is to be noticed in expression (26), giving τ by u, that the denominator $1-\beta^2$ is negative as well as the term $a\,u + \beta x$ in the numerator, the latter being so because we are in region III. From this follows, that the negative sign of the root in (26) belongs to the interval of the larger values of τ $(\tau_2'' < \tau < \tau_1'')$, the positive sign to that of the smaller ones $(\tau_1' < \tau < \tau_2')$. Accordingly we have to put in the second integral of equation (31), which is extended between the two largest roots τ_2'' and τ_1'':

$$\frac{c\,d\tau}{a\,R} = -\frac{du}{\sqrt{(x + a u \beta)^2 + (1-\beta^2)(y^2+z^2)}}\,,$$

whereas we have to use in the first integral the former equation (28). It follows that

$$4\pi\varphi = \frac{3\varepsilon}{4}\int\limits_{-1}^{+1}\frac{(1-u^2)\,du}{\sqrt{(x+au\beta)^2+(1-\beta^2)(y^2+z^2)}}$$

$$-\frac{3\varepsilon}{4}\int\limits_{+1}^{-1}\frac{(1-u^2)\,du}{\sqrt{(x+au\beta)^2+(1-\beta^2)(y^2+z^2)}}, \quad . \quad . \quad . \quad (32)$$

As the two integrals equal each other, we get the following rigorous expression:

$$4\pi\varphi = \frac{3\varepsilon}{2}\int\limits_{-1}^{+1}\frac{(1-u^2)\,du}{\sqrt{(x+au\beta)^2+(1-\beta^2)(y^2+z^2)}} \quad . \quad . \quad (33)$$

We dispense with the evaluation of the integral, which is likewise possible in an elementary way as in the case $r < c$, and we put $a = 0$. Then

$$4\pi\varphi = \frac{2\varepsilon}{\sqrt{x^2+(1-\beta^2)(y^2+z^2)}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

The equipotential surfaces are now hyperboloids of revolution about the direction of motion with two shells. Yet only one of these two shells concerns us as lying in region III.

Region III is bordered by the cone K_2; in its points we have according to (22)

$$(x+a\beta)^2 = (\beta^2-1)(y^2+z^2).$$

If we substitute in (34) and write $x = -|x|$ on account of the negative sign of x in region III, we get by neglecting a^2:

$$4\pi\varphi = \frac{2\varepsilon}{\sqrt{2a\beta|x|}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

This value is large of a higher order than those in the interior of III, because it contains $\sqrt{a}$ in the denominator, but it is nevertheless finite. Yet you can doubt its legitimacy, as we already omitted members of the range a in passing from (33) to (34). However you confirm the value (35), if you calculate the integral (33) rigorously, which does not give much trouble for the points of the cone K_2. For if you expand it in powers of $\frac{a\beta}{|x|}$ and restrict yourself to the lowest power, the rigorous value becomes:

$$4\pi\varphi = \frac{8}{5}\,\frac{\varepsilon}{\sqrt{a\beta|x|}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

The number $\frac{8}{5} = 1{,}6$ here takes the place of $\sqrt{2} = 1{,}4\ldots$ in equation (35).

I. If the point in question is situated in region I, there are no positive roots τ_1 and τ_2; here therefore stands:

$$\varphi = 0.$$

II. In region II, where only the pair τ_1', τ_1'' is to be considered, we have according to (13) and (14) in the first instance the following expression:

$$4\pi\varphi = \frac{3\varepsilon c}{4a}\int\limits_{\tau_1'}^{\tau_1''}\left(1-\left(\frac{R-c\tau}{a}\right)^2\right)\frac{d\tau}{R}. \quad . \quad . \quad . \quad . \quad (37)$$

While τ goes from τ_1' to τ_1'', our variable u passes from -1 to a certain value $u_0 < 1$ and returns to -1.

At the turning-point u_0, for which $\frac{du}{d\tau} = 0$, the square root on the right of (27) vanishes also (see (25) and (27)) and changes its sign. So the integral, extended forwards from -1 to u_0, equals the integral, extended backwards from u_0 to -1, and we get instead of (37):

$$4\pi\varphi = \frac{3\varepsilon}{2}\int\limits_{-1}^{u_0}\frac{(1-u^2)du}{\sqrt{(x+au_1\beta)^2+(1-\beta^2)(y^2+z^2)}} \quad . \quad . \quad . \quad (38)$$

Here it would no longer be permitted to put $a = 0$, as, by neglecting it, the denominator would become very small in the whole of region II and the value of the integral would become very inexact. We content ourselves with stating, that u_0 grows continually from -1 to $+1$ and therefore φ increases continually from 0 to the high value given by (35), as we traverse the region II from its front border, the cone K_1, to its back border, the cone K_2. It is hardly worth while computing the manner of this increase in detail, as the whole of the region II (the so called border of shadow) is of the same thickness as the diameter of the electron.

§ 5. *The force exerted on the electron by its own field, especially if the velocity is stationary and exceeds that of light.*

Whilst in general only such parts of the field would be of interest, that are at a great distance from the electron, viz. a distance great in comparison with the radius of the electron, we need just the field in the interior or at the surface of the electron in order to calculate the force caused by its motion. For this purpose the approximations, mentioned in the beginning of the last §, are not sufficient and we have to resort to the rigorous formulae of § 3. Using the latter always in the form of equations (17) und (18), I have succeeded in my second paper in computing the force exerted on the electron by its own field for any given translation, excluding simultaneous rotations; performing the integrations extended over the charge of the electron I merely had to use GREEN's theorem once more.

I here put these formulae less explicitly; whilst the final formulae there only contain one integration with respect to the former time τ, I shall here refrain from performing the integration with respect to s as well as that with respect to τ. This means a decided simplification of the following calculation, at least in the simplest case of stationary motion.

Let $\mathfrak{F}$ be the required force for the moment t, $\mathfrak{T}$ the chord of the path, traversed by the centre of the electron during the interval from $t-\tau$ to t, T the length of this chord; in the case of surface charge we have according to the equation (48) and (50) of my second paper:

$$-\frac{2\pi^2 a^2 c}{\varepsilon^2}\mathfrak{F} = \underset{r=a}{Lim}\int\limits_0^\infty \left\{c^2 - (\mathfrak{v}_t \mathfrak{v}_{t-\tau})\right\}\frac{\mathfrak{T}}{T}\,d\tau \int\limits_0^\infty \frac{\partial}{\partial T}\frac{\sin sT}{T}\sin sr \sin as \sin cs\tau \frac{ds}{s^2} +$$

$$+ \underset{r=a}{Lim}\frac{\partial}{\partial t}\int\limits_0^\infty \mathfrak{v}_{t-\tau}\,d\tau \int\limits_0^\infty \frac{\sin sT}{T}\sin sr \sin as \sin cs\tau \frac{ds}{s^2}. \quad . \quad . \quad (39)$$

in the case of bodily charge according to equation (48) and (50′)

$$-\frac{2\pi^2 a^2 c}{9\varepsilon^2}\mathfrak{F} = \int\limits_0^\infty \left\{c^2 - (\mathfrak{v}_t \mathfrak{v}_{t-\tau})\right\}\frac{\mathfrak{T}}{T}\,d\tau \int\limits_0^\infty \frac{\partial}{\partial T}\frac{\sin sT}{T}\left(\frac{\sin as - as\cos as}{a^2 s^2}\right)^2 \sin cs\tau \frac{ds}{s^2} +$$

$$+ \frac{\partial}{\partial t}\int\limits_0^\infty \mathfrak{v}_{t-\tau}\,d\tau \int\limits_0^\infty \frac{\sin sT}{T}\left(\frac{\sin as - as\cos as}{a^2 s^2}\right)^2 \sin cs\tau \frac{ds}{s^2} \quad . \quad . \quad (40)$$

We are not allowed to pass to the limit $r = a$ in (39) before performing the integration because the electrical intensity behaves discontinuously at the surface of the electron, where charge is concentrated. The force $\mathfrak{F}$ is determined by the foregoing state of motion, that is by the path $\mathfrak{T}$ and the velocity $\mathfrak{v}_{t-\tau}$. It would seem from the foregoing formulae, as if all the former states, from $r = 0$ to $\tau = \infty$, contributed to the value of $\mathfrak{F}$; in reality only the states during a short interval preceding the time t come into account, as is seen from the more explicit value of $\mathfrak{F}$ given in the equations (54) and (54′) of my second paper.

If the motion is rectilineal, $\mathfrak{E}$ and $\mathfrak{v}$ and therefore $\mathfrak{F}$ have the same direction. In this case we may replace $\frac{\mathfrak{E}}{T}$ by 1, $\mathfrak{v}_t$ by v_t, dispensing with expressing the direction of $\mathfrak{F}$. Moreover if the motion is stationary, we get:

$$v_t = v_{t-\tau} = v \quad , \quad T = v\tau \quad ,$$

at the same time the path and the velocity will become independent of t and the differential coefficients with respect to t will disappear in (39) and (40). By taking out the constant factors and expressing the differentiation with respect to T by that with respect to τ and reversing the order of integration we get:

$$-\frac{2\pi^2 a^2 c}{\varepsilon^2}\mathfrak{F} = \frac{c^2-v^2}{v^2}\,\underset{r=a}{Lim}\int_0^\infty \frac{ds}{s^2}\sin sr \sin as \int_0^\infty \frac{\partial}{\partial\tau}\frac{\sin vs\tau}{\tau}\sin cs\tau\, d\tau, \quad . \; (41)$$

$$-\frac{2\pi^2 a^2 c}{9\varepsilon^2}\mathfrak{F} = \frac{c^2-v^2}{v^2}\int_0^\infty \frac{ds}{s^2}\left(\frac{\sin as - as\cos as}{a^2 s^2}\right)^2 \int_0^\infty \frac{\partial}{\partial\tau}\frac{\sin vs\tau}{\tau}\sin cs\tau\, d\tau \; . \; (42)$$

Integrating by parts:

$$\int_0^\infty \frac{\partial}{\partial\tau}\frac{\sin vs\tau}{\tau}\sin cs\tau\, d\tau = -\,cs\int_0^\infty \sin vs\tau \cos cs\tau \frac{d\tau}{\tau} =$$

$$= -\frac{cs}{2}\left\{\int_0^\infty \sin\,(v+c)\,s\tau\,\frac{d\tau}{\tau} + \int_0^\infty \sin\,(v-c)\,s\tau\,\frac{d\tau}{\tau}\right\}.$$

Of the two last integrals the first always equals $\frac{\pi}{2}$, the second equals $-\frac{\pi}{2}$ or $+\frac{\pi}{2}$, according as $v < c$ or $v > c$ (see equation (15) in § 3). We therefore have:

$$\int_0^\infty \frac{\partial}{\partial\tau}\frac{\sin vs\tau}{\tau}\sin cs\tau\, d\tau = \begin{cases} 0 \ldots\ldots\ldots v < c \\ -\frac{cs\pi}{2} \ldots v > c \end{cases} \quad . \quad . \quad . \quad . \quad (43)$$

The result of the equations (41)—(43) consequently is: *In case of stationary motion with a velocity less than that of light we have* $\mathfrak{F} = 0$; *this motion is a free possible movement of the electron.*

Further the equations (42) and (43) give, in the case of bodily charge if $v > c$:

$$-\frac{4\pi a^2}{9\varepsilon^2}\mathfrak{F} = \frac{v^2-c^2}{v^2}\int_0^\infty \left(\frac{\sin as - as\cos as}{a^2 s^2}\right)^2 \frac{ds}{s}\,.$$

The value of the integral, still to be calculated, is a mere number, namely $\frac{1}{4}$, as one sees, on introducing the new variable $p = as$ and transforming as follows (note, that the expressions taken in [ ] disappear):

$$\int_0^\infty (\sin p - p\cos p)^2 \frac{dp}{p^5} = -\left[\frac{(\sin p - p\cos p)^2}{4p^4}\right]_0^\infty + \frac{1}{2}\int_0^\infty \sin p\,(\sin p - p\cos p)\frac{dp}{p^3} =$$

$$-\left[\frac{\sin p\,(\sin p - p\cos p)}{4p^2}\right]_0^\infty + \frac{1}{4}\int_0^\infty (\cos p\,(\sin p - p\cos p) + p\sin^2 p)\frac{dp}{p^2} =$$

$$\frac{1}{4}\int_0^\infty \left(\frac{1}{2}\frac{\sin 2p}{p^2} - \frac{p\cos 2p}{p^2}\right)dp = -\frac{1}{8}\int_0^\infty \frac{d}{dp}\frac{\sin 2p}{p}\,dp = \frac{1}{8}\left(\frac{\sin 2p}{p}\right)_{p=0} = \frac{1}{4}\,.$$

Thus the force exerted by its own field on an electron bodily charged and moving with a velocity exceeding that of light becomes:

$$4\pi\mathfrak{F} = -\frac{9}{4}\left(1 - \frac{c^2}{v^2}\right)\frac{\varepsilon^2}{a^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

This force acts contrary to the movement. The opposite force is to be exerted in order to maintain the motion and to balance the loss of energy caused by radiation. The force is absolutely finite and and remains so for $v = \infty$. For $v = c$ we have $\mathfrak{F} = 0$, a value which is connected continually to the case of velocity less than that of light; for $v = \infty$ we get

$$\mathfrak{F} = -\frac{1}{4\pi}\frac{9}{4}\frac{\varepsilon^2}{a^2},$$

this equals the attraction of two point charges $\frac{3\varepsilon}{2}$ in the distance a, according to COULOMB's LAW.

Although the stationary motion with velocity exceeding that of light is no free possible movement of the electron, yet this motion is not impossible from a physical point of view as requiring (even if the velocity is infinite) *in every moment only a finite expense of force and also for every finite path only a finite expense of work.*

We finish by studying the motion of a *surface charge* with a *velocity exceeding that of light*, returning to equations (41) and (43). These give us with $v > c$:

$$-\frac{4\pi a^2}{\varepsilon^2}\mathfrak{F} = \frac{v^2 - c^2}{v^2}\lim_{r=a}\int_0^\infty \sin rs\,\sin as\,\frac{ds}{s}. \quad . \quad . \quad . \quad (45)$$

In order to evaluate this integral we divide it into one part from 0 to a quantity ε to be conveniently chosen and another from ε to ∞. In the second part we express the product of the sines by the difference of the cosines:

$$\int_0^\infty sin\, rs\, sin\, as \frac{ds}{s} = \int_0^\varepsilon sin\, rs\, sin\, as \frac{ds}{s} + \frac{1}{2}\int_\varepsilon^\infty cos\,(r-a)\,s \frac{ds}{s} - \frac{1}{2}\int_\varepsilon^\infty cos\,(r+a)\,s \frac{ds}{s}.$$

In the second and third integral we introduce the new variable of integration $p=(r-a)\,s$ and $p=(r+a)\,s$ respectively. Then the difference of these two integrals becomes:

$$\frac{1}{2}\int_{\varepsilon(r-a)}^\infty cos\, p \frac{dp}{p} - \frac{1}{2}\int_{\varepsilon(r+a)}^\infty cos\, p \frac{dp}{p} = \frac{1}{2}\int_{\varepsilon(r-a)}^{\varepsilon(r+a)} cos\, p \frac{dp}{p} = \frac{1}{2}\int_{\varepsilon(r-a)}^{\varepsilon(r+a)} \frac{dp}{p} +$$

$$+\frac{1}{2}\int_{\varepsilon(r-a)}^{\varepsilon(r+a)} \frac{cos\, p-1}{p}\, dp = \frac{1}{2}\, log\, \frac{r+a}{r-a} - \int_{\varepsilon(r-a)}^{\varepsilon(r+a)} sin^2 \frac{p}{2} \frac{dp}{p},$$

or, if we sum up:

$$\int_0^\infty sin\, rs\, sin\, as \frac{ds}{s} = \int_0^\varepsilon sin\, rs\, sin\, as \frac{ds}{s} + \frac{1}{2}\, log\, \frac{r+a}{r-a} - \int_{\varepsilon(r-a)}^{\varepsilon(r+a)} sin^2 \frac{p}{2} \frac{dp}{p}.$$

Now if we choose ε sufficiently small, the first and second integral of the right-hand side may be made as small as we like. Namely in both cases we have to integrate an entirely finite function within two limits indefinitely close to each other. Therefore for any given r and a $(r>a)$ there results rigorously:

$$\int_0^\infty sin\, rs\, sin\, as \frac{ds}{s} = \frac{1}{2}\, log\, \frac{r+a}{r-a}, \quad \ldots\ldots \quad (46)$$

Making r converge to a, our integral becomes positively logarithmic infinite. It follows, that the force necessary to act on the electron in order to maintain its uniform motion also becomes infinite.

The stationary motion of an electron, charged uniformly over its surface, with a velocity exceeding that of light, is actually impossible; it would require an infinitely great expense of force and energy.

Meteorology. — *Oscillations of the solar activity and the climate* by Dr. C. Easton. (Communicated by Dr. C. H. Wind).

The parallelism between the oscillations in the "solar activity" and the variations of the magnetic elements of the earth is certain, and a similar parallelism is suspected for some other terrestrial phenomena. The meteorological elements, however, have always seemed to be subject to so many different perturbations, as to obscure the corresponding parallelism, which most probably does exist in this case also. Brückner has considered this point in his well-known investigations on oscillations of climate [1]), but he only reached a negative result. It is true that Köppen and Nordmann [2]), restricting themselves to tropical countries, have established a parallelism with the 11-year period of the solar spots for the period from 1840 to 1900, and Köppen's curve also shows this parallelism tolerably well for the southern temperate zone, while for the northern temperate zone Langley's bolometric observations [3]) give us a right to expect much from his method for the future. For the non-tropical zones on the whole, however, (and therefore also for the earth as a whole) the disturbing influence of terrestrial causes would seem to be such that the oscillations produced by a cosmical cause are entirely obscured.

The reason of this is apparent. The direct influence of the solar radiation can only be visible in the *general* temperature-curve for regions where the difference between the seasons is neither very large, nor their change very irregular. This reason is already sufficient to explain why Brückner's so-called "temperature-curve for the whole earth" [on which the observations in the northern temperate zone have a preponderating influence] differs so widely from the curve representing Rudolf Wolf's "Relativzahlen" for the sunspots. It appeared to me therefore that this question must be considered from a different point of view.

Dr. W. J. S. Lockyer has recently published an investigation [4]) in which he reaches the result that Brückner's period of 35 years in the climate is also found in the irregularities of the 11-year period of solar activity. He tries to show this by comparing the variable quantity $M—m$ (which represents the interval of time between a minimum of sunspots and the following maximum), with Brückner's

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[1]) E. Brückner. Klimaschwankungen seit 1700., Geogr. Abh. IV, 2 (1890).

[2]) W. Köppen. Zeits. Oesterr. Ges. f. Met. VIII, XV, XVI. — Ch. Nordmann. Comptes rendus T. 136, p. 1047 (1903).

[3]) S. P. Langley. Astroph. Journal XIX, p. 305 (1904).

[4]) W. J. S. Lockyer. Proc. Roy. Society, LXVIII (1901).

curve for the rainfall. This meteorological element appeared to me to be a very unsuitable one for comparison on account of its exceedingly large local variations, it might however be of some interest to compare BRÜCKNER's curve for severe winters. Further the very few oscillations recorded by LOCKYER proved very little, in my opinion, unless the previous oscillations of the solar activity, though less accurately recorded, agreed at least approximately with the result.

An investigation in this direction led me to a negative result with reference to the confirmation of BRÜCKNER's climate-period, which was suspected by LOCKYER. Another very surprising result appeared however, viz. a parallelism (though imperfect) between the $M—m$ curve of solar activity mentioned above and the curve of the frequency of severe winters.

I do not give these curves here, since they are of no direct further use. This parallelism suggested however two important conclusions, *viz.* 1st that the $M—m$ curve [or preferably the deviations of the maxima and minima of solar activity from their normal positions ás determined by NEWCOMB [1])] could be of great value along with the frequency-curve of sunspots (Relativzahlen), while it appeared at the same time that these deviations are real, at least for the greater part, and 2nd that in the records about severe winters we possess a rough but important material from which we can derive a judgment concerning the general course of the weather in the past.

The parallelism which I found is in this sense that the more severe cold corresponds with the larger number of sunspots (i.e. with the greater solar activity, to retain this term). This does not agree with Sir NORMAN LOCKYER's views. It is in accordance however with the view, which is now generally accepted, that the spots do not represent excessively heated areas. It is also well in keeping with the result of an experiment by SAVÉLIËF [2]), and with the conclusions arrived at by Prof. JULIUS in his solar theory [3]).

That the inequalities in the eleven year solar period cannot be attributed in the main to errors of observation had already been indicated by the investigations of FRITZ and LOOMIS on the aurora [4]) and of HALM on corrections to the inclination of the ecliptic, on the variations of latitude, etc. [5]), which show corresponding inequalities.

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[1]) S. NEWCOMB. Astrophys. Journal, XIII, 2 (1901).

[2]) SAVÉLIËF. Comptes rendus T. 118, (1894).

[3]) W. H. JULIUS. Archives néerlandaises, Série II, Ts. VII, VIII, IX.

[4]) H. FRITZ. Das Polarlicht. Leipzig 1881; — E. LOOMIS, quoted by HALM, A. N. 3649.

[5]) J. HALM. Astron. Nachrichten 3619, 3649; Nature Vol. 62, 1610.

The records concerning severe winters naturally are a very rough material, though the remark has already been made that they are far more reliable than *e.g.* records about hot summers, the exceptional formation of ice being an unmistakable criterion. The data must however be carefully and critically arranged and compared. This has already been done by Prof. W. **Köppen** in his well known investigations on the periodicity of severe winters. The data as given by **Köppen** have therefore been used instead of those of **Brückner**, which are simply taken from **Pilgram**.

On comparing **Köppen**'s list with **Brückner**'s curve I was struck by an indication of periodicity in very long periods, different however from what **Köppen** sought (*viz.* the regular occurrence of severe winters in determined, equidistant years), and also not consisting of regular oscillations like those suspected by **Brückner**, but of a recurrence of the *general character of the weather* in periods of about 180 years. The distribution of the winters within each of these periods is the same, *viz.* very many severe winters in the first 60 or 70 years of the period (e.g. the 60 years following 1220, 1400 or 1580), very few in the next 20 years, many in the following 20, few and irregularly distributed winters in the remaining part of the period.

In accordance with what was said above this phenomenon, if it is real, must be attributed to a secular oscillation in the solar activity, presenting itself to us in the form of systematic variations of the eleven-year period. For this reason I took as the basis of my investigation a period of 16 × 11.13 = about 178 years, 11.13 years being the normal period according to **Newcomb**. The available material covers a period of more than a thousand years, *viz.* from the middle of the ninth century to our own time, including the additional data procured by **Köppen** himself. The reality of this periodicity was made very probable by a statistical investigation in which the year 848 was taken as the first of a period of 178 years. We denote the influence of a "normally severe" winter on the climate by a "cold-coefficient" unity. To an exceptionally severe winter ("winter of first class" of **Köppen**) the coefficient 3 is assigned, and 2 to winters of intermediate severity. It then appears — taking all the periods since 848 together — that the four sub-periods of 67, 22, 22 and 67 years have total coefficients of 114, 15, 39 and 62 respectively, *i.e.* 1.70, 0.68, 1.77 and 0.93 respectively for one year. These oscillations are of such amplitude that the proportional number of severe winters in these cold periods of 67 years (*e.g.* from 1561 to 1628 is nearly twice that of the succeeding relatively mild periods of 22 years, the ratio in the case of exceptionally severe winters being seven to one. The mild 22-year periods have, up to the present time, contained altogether 12 severe winters, only one of which was exceptionally severe.

It is now important to ascertain the character of this oscillation. On the one hand there seemed to be some indication of a period consisting of two consecutive 178-year periods (i. e. of 356 years), but even our material does not cover a sufficiently long interval of time to allow any reliable result in this direction to be derived. On the other hand the rise and fall of the curve in the middle of the 178 year period is the most characteristic feature, and points to the possibility of dividing the period into two. In fact the period can be divided into two halves of 89 years, which show a remarkable curve, somewhat different on the two sides (see diagram fig. II). Perhaps this period of 89 years may be further divided into two periods of 44.5 years. The depression in the middle of the 89-years period is but indifferently indicated for all the severe winters together, but becomes more marked, if we take into account only the exceptionally severe winters. In the following list (Table I) the twelve 89-year periods which are available since 848, have been entered, each divided into intervals of 11 years, corresponding to the computed normal maxima of solar activity (according to NEWCOMB). The last interval of each period contains 12 years, which however has only

TABLE I.

Distribution of severe winters in periods of 89 years (848—1916)
(divided into intervals of 11.1 years).

I	848	—	4	4	1	1	1	—	1
II	937	—	—	—	3	1	1	—	1
III	1026	—	4	—	1	5	—	—	—
IV	1115	4	4	1	1	—	3	—	—
V	1204	1	4	6	—	1	1	2	1
VI	1293	—	3	7	—	—	—	3	—
VII	1382	2	—	4	4	7	4	1	1
VIII	1471	—	4^5	1	2	1	1	2	1
IX	1561	8	3	2	6	4	5	1	1
X	1650	5	9	2	3	4	3	4	1
XI	1739	4	4	7	2	9	5	6	1
XII	1828	7	2	4	3	6	3	—	1 ?
		31	41^5	38	26	39	27	19	9 ?

an appreciable effect on the total of this interval. The totals of the *exceptionally* severe winters alone are: 7, 11, 6, 2, 10, 6, 3, 0. — In order to keep the division according to whole years I have dropped one year — the year 1560 — near a minimum of the period. The last interval of the last period being of course unknown, I have taken for this interval the mean of the last column, viz: 1, but even a much higher coefficient would not appreciably alter the general results.

The division of the period can certainly not be continued beyond a period of 4 × 11.13 years. In our material there is no indication of a regular alternation (at least not in the majority of the cases) of cold and mild periods of 22 years. There is even less evidence of a regularity in the succession of the 11-year-periods.

Taking a period of $44^{1}/_{2}$ years as a basis, we can express our results as follows:

There exist oscillations of climate with a periodicity of $44^{1}/_{2}$ years and multiples thereof, chiefly thus, that one period of 11.13 years contains less cold than the three preceding and the three following ones; that at intervals of 89 years there is one period with very little cold; that in two consecutive intervals of 178 years the last 5 or 6 periods of one of them are colder than the corresponding periods of the other interval. This oscillation of climate corresponds to an oscillation in the "solar activity", of a higher order than the well known eleven-year period.

The very doubtful difference between two consecutive 178-year periods, which was indicated above, would be in this sense that the greatest amplitude of the oscillations in one period occurs in the beginning of the period, and is displaced in the next towards the middle of the first 89-year sub-period. Nothing however can be ascertained on this point, and still less on the existence of still longer periods.

It seemed interesting to investigate whether the 11-year variation of the solar activity itself is shown by this material. For this purpose the distribution of the "cold-coefficients" over five phases of the eleven-year sunspot period was investigated, *viz.*: $m = 2$ years on both sides of the observed minimum, $M = 2$ years on both sides of the maximum, $ap =$ ascending phase, dp_1 and $dp_2 =$ two halves of the decreasing phase. The observed maxima and minima are taken in accordance with NEWCOMB (the deviations from R. WOLF's last list [1]) are of no importance). The unequal duration of the phases has, of course, been taken into account. The periods have been arranged in four groups, *A*, *B*, *C*, *D* in order of decreasing cold. We then find the following values of the frequency for one year. The values in parentheses are derived from those periods only for which the weights assigned by NEWCOMB (l.c. p. 7) to the determination of the maximum and minimum are together at least equal to 8.

TABLE II.

Distribution of cold winters over the phases of the 11-year sunspot period.
(Groups arranged in order of coldness).

	A	*B*	*C*	*D*
m	1.50 (1.67)	0.75 (0.75)	0.125 (0.125)	0.17 (0.17)
ap	1.13 (1.44)	1.13 (1.13)	0.60 (0.50)	0.32 (0.32)
M	1.08 (1.50)	1.25 (1.25)	0.33 (0.25)	0.25 (0.25)
dp_1	0.98 (1.09)	0.21 (0.21)	0.76 (0.65)	0.57 (0.57)
dp_2	1.06 (1.03)	0.48 (0.48)	0.36 (0.22)	0.24 (0.24)

For all the groups together, and also for the two coldest groups, we find a curve corresponding with the sunspot curve; for the two mild groups the cold-maximum seems to be displaced towards the descending phase. This phenomenon however does not necessarily depend on a really different distribution of the cold winters within the eleven-year periods, no more than the high value of the minimum in the coldest group. The reason probably is that the variations of temperature precede or follow those of solar activity by a certain interval of time.

This is apparent from a comparison of the temperature variations with the curve of the Relativzahlen for the sunspots. In the diagram fig. I, A is the latter curve according to R. WOLF, B is the second half of the temperature-curve the period being taken at 356 years, C is the temperature curve, if a period of 178 years is adopted, D is the last 178-year period alone [2]). In presenting these curves it is not my intention to contend that they agree with each other in details, — as is the case with the curves of the variations of magnetic elements and the sunspots. Such a parallelism could not be expected

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[1]) R. WOLF. Astron. Mittheilungen LXXXII (1893).

[2]) In drawing the curves *B*, *C* and *D* no other process of smoothing was applied than that given by the formula $b_s = \frac{a+2b+c}{4}$. The cold-coefficients have been taken for each year, only in the case of *D* for every two years on account of the small number.

The scale is: coefficient unity = 40 Relativzahlen.

a priori having regard to the material on which the curves are based. I only wish to show that the general character of the temperature curve is the same as that of the curve of solar activity. It is important to remark that the mean curve B is more similar to A than D. The deviations in *position* of the variations of temperature relatively to those of solar activity seem to be at least partly systematic. On comparing the temperature curve and the solar curve in the separate eleven-year periods we must however not only consider the greater or smaller number of spots, but also another phenomenon (which, it is true, is certainly connected with the abundance of spots) *viz.* the deviations of the minimum and maximum from the normal.

This phenomenon appears already vaguely in the correspondence of the values $M-m$ with the number of cold winters, to which I referred in the beginning of this paper. It is shown more clearly however in fig. III on the plate. For the last 17 periods of 11 years the dotted line represents the acceleration (—) or retardation (+) (expressed in years) of the observed solar minima and maxima, compared with the normal period of 11.13 years. The corresponding cold-coefficients are represented by the continuous line having four different ordinates corresponding to the four degrees (A, B, C, D) of cold. On the whole we find that to an acceleration of the solar period corresponds a more intense cold, and to a retardation a greater heat.

This rule also holds for the individual periods, provided the deviations are large. Combining this result with the distribution of cold-coefficients over the phases of one and the same eleven-year period which was mentioned just now, and with the larger oscillations found above, we find the following rule, which is presented as a hypothesis:

On the whole the oscillation of terrestrial temperature is accelerated relatively to the eleven-year variation of solar activity in the colder part of the larger period, and retarded in the hotter part. In cold 11-year periods the centre of gravity of cold is near the minimum of sunspots, and often there are very cold years preceding the minimum; in warm periods it is situated near the maximum or thereafter; in periods of intermediate character it falls between the minimum and the maximum.

For the individual cases we find that, in cases of considerable retardation or acceleration of the solar minimum or maximum, the centre of gravity of cold tends to be exceptionally retarded or accelerated. If the minimum of a sunspot period occurs very early and the subsequent maximum is retarded, the cold period also is largely extended.

Mathematics. — *The values of some definite integrals connected with Bessel functions*". By Dr. W. Kapteyn.

The integrals referred to are

$$P = \int_0^{2\pi} \frac{\cos(x \sin\theta) - \cos(x \sin\varphi)}{\cos\theta + \cos\varphi}\, d\theta,$$

$$Q = \int_0^{2\pi} \frac{\sin(x \sin\theta)\sin\theta - \sin(x \sin\varphi)\sin\varphi}{css\,\theta + \cos\varphi}\, d\theta,$$

$$R = \int_0^{2\pi} \frac{\cos(x \cos\theta) - css\,(x \cos\varphi)}{\cos\theta + \cos\varphi}\, d\theta,$$

$$S = \int_0^{2\pi} \frac{\sin(x \cos\theta)\cos\theta - \sin(x \cos\varphi)\cos\varphi}{\cos + \cos\varphi}\, d\theta.$$

If in these integrals we insert the wellknown equations

$$\cos(x \sin\theta) = I_0 + 2\, I_2 \cos 2\,\theta + 2\, I_4 \cos 4\,\theta + \ldots$$
$$\sin(x \sin\theta)\sin\theta = I_1\,(1 - \cos 2\,\theta) + I_3\,(\cos 2\,\theta - \cos 4\,\theta) + \ldots$$
$$\cos(x \cos\theta) = I_0 - 2\, I_2 \cos 2\,\theta + 2\, I_4 \cos 4\,\theta - \ldots$$
$$\sin(x \cos\theta)\cos\theta = I_1\,(1 + \cos 2\,\theta) - I_3\,(\cos 2\,\theta + \cos 4\,\theta) + \ldots$$

where I_p stands for the Bessel function $I_p(x)$ of order p, and if we write

$$A_{2n} = \int_0^{2\pi} \frac{\cos 2\,n\,\theta - \cos 2\,n\,\varphi}{\cos\theta + \cos\varphi}\, d\varphi$$

it is easy to find

$$P = I_0\, A_0 + 2\, I_2\, A_2 + 2\, I_4\, A_4 + \ldots$$
$$Q = I_1\, A_0 + (I_3 - I_1)\, A_2 + (I_5 - I_3)\, A_4 + \ldots$$
$$R = -\, 2\, I_2\, A_2 + 2\, I_4\, A_4 - 2\, I_6\, A_6 + \ldots$$
$$S = I_1\, A_2 - I_3\,(A_2 + A_4) + I_5\,(A_4 + A_6) - \ldots$$

In order to determine A_{2n} I notice that

$$(a) \qquad \sin\varphi\, \frac{\cos 2n\theta - \cos 2n\varphi}{\cos\theta + \cos\varphi} = -\sin 2n\varphi + 2 \sin(2n-1)\,\varphi \cos\theta -$$
$$- 2 \sin(2n-2)\,\varphi \cos 2\theta + \ldots$$
$$+ 2 \sin\varphi \cos(2n-1)\,\theta$$

This formula can be proved as follows :

If we multiply the 2nd member of this equation by $\cos\theta + \cos\varphi$ we find

$$\text{2nd member}\left\{\begin{array}{l} \times\cos\theta = \sin(2n-1)\varphi + \sum\limits_{p=1}^{2n-1}(-1)^p[\sin(2n-p+1)\varphi + \sin(2n-p-1)\varphi]\cos p\theta + \\ \quad + \sin\varphi\cos 2n\theta \\ \times\cos\varphi = -\sin 2n\varphi\cos\varphi + \sum\limits_{p=1}^{2n-1}(-1)^{p-1}[\sin(2n-p+1)\varphi + \sin(2n-p-1)\varphi]\cos p\theta; \end{array}\right.$$

so the sum becomes

$$\sin(2n-1)\varphi - \sin 2n\varphi\cos\varphi + \sin\varphi\cos 2n\theta = \sin\varphi(\cos 2n\theta - \cos 2n\varphi).$$

From the formula (a) follows immediately

$$A_{2n} = -2\pi\frac{\sin 2n\varphi}{\sin\varphi}.$$

If we replace this value in the expressions just found, we arrive at

$$P = -\frac{4\pi}{\sin\varphi}[I_2\sin 2\varphi + I_4\sin 4\varphi + I_6\sin 6\varphi + \ldots].$$

$$Q = -\frac{2\pi}{\sin\varphi}[(I_3 - I_1)\sin 2\varphi + (I_5 - I_3)\sin 4\varphi + \ldots]$$

$$= \quad 4\pi[I_1\cos\varphi + I_3\cos 3\varphi + I_5\cos 5\varphi\ldots],$$

$$R = \frac{4\pi}{\sin\varphi}[I_2\sin 2\varphi - I_4\sin 4\varphi + I_6\sin 6\varphi - \ldots].$$

$$S = -\frac{2\pi}{\sin\varphi}[I_1\sin 2\varphi - I_3(\sin 2\varphi + \sin 4\varphi) + I_5(\sin 4\varphi + \sin 6\varphi)\ldots],$$

$$= -\frac{4\pi\cos\varphi}{\sin\varphi}[I_1\sin\varphi - I_3\sin 3\varphi + I_5\sin 5\varphi - \ldots].$$

Moreover from the formula (a) we can deduce another result: When we develop

$$\frac{\cos 2n\theta - \cos 2n\varphi}{\cos\theta + \cos\varphi} = \tfrac{1}{2}a_0 + a_1\cos\theta + a_2\cos 2\theta + \ldots$$

then we know that

$$a_p = \frac{2}{\pi}\int_0^\pi \frac{\cos 2n\theta - \cos 2n\varphi}{\cos\theta + \cos\varphi}\cos p\theta\, d\theta$$

If we compare this to the equation (a) we arrive at

$$a_p = (-1)^{p-1}\, 2\,\frac{\sin(2n-p)\varphi}{\sin\varphi}$$

for $p = 0, 1, 2, \ldots, (2n-1)$, whilst for greater values of p we have $a_p = 0$.

Physics. — *"The validity of the law of corresponding states for mixtures of methyl chloride and carbon dioxide."* By Prof. H. Kamerlingh Onnes and Dr. C. Zakrzewski. (Communication N°. 92 from the Physical Laboratory at Leiden by Prof. Dr. H. Kamerlingh Onnes) (Continued).

(Communicated in the meeting of October 29, 1904).

§ 5. *Further approximations.* By second approximation we get by taking also B^2 into consideration:

$$\frac{p_1 v_1}{p_2 v_2} - 1 = \frac{B}{A^2}(p_1 - p_2) - \frac{B^2}{A^4}(p_1 - p_2)(p_1 + 2p_2). \quad . \quad . \quad (2)$$

If, however, we take B^2 into consideration, it is more rational to do the same with C, and we have:

$$\frac{p_1 v_1}{p_2 v_2} - 1 = \frac{B}{A^2}(p_1 - p_2) - \frac{B^2}{A^4}(p_1 - p_2)\left\{ p_2 + \left(1 - \frac{CA}{B^2}\right)(p_1 + p_2)\right\}. (3)$$

According to the reduced equation of state $\frac{CA}{B^2}$ is about 1/3 for methyl chloride at 20°.

The repetition of the calculations of § 2 yields:

TABLE III. Second virial coefficients of mixtures of carbon dioxide ($x = 0$) and methyl chloride ($x = 1$) to the 2nd and 3rd approximations.

approxim.	composit. x	$\frac{B}{A^2}$ from I a. II	$\frac{B}{A^2}$ from I a. III	$\frac{B}{A^2}$ mean	B_{20°
2nd	1	— 0.01698	— 0.01710	— 0 01704	
3rd		— 0.01711	— 0.01723	— 0.01717	— 0.01978
2nd	0.6945	— 0.01246	— 0.01269	— 0.01258	
3rd		— 0.01260	— 0.01282	— 0.01271	— 0.01464
2nd	0.5030	— 0.01001	— 0.00976	— 0.00988	
3rd		— 0.01009	— 0.00983	— 0.00396	— 0.01147
2nd	0 [1]	— 0.00572	— 0.00545	— 0.00558	
3rd		— 0.00575	— 0.00547	— 0.00561	— 0.00646

The repetition of the calculations of § 3 and § 4 with these corrected values gives:

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[1] Here are two determinations of Keesom agreeing with I and II and I and III, calculated according to (2) and (3) (data see Comm. N°. 88).

$$ {}^{(Cl\,Me.)}B_{20^\circ} = -\,0.01983 $$

$$ {}^{(Cl\,Me,\;CO_2)}_{\quad(12)}B_{20^\circ} = -\,0.01005 $$

$$ {}^{(CO_2)}B_{20^\circ} = -\,0.00644 $$

The comparison of the values found with those of the quadratic formula and the law of corresponding states (using BRINKMAN's[1]) critical data) gives:

TABLE IV. Deviations of the second virial coefficients of mixtures of carbon dioxide ($x = 0$) and methyl chloride ($x = 1$) from the quadratic formula and from the correspondence.

x	B from law of corresponding states.	B quadrat. form. — B corresp.	B observ. — B quadrat.	B observ. — B corresp.
1	— 0.02156	+ 0.00173	+ 0.00005	+ 0.00178
0.6945	— 0.01470	+ 0.00027	— 0.00021	— 0.00006
0.5030	— 0.01135	— 0.00029	+ 0.00016	— 0.00013
0	— 0.00650	+ 0.00006	— 0.00002	+ 0.00004

In the conclusions of § 3 and § 4 no further modification is brought about by these further approximations. It is noteworthy that the deviation now only applies to the methyl chloride.

§ 6. *Comparison of the results with those of* LEDUC *and* CHAPPUIS. The compressibility of methyl chloride with small densities has been examined by LEDUC[2]) in collaboration with SACERDOTE. He does not give the observed results but the quantity calculated from it at 16°, viz.:

$$ \pi\,\mathcal{A}_\pi = -\,\pi\,\frac{1}{pv}\,\frac{\partial(pv)}{\partial p} \text{ at } \pi = 73 \text{ cm.} $$

According to KAMERLINGH ONNES' empirical equation of state:

$$ -\left(\frac{1}{pv}\,\frac{\partial(pv)}{\partial p}\right)_p = -\,\frac{B}{A^2} + \frac{3B^2}{A^4}\left\{1 - \frac{2\,CA}{3B^2}\right\}p. $$

In order to pass from our ${}^{(Cl\,Me.)}B_{20^\circ}$ to ${}^{(Cl\,Me.)}B_{16^\circ}$ we have calculated ${}^{(Cl\,Me.)}\dfrac{\partial B}{\partial t}$ according to the formula given in § 4 for the reduced value of

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[1]) BRINKMAN, Thesis for the doctorate, Amsterdam 1904.

[2]) Recherches sur les gaz, p. 82.

$B, \mathfrak{B}$, and found $\dfrac{\partial \overset{(Cl\,Me.)}{B}}{\partial t} = 0.0001194$, so that $\overset{(Cl\,Me}{B}_{16^\circ} = -0.02026$, while $A_{16^\circ} = 1 + 16\,\alpha_\infty$. Thus we find

$$\pi : A_\pi = 0.01814 \text{ (K. O. and Z.)}$$

while

$$\pi : A_\pi = 0.0195 \text{ (L.)}$$

was found by LEDUC (l.c.). The uncertainty of $\dfrac{\partial B}{\partial t}$ contributes probably but little to the difference. It is noteworthy that in contradiction with our result the value of B derived from LEDUC's observations $\overset{(Cl\,Me)}{B}_{20^\circ} = -0.0215$ perfectly agrees with that according to the law of corresponding states: -0.0216.

Measurements on the compressibility of CO_2 have been made by CHAPPUIS [1]) at 20° C. He found (mean from some determinations with about the same pressure each time):

	p		pv
I	$p = 1260.670$	mm.	$pv = 1312485$
II	1117.228	,,	1313826
III	992.911	,,	1314981

By third approximation yield

$$\left.\begin{array}{lcr} \text{I and II:} & \dfrac{\overset{(CO_2)}{B}_{20^\circ}}{A^2_{20^\circ}} = & -0.005309 \\ \text{II and III} & ,, & -0.005282 \\ \text{I and III} & ,, & -0.005297 \end{array}\right\} \text{assumed mean } -0.005296,$$

from which follows $\overset{(CO_2)}{B}_{20^\circ} = -0.006100$, whereas according to KEESOM $\overset{(CO_2)}{B}_{20^\circ} = -0.00646$.

From the observations of LEDUC on carbon dioxide KEESOM derived $\overset{(CO_2)}{B}_{20^\circ} = -0.0059$.

II. *Conditions of coexistence at low temperatures.*

§ 7. *Determination of the begin condensation pressure* at -25°. In the introduction we mentioned a determination of the begin condensation pressure at -25° for testing the results obtained with the ψ-surface. This determination was made with a mixture with the composition $x = 0.5042$ of methylchloride.

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[1]) Trav. et Mém. du Bureau Intern. des Poids et Mesures, t. 13, 1903.

A condensation was seen on the mirror of the dew-point apparatus (see § 1 and Comm. N°. 92 p. 233) at a pressure of 157.4 cm. mercury and disappeared at 154.6 cm. As mean we may take 156.0 cm., and the accuracy may be put at 1 %.

§ 8. *Determination of the end condensation pressure.* In the first place the condensation pressure (vapour tension) of pure methyl chloride was determined with the aid of the small piezometer (§ 5 Comm. N°. 92). At — 25° we found 72.9 cm. when the piezometer was filled to the capillary tube, 72.8 cm. when the liquid had nearly all evaporated. In both cases the liquid in the piezometer was stirred. The agreement of these values speaks for the purity of the methyl chloride. At — 37°.4 the vapour tension was found to be 42.7 cm.

In order to determine the end condensation pressure of the mixture with $x = 0.5042$ of methyl chloride the temperature of the piezometer had to be lowered down to — 38°.5; at higher temperatures condensation took place at other places in the apparatus. (Cf. § 5 of the Comm. N°. 92 "On the determination of the conditions of coexistence etc." It may further be observed, that no arrangement was applied to heat the press tube and the capillary tube above the ordinary temperature). For the determination of the conditions of coexistence (according to § 5 just mentioned), are wanted: in the first place the observed end pressure p_{lxT}, for which 6.13 atms. was found. Then the volume V_v of the vapour with the composition x_{vTp}. The vapour occupied 0.488 cc. under 6.13 atms. at — 38°.5. Finally the volume V, which vapour and liquid phase together would occupy in normal circumstances; by blowing off in the volumenometer we found 347.7 cc. at 20° C. and 760 mm. (reduced according to the law of BOYLE, GAY-LUSSAC). The composition x_{vTp} was determined with VAN DER WAALS' hyperbolic formula, which yields $x = 0.0375$. From these data follows (see l.c. § 5)

$$x_{lpT} = 0.5084, \quad p_{lxT} = 6.13, \quad t = -38°.5.$$

The circumstances were not favourable for an accurate determination of the correction. It appears, however, to be so slight, that we may safely assume the composition to be accurate down to 1 %.

§ 9. *Comparison of the conditions of coexistence with theory.* For this purpose it is required in the first place to know the vapour tension of methyl chloride and carbon dioxide at — 25° C. and — 38°.5 C. We have calculated the coefficients for methyl chloride in the formula of DUPRÉ and RANKINE $ln.\, p = A - \frac{B}{T} - C ln T$ with HARTMAN's value

(3.48 atms. at 9°.5 C.)[1]), and the two values found by us (§ 8). Extrapolation to —38°.5 C. gives 0.53 atms. For carbon dioxide follows from KUENEN's observations[2]) at —25° C., $p_{max} = 16.5$ atms., at —38°.5 C., $p_{max} = 10.4$ atms.

From our model for —25° C. (Comm. Suppl. N°. 8) follows for methyl chloride at —25° C. $p_{max} = 0.59$ atms. and for carbon dioxide $p_{max} = 16$ atms. (instead of 0.96 and 16.5). The begin condensation pressure of the mixture $x = 0.5084$ is according to the model 1.30 atms., instead of 2.05 atms., as was found by us.

The insufficient concordance on the side of methyl chloride shows once more clearly that for methyl chloride and ether the agreement required for the validity of the law of corresponding states leaves much to be desired.

In order to judge about the degree of deviation of the mixtures from this law, we must first free ourselves as much as possible from the deviations of the separate components. We have tried to do so by raising the px-curve 0.4 atms. Then we get for p_{max} 0.99 atms. for methyl chloride, 16.4 atms. for carbon dioxide, and $p_{rx} = 1.7$ atms. for the examined mixture. The remaining difference with the observed $p_{rx} = 2.05$ atms. is, no doubt, partly due to the fact that the surface had not yet been constructed with sufficient care, to determine with sufficient certainty the place of the points of contact when the plate of glass is rolled over the ridge and over the convex part. More points should have been calculated if we wished to render the model sufficiently precise for an accurate determination.

This uncertainty when rolling, makes it also doubtful whether on account of the law of corresponding states, with an accurately executed theoretical model, a straight line would really be found for the liquid branch of the border curve in the px-diagram, as was derived from our model. We got the impression, that a curve of the same character as that derived by HARTMAN in his experiments and from his model, ought to be found also by us, on our model (Comm. Suppl. N°. 8), but we had not enough data for ascertaining the deviations from the straight line, and had therefore to adopt the straight line as the simplest approximation.

That the experimental liquid branch of the border curve in the

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[1]) Comm. N°. 64.

[2]) Phil. Mag. Jan. 1902.

px-diagram at — 25° C. is not straight, could not be proved with our mixtures and our apparatus, as has been said. The measurements at — 38°.5 C. raised it however beyond doubt, that the line under consideration is not straight at — 38°.5 C., but is for the greater part convex to the x-axis. According to the straight line p_{lx} would have to be 5.38 atms. for $x = 0.5084$, instead of the value 6.13 atms. found. This difference is much too large to be accounted for by errors of observation or of the value ascribed to the composition. There is therefore no doubt but that the liquid branch is curved in the same way at — 25° C. In concordance with this deviation is also the fact that the begin pressure at the same temperature does not agree with the hyperbolic function for the composition (VAN DER WAALS, Continuität II, p. 154). For according to this formula the begin pressure would have to be 1.78 atms. instead of 2.05 atms., as was found (§ 6).

It appears from all this, that *from the conditions of coexistence deviations from the law of corresponding states follow* for isothermals of mixtures of methyl chloride and carbon dioxide, which become very distinct *for liquid densities and low temperatures.*

The comparison of the conditions of coexistence, derived from the law of corresponding states by means of the ψ-surface, with the really observed data, is an *indirect method* for judging about the deviations from the law of corresponding states for the isothermals of mixtures. It was our purpose to give an instance of the application of this method and to do this at low temperatures.

In order to ascertain the accurate amount of the deviations new measuremens at low temperatures will be required, and for the temperature of observation a ψ-surface will have to be constructed with more precision than that devised in Comm. Suppl. N°. 8 for the sake of preliminary elucidation and for the sake of corrections.

Corrigenda et addenda to the paper "*On an equivalent of the* Cromer Forest-Bed *in the Netherlands,*" in this Vol. of the Proceedings, pag. 214—222.

Page 214, line 14 from top and line 10 from bottom, *for* "mass" *read* "massif".
,, 215, ,, 4 from bottom, *after* "Belfeld" *add* "and".
,, 215, ,, 10 ,, ,, *for* "14" *read* "13.5".
,, 215, ,, 14 and 16 from bottom, *for* "her" *read* "its".
,, 216, ,, 2 from top, *dele* "and probably also to the east".

Page 216, line 4 from top *after* "removed" *add* "by denudation"
,, 216, ,, 6 ,, ,, *for* "under layer" *read* "underlying".
,, 216, ,, 8 ,, ,, *dele* "even".
,, 218, ,, 3 ,, ,, *for* "uningured" *read* "uninjured".
,, 218, ,, 14 ,, ,, *after* "strong" *add* "undoubtedly artificial".
,, 218, ,, 16 ,, ,, *for* "straighter" *read* "rather straight".
,, 218, ,, 4 from bottom, *read* "process of the development of".
,, 218, bottom-line, *after* "level", *add* "it".
,, 219, line 19 from bottom, *after* "possession" *add* "of Rhinoceros etruscus,".
,, 219, ,, 18 ,, ,, *for* "an" *read* "two".
,, 219, ,, 14 ,, ,, *after* "species" *add* "of".
,, 219, ,, 5 ,, ,, *after* "of" *add* "*Cervus Sedgwickii,*".
,, 220, ,, 18 ,, top, *for* "indignous" *read* "indigenous".

(December 21, 1904).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday December 24, 1904.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 24 December 1904, Dl. XIII).

CONTENTS.

The following papers were read:

Mathematics. — "*Multiple umbilics as singularities of the first order of exception on point-general surfaces*". Communicated by Prof. D. J. KORTEWEG and Mr. D. DE LANGE.

(Communicated in the meeting of November 26, 1904).

1. Let us suppose a point-general surface, i. e. general if considered as a geometrical locus of points, in whose Cartesian equation parameters appear; then for a continuous change of those parameters also the surface will in general vary continuously in shape [1]). If then we fix our attention on any kind of singular points, plaitpoints, umbilics, etc. appearing on a point-general algebraic surface in finite number, it may happen during the deformation that two or more of those singular points coincide. Such a point where this takes place may be called a twofold or multiple singular point of that kind.

Now such a coincidence may generally occur, as the results tell us, in more than one way. For some of these ways the coincidence depends on a single relation between the coefficients of the Cartesian equation being satisfied, whilst for others it depends on more suchlike relations. The former cases belong to the singularities of the first order of exception, the latter to those of a higher order. It is only with the former that we shall occupy ourselves in this paper [2]).

For plaitpoints the singularities of the first class, which must be regarded as multiple plaitpoints, were investigated by the first mentioned [3]). Two entirely different kinds of double plaitpoints were found (the homogeneous kind and the heterogeneous one); furthermore the points of osculation proved to be threefold plaitpoints, the nodes of the surface twentyfourfold plaitpoints.

It seemed advisable to make an investigation also for other singular points. This we have done for the umbilics. The results obtained are communicated in this paper. For proofs and more elaborate considerations see the dissertation by the second mentioned Mr. D. DE LANGE issued recently.

a. *The double umbilic at finite distance.*

2. If we place the origin of a rectangular system of coordinates at an umbilic and if we use the tangent plane in this point as xy-plane

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[1]) See for more general considerations of the same kind as follow here: „Ueber Singularitäten verschiedener Ausnahmeordnung und ihre Zerlegung", Math. Ann. 41, p. 286—307 (1893).

[2]) See for the reason why these are asking in the first place our attention the paper just quoted, on page 287.

[3]) D. J. KORTEWEG, „Ueber Faltenpunkte", Wien. Ber. 98, p. 1151—1191, (1889) also Arch. Néerl. 24, p. 57—98, (1890).

the equation of the surface can be written in the form:

$$z = c_1(x^2 + y^2) + d_1x^3 + d_2x^2y + d_3xy^2 + d_4y^3 + e_1x^4 + \quad . \quad (1)$$

By a slight deformation we arrive for the new surface at the equation:

$$z = \alpha + \beta_1 x + \beta_2 y + c_1x^2 + \gamma_2 xy + (c_1 + \gamma_3)\,y^2 + d_1x^3 + d_2x^2y \; . \quad (2)$$

where the Greek letters represent small quantities, which can all be regarded as of the same order, namely of the order of the small variation which an arbitrary parameter appearing in the coefficients, has had to undergo. Also the Latin letters must be regarded as having been varied somewhat, which is however immaterial.

Let us now calculate by means of the wellknown conditions:

$$\frac{\dfrac{\partial^2 z}{\partial x^2}}{1+\left(\dfrac{\partial z}{\partial x}\right)^2} = \frac{\dfrac{\partial^2 z}{\partial x\,\partial y}}{\dfrac{\partial z}{\partial x}\cdot\dfrac{\partial z}{\partial y}} = \frac{\dfrac{\partial^2 z}{\partial y^2}}{1+\left(\dfrac{\partial z}{\partial y}\right)^2} \quad . \; . \; . \quad (3)$$

the position of the displaced umbilic; then we shall find after neglecting all terms which are small with respect to those which are retained, the two linear equations:

$$\gamma_2 + 2\,d_2\,x + 2d_3\,y = 0;\ \gamma_3 + (d_3 - 3d_1)\,x + (3d_4 - d_2)\,y = 0 \quad . \quad (4)$$

from which in general we deduce without difficulty the sought for displacement.

This however is different when the determinant

$$K_1 \equiv \begin{vmatrix} d_3 - 3d_1 & 3d_4 - d_2 \\ d_2 & d_3 \end{vmatrix} \equiv d_2^2 + d_3^2 - 3\,(d_1\,d_3 + d_2\,d_4) \quad (5)$$

disappears. In that case no finite values satisfy the linear equations (4). This proves, however, only that the displacement of the umbilic has become of a lower order than the quantities indicated by the Greek letters and that therefore the terms of the second order in x and y must be included in the equations (4). If we do so we obtain by comparing the two new equations and eliminating the linear terms the new equation:

$$\begin{aligned}&(d_3 - 3d_1)\gamma_2 - 2d_2\gamma_3 + [12d_2e_1 + 3(d_3 - 3d_1)e_2 - 2d_2e_3 - 8c_1{}^3d_2]x^2 + \\ &+ [6d_2e_2 + 4(d_3 - 3d_1)e_3 - 6d_2e_4 - 2c_1{}^3(d_3 - 3d_1)]xy + [2d_2e_3 + 3(d_3 - 3d_1)\,e_4 - \\ &- 12d_2e_5 + 8c_1{}^3d_2]y^2 = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)\end{aligned}$$

which must be combined with one of the equations (4).

This equation (6) is of order two in x and y, from which therefore ensues: 1st that the displacement becomes of order $\frac{1}{2}$ with respect to that of the Greek letters used in (2), 2nd that the umbilic originally situated at the origin of the system of coordinates on the surface (1) is broken up into two at the deformation of this surface, which two umbilics diverge in general, real at a variation of the parameter in one sense, and imaginary in the other. So we have to do with a double umbilic, namely with such a one at whose effective [1]) occurrence a transition takes place from the real to the imaginary.

3. Before considering the further properties of this double umbilic we wish to observe that the condition $K_1 = 0$ was already known as an important characteristic. It characterises namely the case of transition between two of the three general kinds of umbilics distinguished for the first time by DARBOUX [2]) according to the manner in which the lines of curvature bear themselves in their neighbourhood.

For the first kind, see fig. 1, lines of curvature are starting from the umbilic in three different directions — namely in each direction a single one, which we have represented by a right line because its curvature depends on the terms of higher order of the equation (1), to begin with those of the fourth. Those three directions have the property that they cannot be represented in one quadrant, i. e. each of them lies inside the obtuse angle formed by the two others. For this kind $K_1 > 0$ [3]).

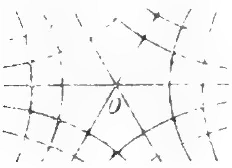

Fig. 1.

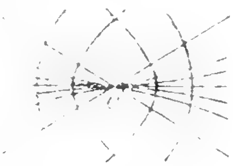

Fig. 2.

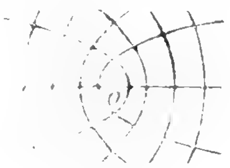

Fig. 3.

For the *second* kind, see fig. 2, also lines of curvature start from the umbilic in three different directions; these directions are however such that *one* of them falls inside the acute angle formed by the two others, so that the three can now be contained in *one* quadrant. Moreover an infinite number of lines of curvature — five of which, the right line included, are indicated in fig. 2 — start in the firstmentioned direction which might be called the middle one. For this kind $K_1 < 0$.

For the *third* kind, see fig. 3, only *one* line of curvature starts from the umbilic, the right line of that figure. The two other directions

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[1]) See for the meaning of this term page 289 of the paper quoted in the first note.

[2]) G. DARBOUX. Leçons sur la théorie générale des surfaces. Quatrième partie. Gauthier-Villars, 1896, p. 448—465.

[3]) This characteristic $K_1 > 0$ means moreover as is proved in the dissertation in a simple way, that the lines of curvature turn in the neighbourhood of O everywhere their convex side to the umbilic, but for $K_1 < 0$ on the contrary their concave side.

of departure have become imaginary. For this kind too $K_1 < 0$. To distinguish it analytically from the preceding one we can notice the sign of the discriminant of the cubic

$$d_3 n^3 + (2d_2 - 3d_4) n^2 + (3d_1 - 2d_3) n - d_2 = 0 \quad . \quad . \quad . \quad (7)$$

which proves to serve for the determination of the three directions of departure. If we call this discriminant K_2, chosen in such a way that for $K_2 > 0$ the three roots are real, we have for the *first* kind $K_1 > 0$, $K_2 > 0$, for the *second* $K_1 < 0$, $K_2 > 0$, for the *third* $K_1 < 0$, $K_2 < 0$. A fourth kind $K_1 > 0$, $K_2 < 0$ does not exist, because as is demonstrated also algebraically $K_1 > 0$ includes $K_2 > 0$.

4. As is apparent from this explanation the double umbilic forms the case of transition between the first and the second kind, for which case of transition K_1 must of necessity be equal to nought, and $K_2 > 0$. The form of the lines of curvature now becomes very simple as long as one confines oneself to the approximation which has led to the figures 1, 2 and 3. Out of the differential equation

$$[d_2 x + d_3 y]\left[1 - \left(\frac{dy}{dx}\right)^2\right] + [(d_3 - 3d_1)x + (3d_4 - d_2)y]\frac{dy}{dx} = 0 \ , \quad (8)$$

which serves to determine the lines of curvature, a factor separates itself namely $d_2 x + d_3 y$, which made equal to zero represents a right line, whilst the remaining furnishes two mutually perpendicular pencils of parallel lines. In this manner, however, from each point of the first mentioned right line three lines of curvature would start, so that there would be an entire line of umbilics. This is of course in general not the case, so that this representation of the lines of curvature must undergo a considerable modification as soon as the terms of higher order are taken into consideration. We shall soon refer to this again.

5. We shall first mention the results of a closer investigation of the deformation of the double umbilic. From this we were able to prove, 1st. that for a variation of parameter in the sense in which the two single umbilics diverge in a real manner, this diverging shall always take place in the direction of the just discussed right line $d_2 x + d_3 y = 0$, which after that represents in first approximation for each of the two separated umbilics one of the directions of departure of lines of curvature, 2nd. that these separated umbilics are always of a different kind, namely one of the first kind, the other of the second. Moreover $d_2 x + d_3 y = 0$ indicates for that of the second kind the middle direction of departure, whilst also the remaining directions of departure of the diverged umbilics nearly correspond to the directions of departure of the original double umbilic discussed in § 4.

All this being stated it is not difficult to guess how in general the form of the lines of curvature must be, shortly after the breaking up of the double umbilic [1]).

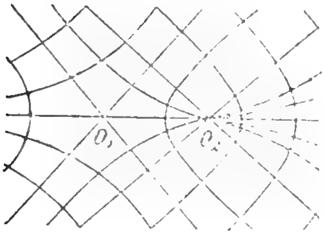

Fig. 4.

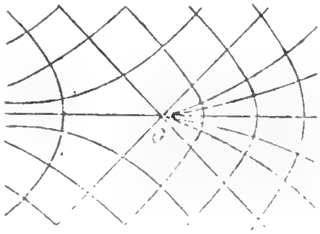

Fig. 5.

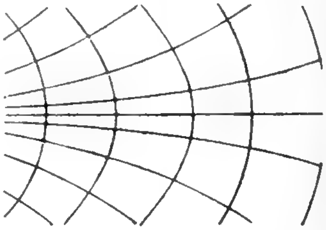

Fig. 6.

That form is represented in fig. 4, where O_1 indicates the umbilic of the first kind, O_2 that of the second. At O_1 the angle of the two other lines of curvature, starting from the umbilic, which contains $O_1\,O_2$ is a little larger than a right angle, at O_2 on the contrary it is a little smaller.

If after that we allow the umbilics to coincide again, they meet at about half the distance and the figure now formed where the lines of curvature situated at some distance to the right and left of O_1 and O_2 must have retained in general the same direction, can hardly be otherwise but such as has been indicated in fig. 5 [2]), apart from the symmetry which in general does not exist of course, no more than in any of the other figures.

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[1]) After the publication of the Dutch version of this paper we found that Mr. A. Gullstrand already in 1900, in his memoir "Allgemeine Theorie der monochromatischen Aberrationen und ihre nächsten Ergebnisse für die Ophtalmologie" (see Nova Acta Regiae Societatis Scientiarum Upsaliensis, ser. 3, vol. 20, pp. 90 and 114) arrived also, starting from other considerations, at the investigation of the double umbilic and its breaking up and that we obtained the same results.

[2]) However, a closer investigation of this subject by another method would not be unwished for. It would have to be a systematic study of the lines, if possible in their entire length, satisfying the differential equation:

$$\left[1-\left(\frac{dy}{dx}\right)^2\right][2d_3y + 3e_2x^2 + 4(e_3 - 2c_1^3)xy + 3e_4y^2] +$$

$$+\frac{dy}{dx}[6d_4y + 2(e_3 - 6e_1 + 4c_1^3)x^2 + 6(e_4 - e_2)xy + 2(6e_5 - e_3 - 4c_1^3)y^2] = 0.$$

For this is the form which the differential equation of the lines of curvature assumes in the neighbourhood of a double umbilic at second approximation, when we place the X-axis in the direction in which the two single umbilics diverge by a slight deformation of the surface. We then have $d_2 = 0$ and $d_3 = 3d_1$; the latter on account of (5).

If we then continue the deformation in the same manner so that now the two umbilics diverge imaginarily, a figure seems to be formed as is represented in fig. 6.

In no case there occurs a transition proper from the first kind to the second on a point-general surface continuously deforming itself. When the relation $K_1 = 0$ meets its fulfilment then we find that two umbilics of different kinds approach each other to disappear from the surface after the coincidence.

b. *The nodes of a point-general surface as twelvefold umbilics.*

6. When there is a node, the equation of the surface in its neighbourhood cannot be given in the form indicated in equation (1). After a fit choice of the axes we can however start from:

$$ax^2 + by^2 + cz^2 + H_3 + H_4 + \ldots = 0 \quad . \quad . \quad . \quad . \quad (9)$$

or after a slight deformation, from:

$$\alpha + \beta_1 x + \beta_2 y + \beta_3 z + ax^2 + by^2 + cz^2 + \ldots = 0 \quad . \quad . \quad (10)$$

It is soon evident that to determine at first approximation the umbilics which appear in the neighbourhood of the place where formerly the node existed, the terms of order two are sufficient. So the surface may be treated there as a quadric, which immediately makes the behaviour of the umbilics clear. If namely we have to do with an *isolated* point, made to appear after the gradual disappearance of a sheet, then at the very instant four real [1]) umbilics disappear, which were situated on that sheet, whilst eight others were imaginary and become so again after the disappearance of the sheet. If the node is a *conical* point then, when the two sheets are disunited, four real [2]) umbilics make their appearance, becoming imaginary at the union, whilst eight others again meet likewise for a moment in the node, but are previously and afterwards imaginary. For an imaginary node of course all the twelve umbilics coinciding there for a moment remain imaginary.

The umbilics at infinity. General considerations.

7. The umbilics are distinguished from the plaitpoints and many other singular points by the fact, that they cannot stand a projective

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[1]) These are at first of the third kind. They can, however, gradually pass during a continued deformation into those of the second kind without giving rise to the appearance of a double umbilic.

[2]) Also for those holds good what was remarked in the preceding note.

transformation. The cause of this is that they are in a definite relation to the plane at infinity and in particular to the spherical points in that plane. This obliges us to give a separate consideration of the cases of the first order of exception, where umbilics reach infinity. It was a priori not improbable that this would be accompanied by the occurrence of multiplicity in all or in some of those cases, as really it proved to be for some.

The method of investigation with respect to this was as follows: first the umbilics were exchanged for a more general kind of singular points which are capable of projective transformation. To this end it is sufficient to observe that an umbilic can be defined as such a point of a given surface which — when regarded as a node of its section of the tangent plane — has the property that both nodal tangents pass through the circular points of the tangent plane.

After applying the general projective transformation the problem of the umbilics of the original surface is in this way reduced to the following:

Given a surface ω, a plane α, and in that plane a conic c; to define on the surface ω the points Ω which have the property that the two nodal tangents of the section of the tangent plane ϱ in Ω pass respectively through the points A_1 and A_2 where c is cut by ϱ.

For this more general problem the plane at infinity has been replaced by the plane α and we have but to study the points Ω which as singularities of the first order may appear in the section d of Ω and α which can be performed by choosing an appropriate system of axes with such a point for origin, by calculating for this system of axes the approximate equation of the surface, and by then applying a slight deformation. The results obtained in this way can be immediately applied to umbilics.

In this manner it became evident that umbilics can appear in four different ways at infinity as singular points of the first order of exception, which we shall successively describe in short.

c. *The point of contact of a point-general surface with the plane at infinity as a fourfold umbilic.*

8. It is clear that whenever the surface ω touches the plane α, such a point of contact must be regarded as an Ω-point; for its tangents in the section of the tangent plane will certainly meet the conic c in the plane α. By regarding the surface as a quadric we can then by returning to the problem of the umbilics decide without calculation that the point under observation is a fourfold Ω-point.

At the same time ensues from the behaviour of the quadrics that when there is a real contact with the plane at infinity, the point of contact, if it appears in the section of the tangent plane as an isolated point, breaks up at the deformation into two real and two imaginary umbilics in whatever direction the deformation may take place. In the opposite case we have to do with four imaginary umbilics. So transition from real umbilics to imaginary ones never takes place in this way.

d. *The point of contact of a point-general surface with the curve of the spherical points at infinity as a double umbilic.*

9. It goes without saying that when ω touches c the point of contact must be an Ω-point, for the points A_1 and A_2 coincide with this point of contact and so they are situated on the nodal tangents in this same point.

By analysis it proves to be a double Ω-point. As the spherical points at infinity are all imaginary, these umbilics and the single ones into which they break up, are also always imaginary.

e. *The points of infinity of the spinodal line as single umbilics, when the tangent of the spinode lies in the plane at infinity.*

10. If we consider a point in which the spinodal line of ω cuts the plane α, it is easy to see that this point must be regarded as an Ω-point as often as the cuspidal tangent of the section of the tangent plane lies in plane α, which is a single condition. It appears, however, that this point cannot be driven asunder by deformation, so it must be regarded as a single Ω-point and the umbilic corresponding to it likewise as a single umbilic. This umbilic can be real or imaginary. The manner indicated here is the only one in which real umbilics can reach infinity without passing into a multiple umbilic, i. e. without meeting other umbilics there.

f. *The points of intersection of the surface with the curve of the spherical points at infinity as single umbilics, when one of the nodal tangents in the section of the tangent plane lies in the plane at infinity.*

11. It is immediately evident that the corresponding points on ω are Ω-points and after investigation they prove to be single ones. As umbilics they are of course always imaginary.

Application to quadrics.

12. The equation of a quadric can be brought with an appropriate

choice of axes when the origin is placed in one of its umbilics, into the finite form:

$$z = c_1 (x^2 + y^2) + k_1 xz + k_2 yz + k_3 z^2 \quad . \quad . \quad . \quad . \qquad (11)$$

Bringing the value of z into the second member this furnishes the development in series

$$z = c_1 (x^2 + y^2) + k_1 c_1 x^3 + k_2 c_1 x^2 y + k_1 c_1 xy^2 + k_2 c_1 y^3 + \ldots \qquad (12)$$

Comparing this to (1) it is immediately evident that for the umbilics on a quadric we always find $d_1 = d_3$, $d_2 = d_4$, so $K_1 < 0$. Furthermore the cubic (7) passes into $(d_1 n - d_2)(n^2 + 1) = 0$; so $K_2 < 0$. From this it is evident, as indeed is known, that on a quadric never other umbilics than those of the third kind can appear.

From this ensues again immediately that on a quadric no common double umbilics can appear. Indeed beside the nodes the only possible multiple umbilics at finite distance on a quadric are the vertices of a surface of revolution; but these are fourfold umbilics whose occurrence on surfaces of higher order would demand more than one relation between the coefficients of the equation. So it is not astonishing that for such vertices the lines of curvature bear themselves in an entirely deviating way.

13. Passing now to the umbilics of quadrics at infinity we observe that the case given sub c appears for paraboloids. If, however, we regard more closely the section with the plane at infinity, then this is evidently degenerated into two right lines. Each of these right lines meets the curve of the spherical points in two points. If we make tangent planes to appear in those points, then also there the section of the tangent plane degenerates, namely, into one of the recently considered right lines and into another. These two must at the same time be regarded as the tangents of the section of the tangent plane. One of these tangents therefore always happens to lie in the plane at infinity and we are in case f.

To the fourfold umbilic at infinity four single umbilics are in this way added for the paraboloid. For finite distances four such points only are thus left, which furnishes here the proof to the sum.

Inversely case d requires as is easy to see, at least for quadrics with real equation, that these should pass into surfaces of revolution. There is then double contact of the surface and the curve of the spherical points. Indeed in this case four umbilics pass into infinity; the eight remaining ones coinciding four by four in both vertices.

The remaining case e cannot make its appearance for quadrics. The case f has just been discussed. It can as is easy to see make its appearance for quadrics only in the manner indicated there.

Chemistry. — *"On the preparation of pure o-toluidine and a method for ascertaining its purity."* By Prof. A. F. Holleman.

(Communicated in the meeting of November 26, 1904).

Whilst *p*-toluidine being a solid, well crystallised substance may be very readily obtained in a perfectly pure state from the commercial product by recrystallisation and distillation, this is by no means the case with the liquid *ortho*-toluidine. The latter stands a good chance of containing its *para*-isomer as it is prepared from *o*-nitrotoluene, which is rather difficult to completely separate from the *p*-nitrotoluene simultaneously formed in the nitration of toluene, particularly because the *ortho*-nitrocompound is liquid. It is further stated that *o*-toluidine sometimes contains aniline.

Of the various ways mentioned in the literature on the subject for the purification of *o*-toluidine, the conversion into oxalate seemed to me the most appropriate. According to Beilsteins Handbuch, the solubility of *ortho*-toluidine oxalate amounts to 2.38 parts by weight in 100 parts of water at 21°; that of the acid oxalate of *p*-toluidine (the neutral compound does not exist) 0.87 parts in 100 parts of water at 10°. If, therefore, the *o*-toluidine contains a few per cent of *para*, the oxalate thereof must remain in the aqueous mother-liquor when the mixture is submitted to recrystallisation, and the use of ether, which is given as an accurate method of separating the oxalates, becomes superfluous. Even any aniline which happens to be present, may be removed in this manner.

In order to see whether a complete purification might indeed be attained in this way, it was necessary to first obtain a characteristic test for ascertaining the purity; for the processes found in the literature for ascertaining the purity of *o*-toluidine, of Häussermann (Fr. **26**,750), Reinhart (Fr. **33**,90) and Lunge (Fr. **24**,459) appeared but little suitable for the detection of very small amounts of impurities.

For this purpose the determination of the solidifying point of the acetyl compound proved serviceable. By determining a portion of the solidifying point curve of *o*- and *p*-acetotoluidide the amount of the impurity could then be ascertained quantitatively at the same time.

The following solidifying point figures were found:

Percentage of *para*.	Solidifying point.
0	109.°15
1.12	108.°45
2.42	107.75
9.58	103.°2
13.6	100.°8

That $109^{\circ}.15$ is the solidifying point of pure aceto-*o*-toluidide was proved by recrystallising the oxalate prepared from a "chemically pure" *o*-toluidine and then recovering the toluidine, which was then treated once more in the same way.

After each crystallisation of the oxalate a small quantity of *o*-toluidine was converted into the acetocompound; the observed solidifying points were both the above figure, which moreover did not suffer any change when the acetocompound was again recrystallised.

In order to ascertain how far small quantities of *para*-toluidine and aniline may de detected by means of the solidifying point figures, the above purified *o*-toluidine was mixed with 2 % of aniline and another portion with 2 % of *p*-toluidine and tested as follows:

25.2 grams of oxalic acid ($^1/_5$ mol.) are dissolved in a litre of boiling water and to this are slowly added 42.8 gram of toluidine ($^2/_5$ mol.). On cooling, the oxalate crystallises out; after placing the flask in ice the liquid is thoroughly removed by suction and the crystals washed once with a little water; the toluidine is then recovered from the crystals as well as from the motherliquor by adding alkali and distilling in a current of steam. In order to avoid loss it is necessary to extract the water, which has also distilled over, twice with ether. The toluidine so obtained is converted into the acetocompound by adding per gram a mixture of 2 cc. of glacial acetic acid and 1 cc. of acetic anhydride. The mass is now evaporated on the waterbath and the dry residue once distilled in *vacuo* when everything passes over leaving but a small black residue. The solidifying point of both products is then determined. We found:

	Added	
	2 % *p*-toluidine	2 % aniline
Solidifying point of the acetotoluidide from the crystals:	109.°15;	109.°15
„ „ „ „ „ „ „ motherliquors:	103.°2 ;	103.°0

This shows that while the oxalate crystallised out, the added impurities remained completely in the motherliquor and that the acetocompound prepared from the latter shows the serious depression of about 6°. If now we consider that the determination of the solidifying point is accurate to 0.°2 and with practice even to 0.°1 it follows that we may detect in this way $^1/_{60}$ part of the impurities now present, viz. $^2/_{60}$ or 0.03 %.

Using this method I have examined two samples of *o*-toluidine from different makers and both marked "chemisch rein" as to their purity with the following result.

I. Converted into oxalate in exactly the same manner as described. Flask cooled in ice water.

From the crystals were obtained 31 grams, from the motherliquor 10.2 grams, total 41.2 grams, 42.8 grams having been started with.

Solidifying point of the acetocompound from the crystals 109.°15. Therefore pure.

" " " " " , motherliquor 107. 15, corresponding with 3.6% of *p*-toluidine or 0.37 gram. The sample therefore contained $\frac{0.37 \times 100}{41.2} = 0.9\ \%$ impurity.

II. 42.8 grams of toluidine converted as before into oxalate. From the crystals are taken 30.5 grams, from the motherliquor 11.2 grams, total 41 7 grams.

Solidifying point of the acetocompound from the crystals 108.°45 so this still contained 1.1 % or 0.34 gram of byproduct. After having been converted once more into oxalate, the newly prepared acetocompound now solidified at 109.°15. Solidifying point of the acetocompound from the motherliquor 101.°9 corresponding with 12.1 % or 1.36 gram. Total impurity present, therefore, 1.36 + 0.34 = 1.70 corresponding with 4.1 %.

Assuming the impurity to be either aniline or p-toluidine the following plan was followed to ascertain which of these two was present. Of a mixture of acetanilide (6 grams.) and aceto*ortho*toluidide (4 grams) the eutectic point was determined. For this was found 64.°6 and 65.°1, mean 64.°8$_5$. On adding to this mixture 0.1 gram of p-acetotoluidide, the said point was found to be 63.°1 and 63.°6, mean 63.°3$_5$; the latter, therefore, seemed rather sensitive to small additions of *para*.

5.64 grams of acetanilide were now mixed with 4.36 grams of the acetocompound prepared from the motherliquor (I) which, according the above examination, contain 4.20 gram of aceto*ortho*toluidide and 0.16 gram of an impurity, which might be p-acetotoluidide.

The point of initial solidification of this mixture was found to be 72.°0 and 71°9, the point of complete solidification 62.°6 and 62.°8. A mixture prepared from 5.64 gram of acetanilide, 4.20 grams of aceto*ortho*toluidide exhibited these same points at 72.°1 and 62.°8, so that the impurity seems to be indeed p-acetotoluide; acetanilide is out of the question as then the point of complete solidification ought to have coincided with the eutectic point of the pure mixture of acetanilide and aceto-*o*-toluidide.

The above method will no doubt be found applicable in a number of other cases as it is based on a general principle. By its means, it is possible to ascertain the purity of organic preparations with a greater degree of quantitative precision than has been the case up to the present, particularly when dealing with liquid substances.

Mr. F. H. VAN DER LAAN has ably assisted me in the experimental part of this research.

Groningen, Chem. Lab. Univers. November 1904.

Botany. — *"On the influence of nutrition on the fluctuating variability of some plants."* By Miss Tine Tammes. (Communicated by Prof. J. W. Moll).

(Communicated in the meeting of October 29, 1904).

That nutrition has an influence on the development of plants has long been known. Also that some parts are much more sensitive in this respect than others and that, for example, the size of the stem and leaf is much more affected by good or bad nutrition than the number of stamens. As yet our knowledge on this point, especially our quantitative knowledge, is very superficial. The introduction of the statistical method, however, into botany has enabled us to formulate more sharply the formerly vague and insufficiently defined question of the influence of nutrition and also to interpret the results obtained easily and accurately.

Although the number of statistical investigations on plant characteristics, carried out in recent years, is fairly numerous, yet the influence of nutrition on the value of these characteristics has not often been studied.

De Vries [1]) carried out an extensive investigation in this direction with *Othonna crassifolia*. He compared plants that had been grown in a greenhouse in pots with very dry ground with garden-cultures and found that with the plants from the greenhouse the median of the length of the leaves was only about half that of the plants that had grown in full ground, the average number of ray-flowers per head being 12 with the former, 13 with the latter. In his work "die Mutationstheorie" de Vries [2]) describes experiments and observations, the chief object of which has been the comparison of the influence of nutrition with that of selection, but which at the same time increase our knowledge about the influence of nutritive conditions as such. He investigated the influence of these two factors on the length of the fruit of *Oenothera Lamarckiana* and *Oenothera rubrinervis*, on the number of umbel-rays of *Anethum graveolens* and *Coriandrum sativum* and on the number of ray-flowers of *Chrysanthemum segetum, Coreopsis tinctoria, Bidens grandiflora* and *Madia elegans*. From his observations de Vries concludes that nutrition and selection act in the same direction and that by stronger nutrition as well as by positive selection the median value of a character is increased. Moreover he generally observes that the variability of the

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[1]) Hugo de Vries, Othonna crassifolia, Bot. Jaarb. Dodonaea, 1900, p. 20.

[2]) Hugo de Vries, Die Mutationstheorie. Bd. I, p. 368.

characters is increased when nutrition and selection act in opposite directions, i. e. when, as in his experiments, strong nutrition goes together with negative selection.

Also the experiments by Reinöhl [1] on the variability of the number of stamens of *Stellaria media* show that with good nutrition the median of this character possesses a higher value than with bad nutrition. Besides Reinöhl finds that the index of variability, which is a measure for the variability, becomes smaller under unfavourable nutritive conditions.

Weisse [2] investigated the influence of nutrition on various characters of *Helianthus annuus* and found that the arithmetical mean for all the characters studied is smaller with plants cultivated on a sandy soil than with well-fed plants. His numbers, (for each culture about forty) are too small, however, to allow us to calculate the constants for median and variability from them and to draw conclusions from these.

Mac Leod [3] made experiments in order to determine the influence of nutrition on the number of ray- and disk-flowers of *Centaurea Cyanus* and found that this number is the smaller the more the nutritive conditions are unfavourable. Besides he investigated the influence of good and bad nutrition on the number of stigmatic-rays of *Papaver Rhoeas coccineum aureum*. He arrived at the result that with the badly-fed plants the median is considerably smaller, but that the variability of the character is increased by the bad nutrition.

From this short summary it will appear that in very few cases only the quantitative change, caused in the median by varying nutrition, has been determined. It is desirable to extend the number of observations on this point, but it is especially important to learn the influence of nutrition on the variability for several characters and plants. Two questions here arise, in the first place whether this influence is different for different parts of the same plant, in agreement with Verschaffelt's [1] result that the variability itself of diffe-

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[1] Friedrich Reinöhl, Die Variation im Andröceum der Stellaria media Cyr. Bot. Zeit. 1903, p. 159.

[2] Arthur Weisse, Die Zahl der Randblüthen an Compositenköpfchen in ihrer Beziehung zur Blattstellung und Ernährung. Jahrb. f. wiss. Bot. Bd. 30, 1897, p. 453.

[3] J. Mac Leod, On the variability of the disk- and ray-flowers in the cornflower (*Centaurea Cyanus*). Hand. v. h. 3de Vlaamsch Nat. en Geneesk. Congres, Sept. 1899, p. 61 (in Dutch) and On the variability of the number of stigmatic-rays in *Papaver*. Hand. v. h. 4de Vlaamsch Nat. en Geneesk. Congres, Sept. 1900, p. 11 (in Dutch).

[1] Ed. Verschaffelt, Ueber graduelle Variabilität von pflanzlichen Eigenschaften. Ber. d. d. bot. Gesellsch. Bd. XII, 1894, p. 350.

rent parts differs considerably, and secondly whether bad nutrition causes either an increase or a decrease of the variability for all characters, or an increase for some and a decrease for others.

With the object of answering these questions, I made some culture experiments in the botanical garden at Groningen in the summer of 1903. The description and results of these experiments will be found in what follows.

For the cultures four beds of 2 metres breadth and 6 metres length were prepared in April. Two of them were manured with hornmeal, about half a kilogram per square metre. The other two beds were dug out to a depth of about half a metre and filled with a very meagre loamy sandsoil, originating from Harendermolen, a sandy region in the neighbourhood of Groningen. In the middle of April on one of the manured beds and on one of sandy soil equal quantities of seed were sown of *Iberis amara Linn.*, obtained from HAAGE and SCHMIDT at Erfurt, *Ranunculus arvensis Linn.*, obtained from various botanical gardens and mixed, and of *Malva vulgaris Fr.* (*Malva rotundifolia Linn.*), obtained from the botanical garden at Leiden. The seeds of three other species, which were sown at the same time on the remaining two beds, did not germinate in sufficient numbers, so that about the middle of June we resolved to weed them all out and to sow afresh. This time *Anethum graveolens Linn.*, from the trade, *Scandix Pecten-Veneris Linn.* and *Cardamine hirsuta Linn.*, both obtained from various botanical gardens were chosen, three species of which it might be expected that, although sown so late in the summer, they might still fully develop. This seed was sown in germinating dishes, each species partly in meagre and partly in fertile earth taken from the beds in the garden. In the course of the following days part of the germplants were placed into small pots with meagre as well as with manured earth, special care being taken that no selection from the germplants should be made. At the middle of July the young plants were placed in the beds at such distances from each other that each could freely develop.

Already at the beginning a considerable difference between the two cultures could be observed in all three species sown in the garden. The seed in the bed that had been manured with hornmeal came up sooner and the plantlets developed much more vigorously. With *Malva vulgaris* the difference between the plants of the two beds was at first very great. Those on the fertile soil showed already abundant leaves and flowers when the plants on the sandy soil had only formed few and small leaves. This difference remained till the beginning of July, when suddenly also the plants on the meagre soil began to develop vigorously, so that in the autumn scarcely any difference could be observed. The reason of this late, very rapid development appeared when the plants were dug out. It turned out, namely, that some of the strongest roots had reached the underlying earth through the layer of sand. As long as the plants only obtained their food from the sand, they remained tiny and backward, but when the roots had penetrated into the fertile earth they still developed vigorously and with great rapidity. Also with *Iberis amara* the roots appeared to have reached the earth underneath but in a much less degree. It was difficult here to trace the fine terminals of the principal roots as far as the underlying earth, whereas the roots of *Malva vulgaris*, where they passed from the sand into the earth below, were strong and penetrated at least a few decimetres. Of *Ranunculus arvensis* only few roots had reached the underground with their tips, the same being the case with *Scandix Pecten-Veneris* and *Anethum graveolens*; the roots of *Cardamine hirsuta* were restricted to the sand, as far as I could see.

Although with most of the species studied the nutrient material was not entirely derived from the sandy soil, yet all these plants were in less favourable nutritive conditions than the plants on the manured soil. So the experiments will show us the consequences of the difference in nutrition.

For the investigation I chose some characters that are easily expressed quantitatively and numerically and took care that the determination was made at the same time for both cultures and that the same parts of both were always taken.

In this way I determined in the first place the length of the leaf of *Iberis amara*. In July the length of the five oldest leaves, which were already adult then, was measured. Besides in the autumn, after the plants had been dug out, the length of the plant was determined from the base to the top of the inflorescence of the principal stem; at the same time were counted the number of branches of the second order, the number of branches of the third order and the number of fruits on the inflorescence of the principal stem.

Of *Malva vulgaris* the number of akenes of the schizocarp, the length of the leaf-blade and the length of the leaf-stalk were determined. These countings and measurements were made in the beginning of July, when a very distinct difference in the development between the two cultures was visible, hence probably before the roots of the plants on the meagre soil had penetrated the layer of sand, and in any case before a better nutrition had any perceptible effect.

In the case of *Anethum graveolens* and *Scandix Pecten-Veneris* the number of lobes of the first leaf was counted in the plants that had survived in germinating dishes. Besides I determined in adult plants of *Scandix Pecten-Veneris* the number of umbel-rays and with *Anethum graveolens* also the number of umbel-rays and at the same time the number of flowers of the umbellet. For the determination of this latter character only the umbellets of the oldest umbel of each plant were taken. Of *Ranunculus arvensis* the number of fruits per flower was determined and of *Cardamine hirsuta* the length of the silique, of each plant the siliques of the principal stem being measured.

For each of the characters mentioned I took of each of the cultures on fertile soil and on sandy soil 300 measurements or countings, a number which, according to the calculations of Prof. Kapteyn, gives in investigations of this kind a sufficient guarantee of accuracy. For certain characters I had to be contented with a smaller number since the material in these cases was deficient. For those cases in which the variability concerns the number, the numbers were noted increasing by unity; for those characters that vary in length, the length was determined in fractions of a millimetre, in millimetres or in centimetres, depending on the absolute size of the parts. By means of the numbers obtained, curves were plotted in order to have a general survey of the observations and to facilitate a comparison of the observations of the culture on fertile soil with that on sandy soil. In most cases the observations were combined into groups, so that from seven to seventeen intervals were obtained. In this way curves are obtained that admit of easy inspection and in which the smaller irregularities have disappeared. Only for the number of branches of the third order of *Iberis amara*, fig. V, the observations of the plants on the fertile soil had to be combined to 28 groups, since only then a comparison with the plants from the sandy soil was possible.

The curves for the various characters are reproduced on the accompanying plate. Since for all cases the frequencies have been calculated, all the curves have the same area and can be mutually compared. For each character the curve of the well-fed plants has been drawn as a continuous line and that of the badly-fed plants as a dotted one, both having the same absciss. Of both the observations have been combined to groups with the same interval. In all the figures the size or the number of the part in question increases from left to right.

These curves now show us the way in which the studied characters vary and the limits of this variation.

Looking at the various figures we notice that the studied characters generally give fairly symmetrical curves, disregarding smaller irregularities. Only in a few cases, as with *Anethum graveolens* for the number of umbel-rays of plants on the sandy soil, fig. VI, for the number of lobes of the leaves of the well-fed plants, fig. VIII, and besides for the number of lobes of the leaves of *Scandix Pecten-Veneris* of the fertile soil, fig. IX, the curve is markedly oblique. Only for the number of branches of the third order of *Iberis amara* from the sandy soil, fig. V, a semi-curve has been obtained.

Examining in the various figures the position of the two curves with respect to each other, it appears that they partly coincide. This means that in the two corresponding cultures plants are found in which the organ under consideration is as large or occurs in equal number in the well-fed and in the badly-fed plants. But at the same time they show that in one culture individuals occur, in which a definite part is so strongly or feebly developed, as are not to be found in the other cultures. The figures further show that in all cases except of the number of akenes of *Malva vulgaris*, fig. XIII, the curve of the plants on sandy soil has been shifted to the left with respect to that of the well-fed plants.

The observations now enable us to determine how great the influence of the nutritive conditions is in the various cases and whether this difference in development between the two cultures is the same for various parts of the same plant.

Examining the figs. I—V, relating to the characters of *Iberis amara*; figs. VI—VIII of *Anethum graveolens* and XI—XIII of *Malva vulgaris* it appears that, whereas with the two former plants the shifting of the curve is very different in the various cases, it is about the same for the three characters of *Malva vulgaris* and for all three of them relatively small. So the curves enable us to form an approximate idea of the influence of various nutritive conditions, but a clear insight is only obtained when the curves are defined by definite constants and these are mutually compared. In this way it is possible to determine what influence feeding has not only on the median value of the character, but also on its variability. In order to obtain these values, the median value M and the quartile Q were deduced from the observations. From these the coefficient of variability $\frac{Q}{M}$, which is a measure of the variability and enables us to mutually compare the variability of different characters, was calculated by the method introduced by VERSCHAFFELT[1]). Also for the

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[1]) ED. VERSCHAFFELT, l. c.

somewhat skew curves these values have been determined, since these curves do not considerably deviate from the symmetrical ones and besides, in all cases the average of both quartiles has been taken. Only from the semi-curve for the branches of the third order of *Iberis amara*, fig. V, no constants were calculated. This curve will be dealt with later on.

I give here the values found for the various characters in the plants studied in the same order as that of the curves of the plate. In the table, *G* means the constants of the well-fed, *B* those of the badly-fed plants. For each character are given: the median value, the quartile, the variability-coefficient and the minimum and maximum value. Besides the differences of these values in the well-fed and the badly-fed plants have been calculated as well for the median as for the variability-coefficient. This difference, divided by the value for the well-fed plants and consequently expressed as a fraction of this value, I will call the *sensibility-coefficient* of the median or the variability. This coefficient is given in the table under the two values. A + sign for the sensibility-coefficient means that the value is greatest with the well-fed plants, a — sign that with these the value is smallest.

It appears from this table as well as from the curves that in general the median value of the characters of the badly-fed plants is smaller than of the well-fed ones. Only with *Malva vulgaris* the median value of the number of akenes of the plants from the sandy soil is slightly larger, the difference being very small, however. The sensibility-coefficient is only — 0.015. With the remaining characters the sensibility-coefficient of the median is positive and differs very much; on the whole it varies between 0.015 and + 0.54.

Let us now see from the table whether nutrition has the same influence on the median value of the different characters of the same species. We shall leave *Malva vulgaris* out of account here since, as was mentioned above, its roots had in the bed of unfertile earth penetrated into the fertile underground and possibly on this account the differences were very slight for all the characters considered. Comparing the sensibility-coefficients of the median of the various characters of one species, we find that they diverge largely.

While the sensibility-coefficient of the median of the number of branches of the second order of *Iberis amara* is + 0,54, it is + 0,15 for the number of silicles of the principal stem; the sensibility-coefficients of *M* for the length of the plant and the length of the leaf lie between these values and amount to + 0,24 and + 0,28. With *Anethum graveolens* the sensibility-coefficient of the median of

		M	Q	$\frac{Q}{M}$	Minimum.	Maximum.
Iberis amara.						
I. Length of the plant	G	41.1 cM.	4.65 cM.	0.114	26 cM.	56 cM.
	B	31.3 »	3.25 »	0.103	12 »	51.8 »
	sensibility coefficient...	+ 0.24		+ 0.09		
II. Length of the leaf	G	7.9 cM.	1.085 cM.	0.137	4.5 cM.	14.2 cM.
	B	5.18 »	0.825 »	0.160	2.3 »	8.5 »
	sensibility coefficient...	+ 0.28		— 0.17		
III. Number of silicles	G	55.4	7.5	0.13	29	91
	B	47	6.8	0.14	11	118
	sensibility coefficient...	+ 0.15		— 0.08		
IV. Number of branches of the 2d order	G	22.4	3 35	0.15	5	35
	B	10.3	3.75	0.36	0	22
	sensibility coefficient...	+ 0.54		1.40		
Anethum graveolens.						
VI. Number of umbel-rays	G	32.8	6.40	0.19	15	59
	B	18.4	6.45	0.35	7	41
	sensibility coefficient...	+ 0.44		— 0.74		
VII. Number of flowers in the umbellet.	G	33.3	6.55	0.19	1	67
	B	26.5	5.7	0.21	4	45
	sensibility coefficient...	+ 0.20		— 0.105		
VIII. Numb. of lobes of the first leaf.	G	18	3.25	0 18	9	40
	B	16.5	2.4	0.127	7	28
	sensibility coefficient...	+ 0.08		+ 0.29		

		M	*Q*	$\frac{Q}{M}$	Minimum.	Maximum.
Scandix Pecten-Veneris. IX. Number of lobes of the first leaf..	*G*	27.2	3.85	0.14	16	56
	B	25.1	2.6	0.104	11	43
	sensibility coefficient ..	+ 0.08		+ 0.26		
X. Number of umbel-rays........ ...	*G*	6.05	0.7	0.101	3	10
	B	5.03	0.55	0.100	4	7
	sensibility coefficient...	+ 0.17		+ 0.01		
Malva vulgaris. XI. Length of the blade	*G*	53.8 mM.	3.85 mM.	0.071	40 mM.	65 mM.
	B	51.9 »	3.95 »	0.075	30 »	70 »
	sensibility coefficient...	+ 0.03		— 0.055		
XII. Length of the leaf-stalk.......	*G*	172.4 mM.	15.4 mM.	0.089	128 mM.	289 mM.
	B	167 »	13.65 »	0.081	115 »	244 »
	sensibility coefficient...	+ 0.03		+ 0.09		
XIII. Number of akenes........	*G*	13.38	0.7	0.05	9	17
	B	13.6	0.6	0.044	11	17
	sensibility coefficient...	— 0.015		+ 0.12		
Ranunculus arvensis. XIV. Number of akenes........	*G*	8.5	0.75	0.09	5	12
	B	6.9	0.775	0.11	4	11
	sensibility coefficient...	+ 0.19		— 0.22		
Cardamine hirsuta. XV. Length of the silique..........	*G*	17.5 mM.	2.75 mM.	0.15	4 mM.	24.1 mM.
	B	14.7 »	2.75 »	0.19	3.2 »	23.2 »
	sensibility coefficient...	+ 0.16		— 0.27		

the number of umbel-rays is + 0,44, that of the number of lobes of the first leaf only + 0,08. To some extent this may be explained by the circumstance that the influence of nutrition on the first leaf is not so great as on characters which appear later, since the food, stored in the seed, is the same for both cultures and possibly has not been entirely used when the first leaf develops. In agreement with this the sensibility-coefficient of the median of the number of lobes of the first leaf of *Scandix Pecten-Veneris* is + 0,08, whereas it is + 0,17 for the number of umbel-rays of the same plant.

From what precedes it will be seen that the influence of nutrition of the median value of different characters of the same plant varies greatly, some organs being very sensitive for differences in nutrition, others experiencing little difference in their development on this account.

Concerning the value of the quartile the table shows that we do not obtain in all the cases studied, a variation in the same sense by bad nutrition, as was the case with the median value. In some cases Q is greater in the plants from the fertile soil, in other cases it is smaller, as great or nearly as great as with the plants from meagre soil. In order to be able to compare the variability of the characters in both cultures, however, and to draw conclusions from this comparison about the influence of nutrition on the degree of variability, we must not take the quartile but the variability-coefficient $\frac{Q}{M}$.

If, to begin with, we consider the value of this variability-coefficient in the various cases, we see from the table that it varies between wide limits 0,044 and 0,36. Also VERSCHAFFELT [1]) found equally divergent values of $\frac{Q}{M}$ for the characters of different plants studied by him. The smallest variability is found with the different characters of *Malva vulgaris*, as well in the well-fed as in the badly-fed plants. Hence this plant appears to be little variable. Comparing the variability of the different characters of the same species with each other, we see that they diverge relatively little with the well-fed plants, as well with *Iberis amara*, as with *Anethum graveolens* and *Malva vulgaris*. For the different characters of *Iberis amara* $\frac{Q}{M}$ is respectively 0,114, 0,137, 0,13, 0,15; for *Anethum graveolens* 0,19, 0,19 and 0,18 and for *Malva vulgaris* 0,071, 0,089 and 0,05.

It will be seen that for the same species these values are nearly

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[1]) VERSCHAFFELT, l. c. p. 353.

the same, while they differ considerably among the three species. Doing the same with the badly-fed plants we find a much greater difference between the variability-coefficients of the various characters of the same plant. For this culture $\frac{Q}{M}$ varies between 0,10 and 0,36, for the characters of *Iberis amara* and between 0,127 and 0,35 for those of *Anethum graveolens*. Hence it follows that the influence of nutrition on the variability of the different properties of a plant is not the same; how much this influence varies will be seen from what follows.

Comparing for each character separately the variability of the well-fed with that of the badly-fed plants, we find that the difference between the variability-coefficients for the two cultures varies greatly in different cases; for some characters it is very considerable, for others small. In order to compare these differences, they were divided by the value of $\frac{Q}{M}$ of the well-fed plants, as stated. The resulting number is the sensibility-coefficient of the variability. This sensibility-coefficient of $\frac{Q}{M}$ appears to vary between $-0,140$ and $+0,29$. In a comparison of various characters of the same species the fact that the roots of the bad culture had more or less penetrated into the subsoil, obviously is of no consequence, so that the results obtained with *Malva vulgaris* are also available here.

The sensibility-coefficient of $\frac{Q}{M}$ of *Iberis amara* is for the four characters respectively $-1,40$, $-0,17$, $-0,08$ and $+0,09$; for the characters of *Anethum graveolens* $-0,74$, $-0,105$ and $+0,29$; and for those of *Malva vulgaris* $-0,055$, $-0,09$ and $+0,12$. Especially with the first two plants these sensibility-coefficients diverge considerably, which proves how very different the influence of nutrition is on the variability of the different characters of a plant. By the same change in nutrition the variability of one character is hardly modified at all and that of another character of the same plant very considerably increased or diminished.

It is very important to know in what direction the nutrition reacts on the variability, whether under unfavourable nutritive conditions the variability is either always greater, or generally smaller or whether the two cases are equally frequent. In this respect the table shows us that for 6 out of 14 characters the sensibility-coefficient of $\frac{Q}{M}$ is positive and the variability-coefficient of the well-fed plants greater than of the badly-fed ones, whereas in the other characters the sensibility-coefficient is negative and the variability-coefficient greatest in the badly-fed plants.

Even with the same species one character shows a greater, another a smaller variability when the cultures grown under favourable and unfavourable nutritive conditions are compared. With *Iberis amara* the length of the plants from the fertile earth is more variable than that of the plants from the sandy soil, other characters, on the other hand, show greater variability in the badly-fed culture. In the same way in *Anethum graveolens* the variability is greatest with the number of lobes of the well-fed plants and with the number of flowers and umbel-rays of the badly-fed ones, while with *Malva vulgaris* the length of the leaf-stalk and the number of akenes of the well-fed plants, but, on the other hand, the length of the blade of the plants from the sand, show the greatest variability.

Summarising the results obtained, we see that nutrition influences the median value and the variability of the characters. Besides it appears that the sensibility-coefficient of the median is very different:

1. for different species compared among each other.
2. for different characters of the same species.

And about the variability we saw:

1. that with good nutrition the variability-coefficient $\frac{Q}{M}$ is fairly constant for different characters of the same species, but very divergent for the different species.

2. that with bad nutrition two of the species studied show great differences between the variability-coefficients of the different characters of the same species, while with one species the variability-coefficients of the various characters diverge relatively little.

3. that the sensibility-coefficient of $\frac{Q}{M}$ diverges greatly for different species and characters and varies between $-1,40$ and $+0,29$.

4. that for some characters the sensibility-coefficient of $\frac{Q}{M}$ is positive and good nutrition results in an increase of the variability; while for other characters, even of the same species, this coefficient is negative.

In what precedes, there has only been question of those characters which show symmetrical or sensibly symmetrical curves and which, when expressed in constants, yielded the results mentioned.

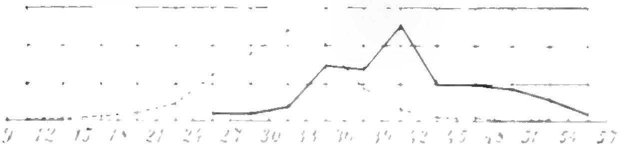
From these the curve of the number of branches of the third order of *Iberis amara*, grown on the sand, deviates entirely, being a semi-curve. For the culture on fertile earth, however, this same character gives a symmetrical curve. In fig. V this latter is very flat and extended in length, as the observations were divided over a great number of intervals in order to allow a comparison of the two curves. If, however, the observations are arranged to a number of groups equal to that of the other figures, the curve thus obtained is not different from those of the other characters. For this culture the median is 53, the quartile 17.25 and the variability-coefficient $\frac{Q}{M}$ 0.32, the minimum number of side-branches being 1, the maximum 162.

With this character now, bad nutrition does not result in a simple shifting of the curve to the left, accompanied by greater or smaller changes in the values of M, Q and $\frac{Q}{M}$, as in the other cases, but here the symmetrical curve changes into a semi-curve of which the apex lies at zero.

We can explain the origin of this semi-curve in the following way. The lower limit for the number of branches of the third order of *Iberis amara* is 0. Since the plant also blooms on the principal stem and on the branches of the second order, it may exist without branches of the third order. Under favourable nutritive conditions the development of the plant is so vigorous that in all individuals branches of the third order are formed, but in greatly diverging numbers, as is shown by the curve of fig. V for this culture. With unfavourable nutrition, however, also individuals arise in which no branches of the third order are originated and as nutrition becomes worse the number of these individuals will become greater. Hence we see that with the very bad nutrition of the sandy soil, a great number of plants has no branches of the third order and so has reached the lower limit, the other specimens bearing a greater or smaller number of these side-branches, as is shown by fig. V for this culture. This leads us to the conviction that the semi-curve for this character is a necessary consequence of the fact that by the unfavourable nutritive conditions the variation-curve is shifted in such a way that it strikes against the lower limit of the whole range of variation of this character, a great many of the individuals showing this lower minimum value.

Also with *Anethum graveolens* a great difference is noticed in the shape of the curves of the number of umbel-rays in the two cultures, fig. VI. The curve of the well-fed plants is nearly symmetrical, while

T. TAMMES. "On the influence of nutrition on the fluctuating variability of some plants."



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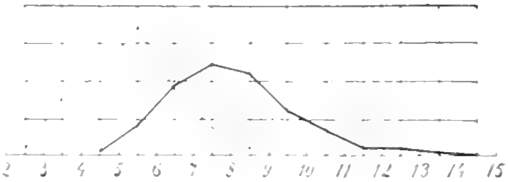

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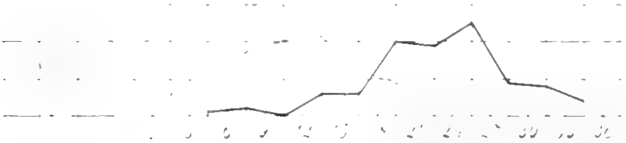

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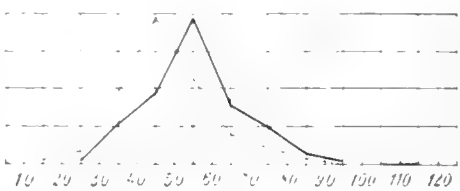

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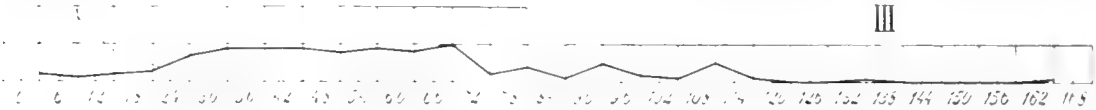

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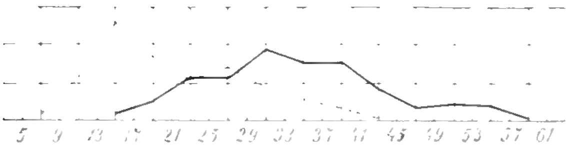

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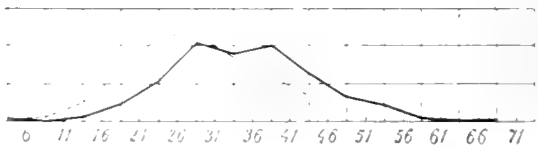

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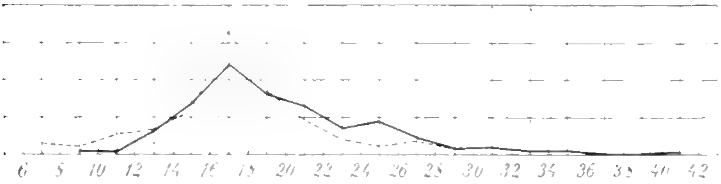

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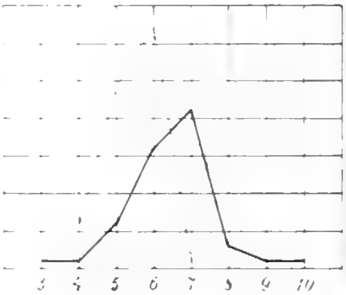

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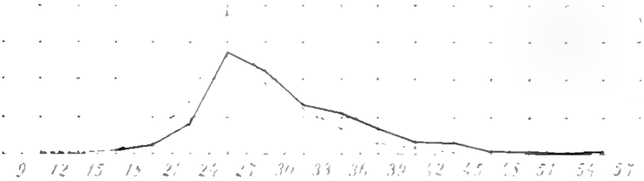

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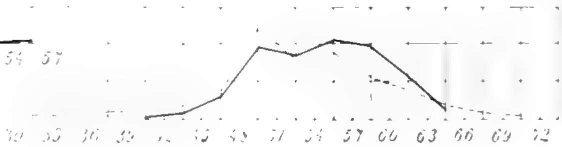

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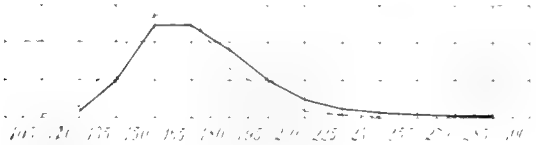

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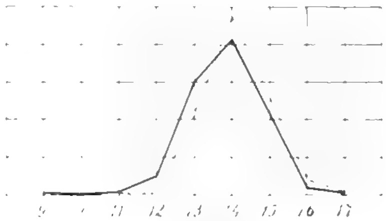

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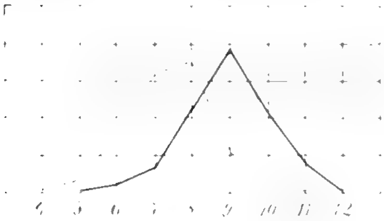

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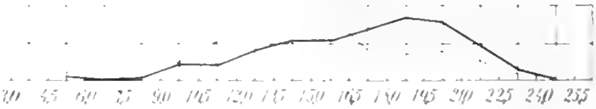

XV

that of the plants from the sandy soil is asymmetrical in such a way that the top of the curve lies nearer the minimum. It can not be stated with certainty whether in this case we have the same phenomenon as with *Iberis amara*, i.e. whether the lack of symmetry of the curve indicates that it has been shifted to the proximity of the lower limit. But the fact that the minimum now obtained, viz. 7, is already very small compared with the maximum 41 and that this lower limit cannot be zero, renders this view probable. Yet we must bear in mind in cases like the present, that the appearance of an asymmetrical curve need not in general be a proof that the curve is located near one of the limits of the range of variation, but that the asymmetry of the curve may also be the consequence of entirely different causes.

Botanical laboratory at Groningen. July 30, 1904.

EXPLANATION OF THE FIGURES.

The figures are all reproduced at about half size. In the original figures the distances of the intervals, placed along the absciss, are 1 cm., each mm. of the ordinates having a value of $1^0/_0$. So we can find from the length of the ordinates the percentage number for each interval. In most figures the ordinates are drawn between the two numbers indicating the interval, only in figs. X, XIII and XIV, where the observations are not arranged in groups, the ordinates stand above the number. The curves of the well-fed plants are drawn in continuous lines, those of the badly-fed plants are dotted.

Fig. I. *Iberis amara.* Length of the plant from the base of the principal stem to the top of the inflorescence of this latter, in cm.
" II. *Iberis amara.* Length of the leaf, in cm.
" III. *Iberis amara.* Number of silicles of the inflorescence of the principal stem.
" IV. *Iberis amara.* Number of branches of the second order.
" V. *Iberis amara.* Number of branches of the third order.
" VI. *Anethum graveolens.* Number of umbel-rays.
" VII. *Anethum graveolens.* Number of flowers in the umbellet.
" VIII. *Anethum graveolens.* Number of lobes of the first leaf.
" IX. *Scandix Pecten-Veneris.* Number of lobes of the first leaf.
" X. *Scandix Pecten-Veneris.* Number of umbel-rays.
" XI. *Malva vulgaris.* Length of the leaf-blade, in mm.
" XII. *Malva vulgaris.* Length of the leaf-stalk, in mm.
" XIII. *Malva vulgaris.* Number of akenes of the schizocarp.
" XIV. *Ranunculus arvensis.* Number of fruits per flower.
" XV. *Cardamine hirsuta.* Length of the silique, in mm.

Botany. — Prof. J. W. MOLL presents the thesis for the doctorate of Mr. B. SYPKENS: "*On the nuclear division of Fritillaria imperialis L.*", and gives a summary of the results.

(Communicated in the meeting of October 29, 1904.)

The subject of this investigation is especially the nuclear division in the embryo-sac of *Fritillaria*, formerly a favourite material for investigations on the subject of nuclear division.

Mr. SYPKENS studied the free nuclear divisions in the parietal layer of protoplasm as well as the nuclear divisions in the first layer of endosperm-cells which are directly followed by tangential cellular divisions. Besides some observations were made on the nuclei in the ovules of *Tulipa* and in the growing-point of the root of *Vicia Faba*.

All the material was fixed by means of the strong chromo-aceto-osmic acid of FLEMMING. It was for the greater part imbedded in paraffin in various ways and was examined in series of sections of 2 to 4 μ thickness, stained with gentian violet. Some observations were also made by means of the method introduced by VAN WISSELINGH, in which the nuclei are dissolved in chromic acid of about $50^0/_0$. These two methods supplement each other; the chromic acid method is to be preferred for observations about the chromatic parts, sections give more information about the nuclear spindle. But in this investigation the excellence of both methods was again proved as compared with the observation of the nucleus as a whole, which in many cases renders it impossible to form an accurate idea about its internal structure.

I will briefly mention the chief results obtained by Mr. SYPKENS for the various stages of nuclear division.

The resting nucleus was studied by means of sections and of chromic acid and the results so obtained were in the main a complete confirmation of the results published by VAN WISSELINGH and by GRÉGOIRE and his co-workers WYGAERTS and BERGHS. The framework of the resting nucleus consists of numerous larger and smaller lumps of chromatin, connected by fine threads so that an anastomosing network is formed. There is no reason for assuming in this network the existence of two constituents, chromatin and linin; the chromic acid method as well as coloured nuclear sections show the contrary, if only partial washing out of the stain is prevented, as Mr. SYPKENS did. Those who wish to maintain the assertion about the existence of linin-connections will have to bring forth new and valid proofs.

Also for the nuclei of the integuments and nucellus of *Fritillaria* and of the ovules of *Tulipa* the same results were obtained.

Concerning the individuality of the chromosomes VAN WISSELINGH has shown that it exists in the spirema, since at that stage a continuous thread is never found. But his further observations as well as those of GRÉGOIRE and WYGAERTS indicate that probably, even in the resting stage, this individuality never entirely disappears. Mr. SYPKENS was led to the same conviction by his observations about the formation of the spireme and of daughter-nuclei from the daughter-spiremes. He speaks of a "centralisation and decentralisation of a number of chromatine masses, which in certain stages form as many chromosomes."

About the behaviour of the chromosomes during the process of division little that was new could be found in this investigation for the reason mentioned. The number of chromosomes was fixed at about 60, but in certain nuclei it decidedly is much smaller. Neither is the shape of the chromosomes constant; in the same nucleus *U*-shaped, as well as *V*- and *J*-shaped ones could be found.

The study of the nuclear spindle on the other hand gave important results, not so much about the formation of the spindle as about its further history and the part played by it in cellular division.

The formation of the spindle could be followed in details. Round the free nuclei in the parietal layer of protoplasm of the embryo-sac granular protoplasm occurs with many very small adventitious vacuoles; round the nuclei of the first endosperm-cells also protoplasm with several small vacuoles. Now, when the nuclei begin to divide and the nuclear membranes are dissolved, the surrounding protoplasm penetrates into the nuclear space, at first without many vacuoles, and forms at the interior the spindle-threads, which at first consist of coherent granules and later become smoother. They gradually assume parallel directions and are connected to a bundle without strongly converging towards its poles. The nuclei are then in the spireme-stage. Later, in the aster-stage, besides the threads already mentioned, others are formed in exactly the same way, which grow thicker and only proceed from the poles to the equator, where they are attached to the chromosomes, which have been formed in the mean time. They are found not only at the circumference of the spindle, but also in the interior part of all the longitudinal sections of a nucleus. STRASBURGER has called the former sort of threads, running from pole to pole, "Stützfasern", the shorter and thicker ones "Zugfasern".

Now metakinesis follows and in the dyaster-stage a separation of the two sorts of spindle-threads has taken place. The shorter and thicker ones have much contracted and form at both poles, adjacent to the daughter-nuclei, two small caps which soon disappear in the protoplasm. The long threads on the other hand remain between the daughter-nuclei, extending from one to the other and hence are often called connecting threads. They occur in numbers from 200 to 300 and cross-sections show that they form a massive bundle lying free in the surrounding protoplasm, which can freely penetrate between them.

Hence Mr. SYPKENS arrives at the conclusion that the nuclear spindle is entirely formed from the cytoplasm within the nuclear space and so agrees with what has been found by most other investigators and on main points also with the results obtained by STRASBURGER and HEUSER for the nuclei of *Fritillaria*.

Now with regard to the part played by the nuclear spindle in cell-division zoologists and botanists have divergent views. Concerning animal cells the general opinion is that the nuclear spindle is dissolved in the cytoplasm after the nuclear division has been completed and takes no active part in cell-division, the cell subsequently dividing by constriction. Botanists on the other hand, attach great importance to the spindle in cell-division and especially in the formation of the wall. Their generally accepted representation is that the above-mentioned connecting threads of the spindle grow thicker in the equatorial plane and form so-called dermatosomes. By fusion of the dermatosomes the so-called cell-plate is then formed, which subsequently participates in some way or other in the formation of the new cell-wall between the nuclei. STRASBURGER is one of the chief representatives of this much spread conception.

It is a consequence of the fact that the study of this phenomenon has for the greater part taken place with nuclei that were seen from the outside. By means of his sections Mr. SYPKENS was enabled to prove that, for the objects studied by him, the opinion now prevailing in botany is incorrect and that, at any rate as far as the behaviour of the nuclear spindle is concerned, the phenomena have great resemblance with those of animal cells.

In describing the later phases of the nuclear spindle it is desirable to distinguish three different cases of nuclear division. In the first place we have the free nuclear divisions in the parietal layer of protoplasm of the embryo-sac of *Fritillaria*, which will be followed by still other nuclear divisions before there is question of cell-divisions. Here in the beginning a system of connecting threads between the daughter-nuclei appears, as in all other cases, but this soon becomes narrower at the equator and so assumes the shape of an hour-glass and is then absorbed in the protoplasm and disappears. So this case needs no further consideration.

The second case regards the parietal layer of protoplasm of the embryo-sac, which has already become partly divided into cells. Now when here also free nuclear divisions take place, the nuclear spindle, consisting of connecting threads, behaves at first in exactly the same manner as in tissue-cells in which the cell-division follows immediately: the system of connecting threads swells laterally and forms a so-called nuclear barrel. After this, however, the spindle here is also lost in the protoplasm and not until later one sees successive divisions take place between these nuclei, progressing regularly from that part of the parietal layer of protoplasm that is already divided into cells, so that finally a complete pavement of endosperm-cells is formed from the protoplasm. This description renders the existence of a connection between the nuclear spindle and cell-division not very probable.

The most important case is the third, in which the just-mentioned endosperm-layer divides into two layers of cells by tangentially directed walls. Here the nuclear divisions are immediately followed by cell-divisions, in the same way as in the formation of various sorts of tissues.

Hence this case, as was proved by comparative observations, must be considered as completely analogous with what happens in the cells of the growing-point of the roots of *Vicia Faba*.

From Mr. SYPKENS' sections it appears that in the two latter cases the connecting threads soon cease to deserve that name, as their extremities are not attached to the daughter-nuclei but end freely in the protoplasm. In *Vicia Faba* moreover, the equatorial parts are soon dissolved so that the system of connecting threads falls asunder into two halves.

Meanwhile the protoplasm round the nuclei of the parietal layer of protoplasm penetrates with its small adventitious vacuoles into the space between the daughter-nuclei where the massive complex of connecting threads is found. These threads are consequently forced asunder towards the circumference and thereby united to spindle-shaped bundles, which lie free in the protoplasm; they form what is usually called the nuclear barrel. The result is that the two daughter-nuclei are at last separated from each other by the same granular protoplasm, which also surrounds them and in which also the remains of the connecting threads are found. The spindle-shaped complexes, formed from these, are united to a barrel-shaped, equatorially swollen, cylindrical mantle, which, if the nuclei are only observed from the outside, still seems to join them, although in reality this is no longer the case by any means. On the contrary, the remains of the connecting threads gradually disappear as if they were dissolved in the protoplasm and this process has long been completed when the cell-walls successively appear between these nuclei also.

Also in the divisions of the endosperm-cells of *Fritillaria* and in the root-tip of *Vicia Faba* mainly the same occurrences take place although there are some points of difference to which I shall refer presently, and although the formation of the cell-wall follows sooner here.

How this wall-formation takes place has for the present not been investigated by Mr. SYPKENS, but that it stands in no relation to the nuclear spindle or to a cell-plate formed by it, is pretty clear from what precedes. A cell-plate in the sense of botanical authors does not even occur.

Although the opinion, so generally spread in botany, that in many cases the formation of cell-walls is dependent on nuclear spindles, may have a certain probability when we only think of the cross-divisions of the cells of growing-points and suchlike, it lacks, generally speaking, every foundation. For any one knows that the formation of cell-walls can in many cases have nothing to do with a nuclear spindle. Not to mention all possible cases of thickening of the cell-wall which do not correspond to the formation of a primary membrane, I will only mention zoospores which, after having come to rest, form a wall; plasmolysed protoplasts of *Spirogyra* and other Algae which cover themselves with a new cell-wall; *Caulerpa* and other Coeloblasts, the protoplasm of which after a lesion produces a new wall-piece.

But also in other cases, which resemble more the cell-divisions in growing-points, it is often easy to show how newly-formed cell-walls cannot possibly have been formed in the nuclear spindle. I mention the antipodal cells, which so frequently are formed projecting inwardly in the embryo-sac connected only for a small part of their surface with the cell-wall of the embryo-sac; in any case no more than a small part of the free wall-surface can have been formed here in a nuclear spindle. A corresponding case is that of the U-shaped walls in the epidermal cells of the leaves of ferns, by which the mother-cells of stomata are formed. More clearly still one sees the same thing in the formation of the stomata of *Aneimia fraxinifolia*: the stomata lie in the middle of an epidermal cell of the leaf and the nucleus of this cell is still pressed against the stoma. A nuclear division has taken place here before the stoma-mother-cell was formed in the epidermal cell, and between the two cells so formed there certainly was a spindle at first. But in the subsequent cell-division a cylindrical wall was formed at a certain distance round one of the nuclei, which consequently could for a small part only have been formed in the spindle. Finally we have the formation of the first pavement of endosperm-cells from the parietal layer of protoplasm of the embryo-sac as well in *Fritillaria* as in many other plants. When the number of nuclei of this layer of protoplasm has very greatly increased, separations between the nuclei arise, so that a layer of flat, pentagonal or hexagonal cells is formed, which at last are separated from each other by cell-walls. These cell-walls are formed at a period when of the originally present nuclear spindles no trace is left.

In relation with these facts the result of Mr. SYPKENS about the negative part played by the nuclear spindle in cell-division cannot surprise us and it even gains in inner probability by them. This result also shows the way to a more profound study of the phenomena of cell-division and wall-formation in the vegetable kingdom. The cell-divisions in growing-points, in the above-mentioned epidermal cells of ferns, also in the parietal layer of protoplasm of the embryo-sac, must now be more closely investigated, preferably by the method applied by Mr. SYPKENS, and important results may be expected of this investigation. Also the study of living, dividing cells, in the same sense as was formerly done by TREUB [1]) deserves again our attention in this respect.

It is by no means impossible that by such investigations the conception of cell-division in plants will come still nearer to that of the same phenomenon in animals than is the case at present.

From all that precedes it appears that the nuclear spindle is formed entirely from the cytoplasm and returns to it. Besides, all investigators agree that in nuclear division the nuclear membrane and the nucleoli are dissolved and later are formed anew in the daughter-nuclei. An uninterrupted individual position with regard to the cytoplasm is consequently, among all the parts of the nucleus, occupied by the chromosomes alone, only here there is question of a hereditary organisation.

The opinion of some authors that the nucleus during the whole process of division would form an isolated whole with respect to the cytoplasm and that at first there would be a sort of vesicle, joining the daughter-cells and separating the spindle from the cytoplasm, must consequently be abandoned.

In relation with this I may briefly point out the complete agree-

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[1]) M. TREUB, Quelques recherches sur le rôle du noyau dans la division des cellules végétales. Publié par l'Académie Roy. Néerl. des Sciences. 1878.

ment between the results of Mr. SYPKENS and the theory of DE VRIES and WENT, which looks upon the vacuoles as hereditary organs of the protoplast. If the nucleus were, during division, an isolated whole, the question about the origin of the vacuoles, present inside the spindle, would perhaps give some difficulty. But we saw, how the observations of Mr. SYPKENS prove that we have here ordinary vacuoles, already present in the granular protoplasm and which are shoved in between the spindle-threads from the outside with the protoplasm.

Yet it will be desirable to give some nearer information about this process, since two somewhat divergent cases occur and here again a distinction must be made between the nuclear divisions in the parietal layer of protoplasm of the embryo-sac and those in the first endosperm-layer or in the meristem of the roots of *Vicia*.

In the latter cases, in which ordinary division of tissue-cells takes place, Mr. SYPKENS observed what follows. In these cells there are a number of vacuoles, which are about equivalent and lie round the nucleus in the granular protoplasm. After nuclear division this protoplasm with its relatively large vacuoles, penetrates into the spindle between the connecting-threads, as we saw above. This penetration here occurs as well in the equator as more in the neighbourhood of the daughter-nuclei. Hence it is the ordinary vacuoles of the mother-cell, which shove in between the daughter-nuclei with the protoplasm in which they lie. Later, when the connecting-threads have been dissolved and cell-division takes place, these vacuoles, as well as those which did not penetrate into the spindle, are divided equally between the two daughter-cells. So the question is here very simple and in complete accordance with what VAN WISSELINGH found in *Spirogyra*. Only in this latter case the mother-cell has not several equivalent vacuoles but a single large one which penetrates laterally into the nuclear spindle.

Somewhat different are the circumstances in the divisions of the parietal layer of protoplasm of the embryo-sac. This cell not only contains many nuclei but has also a somewhat different structure with regard to its vacuoles. It has namely one single large vacuole, filling the middle part of the cell, but besides in the parietal layer of protoplasm a great number of very small adventitious vacuoles, which were very conspicuous in the preparations of Mr. SYPKENS, stained without washing out of the stain. Now, after nuclear division, the granular protoplasm with its many adventitious vacuoles penetrates between the daughter-nuclei and the free extremities of the connecting threads. From there it penetrates further towards the equator between the connecting threads. Hence the daughter-nuclei are finally separated from each other by granular protoplasm with adventitious vacuoles of the embryo-sac. Now, when later the parietal layer of protoplasm divides into cells, the large embryo-sac vacuole does not partake in this process, but each newly formed endosperm-cell is provided with a certain number of adventitious vacuoles.

So there is a certain antithesis here with what happens in ordinary cell-divisions in young cells, but with the vacuole theory of DE VRIES and WENT this process also is in complete harmony, for WENT has shown that small adventitious vacuoles can occur in large numbers in all sorts of ordinary cells and can in all respects be compared with the large vacuole, from which they can also be produced by division. I should not be surprised if further investigation showed that their occurrence is much more general still than is now supposed.

The case met with in the embryo-sac of *Fritillaria* and many other plants stands by no means isolated, and is also met with in the division of other multinuclear cells. WENT mentions some cases of this kind in his investigation about the vacuoles of Algae. (*Chaetomorpha aerea, Acetabularia mediterranea, Codium tomentosum*).

I had an opportunity personally to observe a similar case of division in the formation of asexual zoospores in the cells of *Hydrodictyon utriculatum*. While the zoospores, which had been formed by division of the parietal layer of protoplasm, were partly in motion and partly had already arranged themselves to a network, all this inside the wall of the large mother-cell, I saw the middle part of this cell occupied by three great tonoplast vesicles, having their origin in the great central vacuole of the cell and which, upon being heated under the microscope, first shrank and then burst. Hence here, no more than in the embryo-sac of *Frittillaria*, the great central vacuole took part in the formation of new cells. That the zoospores were provided with very small vacuoles, present in the granular protoplasm, cannot be doubted according to the above-mentioned investigations of WENT. I also observed them very distinctly in the cells of the young nets very soon after their formation.

Finally it requires to be mentioned that the doctoral dissertation of Mr. SYPKENS will soon appear in a German translation in the second Part of Volume I of the Recueil des travaux botaniques Neerlandais.

Botany. — "*An investigation on polarity and organ-formation with Caulerpa prolifera.*" By Prof. J. M. Janse. (Communicated by Prof. Hugo de Vries).

(Communicated in the meeting of October 29, 1904).

Polarity is a property of very many of the lowest organisms as well as of a great part of the cells in the body of the higher plants and animals.

The regular exterior shape and internal structure of organs must be partly attributed to the agency of polar influences during their development, while the definite vital phenomena of organs must also, among other causes, be ascribed to polar actions of the constituent cells.

The cause of this polarity, i. e. the property of acting or reacting in a certain direction otherwise than in the opposite direction, is unknown, and the great difficulty of finding suitable material for investigation is perhaps the principal cause of this.

Former observations made with *Caulerpa prolifera* had convinced me [1]) that this unicellular, relatively gigantic and morphologically highly differentiated alga must be suitable for this purpose.

Having had the opportunity during last summer, of submitting this plant to a renewed investigation at the Zoological Station at Naples, I wish to relate briefly the principal results obtained.

For a description of the structure of *Caulerpa prolifera,* as well as of its protoplast and the very intense currents that take place in it, I refer to my quoted paper.

For the new experiments the "leaves" were exclusively used, namely the outgrowths of the "rhizome" measuring in extreme as much as 22 centimetres in length and 20 millimetres or a little more in breadth. Their little thickness allows us to examine them also microscopically in a living condition, while their considerable length and breadth make them particularly fit for experiments.' Moreover cut leaves or parts of leaves can form new rhizomes and rootlets and so can regenerate to complete plants by neo-formation.

Formerly already I used these leaves for experiments concerning the course of the protoplasm-currents, in which it was often required to make large incisions in the leaves.

These plants, to be true, often sustain serious lesions which heal

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[1]) Die Bewegungen des Protoplasma von *Caulerpa prolifera,* Pringsheim's Jahrb. f. wiss. Bot. 1889, Bd. XXI, pag. 163—284, with 3 plates.

in one day, but this is always accompanied by a great loss of protoplasm by which the cell is much enfeebled.

This time I succeeded in finding a new method in order to get at the same result, based on the observation that every laceration of a part of the numberless protoplasm-threads, which run through the whole plant as an extremely fine network, is immediately followed by the local secretion of a white, tough, wiry substance, which very soon becomes stiffer, assumes a bright yellow colour and then forms a perfect partition. If at the same time the cell-wall had been injured, the external wound is closed in this way. But the same laceration of the plasm-threads can be brought about by pressure and without external lesion; the partition is then restricted to the place where sufficient pressure was exerted. In this manner one can at any arbitrary point of the leaf produce, as it were, a cross-wall, to which any desired direction and length can be given. If one proceeds with care this partition is no broader than $^1/_4$ millimetre.

In this way one can also physiologically, namely without external lesion, divide a leaf into two or more parts.

This treatment, which in all respects has the same consequences as are observed with a wound, is not accompanied by weakening of the cell, since no protoplasm is lost, and besides the plant is already after a minute fit for further manipulations or for examination.

Caulerpa prolifera derives its specific name from the circumstance that the "leaves" which spring forth from the "rhizome" very often produce new leaves, prolifications. Especially by this circumstance I succeeded formerly in showing that, in accordance with DE VRIES' views, there exists also in this plant a direct relation between the intensity of the motion of the protoplasm in various places and that of the nutrition in these places. The bundles of protoplasm bands, coloured dark green by chlorophyl grains and very often visible to the naked eye, which pass from the stalk of the prolification into the primary leaf and then tend to the leaf-stalk of this latter were a very important aid in this investigation.

These bundles are lacking where very young prolifications are found and only gradually develop in the leaf, and in doing so always begin at the stalk of the prolification and extend towards the base of the leaf. These stream-bundles are never seen developing in the opposite direction, i. e. beginning at the leaf-stalk and extending towards the stalk of the prolification, neither do they proceed from the prolification to the top of the leaf. So they originate from above and tend downward.

Moreover if an existing prolification is cut off, one sees the bundles gradually disappear: this disappearance also proceeds from above downward.

Both phenomena point to the existence of a polarity in the regulation of the protoplasmic currents, of which the impulse proceeds in the direction from the organic top to the base.

If this stream-bundle is interrupted by a large cross-wound the communication is restored round the end of the wound. Now, however, the currents above and below the wound behave quite differently: the bands which proceed from the stalk of the prolification remain on the whole unchanged until they have arrived near the wound; they then partly deviate transversely and bend round the end of the wound, after which they go in a straight line to the leaf-stalk. Another part often turns back with a bend, namely if the currents are strong. So above the wound there occurs as it were a thrust and often a reflection which are entirely absent below the wound.

Also this difference in the course of the currents above and below the wound points to a polarity in the regulation of the protoplasmic currents, the impulse evidently here also proceeding from the top and being directed to the organic base.

We must add here in the first place that the currents, running in a non-proliferous leaf, which assemble like a fan from the top and the edge of the leaf and all pass into the leaf-stalk, behave in exactly the same manner, when interrupted, as the stream-bundle which proceeds from a prolification downward; only this latter is generally more powerful and so more suitable for experimenting.

Secondly we must remember that everywhere in the leaf there exists a very complicated network of currents, stretching between the numerous (± 800 per sq.mm.) cross-beams which join the two sides of the leaf; so there exists an almost straight, but little intensive connection between any arbitrary pair of points on the leaf; so when we speak here for simplicity's sake of the generation of currents, we mean the strengthening or thickening of the currents in such a way that they become visible with the naked eye or with the eye-glass.

Thirdly the protoplasm in all currents moves continually or alternately in both directions and this applies also to those which develop from above and to those which disappear from above.

Thus far my previous investigations had led me.

The renewed investigation was begun again with these experiments; they gave entirely concordant results.

As the experiments with cross-wounded leaves had shown that it is possible to deviate the large nutritive currents from their way and to cause them to assume a lateral direction, the question was

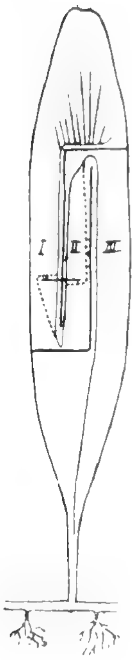

Fig. 1.

whether it would be possible to go farther still and to lead the current in an opposite direction.

Formerly already I had made similar experiments, which had given a favourable result, but there was reason to repeat them now on a more extensive scale.

The arrangement of the experiments was such that two internal partitions were produced forming two hooks, embracing each other, and the short arms of which extended as far as the edge of the leaf (fig. 1).

Hence the connection between top and base lay through the whole middle piece between the two longitudinal partitions and in this piece the development of the current would have to take place in a direction opposite to that in the normal leaf.

Now the experiments proved that indeed such a development, and thus so to say the "reversion", in this middle piece is possible, and that the typical direction of the currents is then, as indicated in the figure by the continuous line. The experiments proved besides:

1. that it takes a long time before by this route a powerful connection between top and base is formed, some weeks being required;

2. that the attempt is successful only when the distance between the cross-wounds is not too considerable, 25—50 mm. being the extreme limit;

3, that for success it is desirable that the impulse from above be powerful, which is the case, for example, if above the highest cross-wound one or more vigorous prolifications occur;

4. that the leaf always strongly opposes the reversion.

Concerning this latter point I must add what follows:

When a leaf of *Caulerpa* is cut off, either at the leafstalk or at a higher level, rootlets are formed at the cut piece and this nearly always exactly at the sectional plane i. e. at the organic lower side; a middle piece from the leaf does exactly the same.

The plant thus makes an attempt at beginning an independent life by neo-formation. (In nature this is the most powerful, if not the only means of propagation for *Caulerpa*, since it seems to have no sexual organs).

Now one sees the same happen with the double-hooked wounds: along the whole breadth above the lower cross-wound rootlets often grow, proving that communication has become so much impeded, that the first piece of the leaf (I, which is in communication with the top) and the middle piece, II, evidently meet their want of connection sooner and perhaps better by means of the neo-formation of rootlets, than by strengthening the existing but feeble communication with the old ones.[1])

The third part of the leaf, III, (which consequently is in direct communication with the base) never shows any inclination to the formation of rootlets, obviously because the communication has remained unimpaired here.

If we must assume that the stream-bundle in the uninjured leaf is regulated by a basally directed impulse, then, when the "reversion" has succeeded, the newly formed current in the middle piece must be directed by an opposite impulse, or, to speak more correctly, by the same impulse, after it has, so to say, been reflected by the cross-wound.

That this current in fact behaves in this manner, follows at once from the fact that the new current is first visible below in the middle piece and is gradually prolonged upward.

A still more convincing proof of this can be given by a further experimental operation: if namely these new currents are interrupted in I and II by a small cross-wound (as in fig. 1) one sees the thrust in I occur above, in II on the other hand below the wound, and the currents take their way as is indicated by the dotted line in the figure. This is a proof that these two adjacent pieces behave oppositely.

Though we finally often succeeded in bringing about the "reversion" in the middle piece, yet this reversion is very incomplete, as I infer from the following observation. In one of the leaves with a double-hooked wound a prolification had been formed above in the middle piece, while the complete reversion was being brought about; the new leaflet lay a little sideways of the current. Proceeding from this leaflet a little bundle of three currents had developed. One of them proceeded along the lower side of the upper cross-wound into the third part of the leaf, after having joined the main current coming from below. The other two, however, took their way straight downward as if the connection with the base of the leaf were still exactly as before the lesion. Hence one of the currents, when coming forth from the leaflet, obeyed the action of the reflected impulse, whereas the other two experienced no influence. In that place of the middle piece the old basipetal impulse must consequently have been preserved.

A similar case, occurring in another experiment, will be mentioned later.

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[1]) Above the upper cross wound also rootlets are sometimes formed, although only when the top-part is large and so powerful enough, or when prolifications occur on it.

Also one of the leaves, mentioned above, in which a small cross-wound was made in the middle piece and at the same time in the first piece (as in fig. 1), showed a phenomenon which I can only explain in this manner. It was pointed out already that above wounds new rootlets are regularly formed: we shall hereafter describe the phenomena preceding the formation of the rootlets, phenomena which always make themselves felt in a basipetal direction. These preliminary phenomena now appeared in that leaf in the first part (1) above the small wound, as usual, and in the middle piece also *above* the small wound. If the polarity of this whole piece had been reversed, these changes should have appeared there *below* the small wound. Now this indicates, in my opinion, that the reflected impulse was localised and had no influence on the lateral part of the middle piece, after it had been withdrawn from its direct action, and this piece, having retained the old impulse, reacted therefore as normally.

After I had succeeded in "reversing" a current, it was probable that it would also be possible to cause a whole plant to develop inversely.

When, however, this experiment was made in such a way that a whole plant, with rhizome and rootlets, was reversed and the leaf-tops were buried in mud, it gave no result; for seven weeks such a plant remained absolutely unaltered; only the top of the leaf became white on account of the loss of chlorophyl-grains, caused by the darkness, while the rhizome grew a little and made some new rootlets.

Cut leaves, freely suspended upside down or planted with their top in mud, gave quite different results, however.

Nearly all the leaves, and especially and most quickly the youngest, first formed new rootlets, which also in this position of the leaf always arose at the end of the stalk; very many appeared already after two days.

After that several prolifications appeared generally in various places, and then a first consequence of the reversion could be observed in the course taken by the stream-bundles coming out of the prolifications and continuing their way through the old leaf.

In a cut but erectly planted leaf these go always, without exception, to the base of the leaf; here in nearly all prolifications the greater part of these currents went to the base also, but some of them took their course towards the top of the leaf, without reaching it however. Gravity, acting in the opposite direction during their formation and development, had evidently deviated them.

Still more clearly the existence of an antagonism between gravity and the basipetal impulse was visible in some of these leaves from the fact that stream-loops were formed. From the young prolifications, namely, some currents were seen going to the top of the leaf, which however later suddenly returned with a very sharp bend and then went back straight to the leaf-stalk. So gravity had first deviated them, but the continuous counteracting influence of the basipetal impulse, which was evidently felt in every point of the leaf, had at last overcome gravity and got the upper hand. These loops had in large leaves a length of 5 to 10 mm.

All these changes took place before at the apical side rootlets developed. This occurred finally with very many leaves; the earliest appeared after 9 days, the majority came later, but after almost four weeks they had not yet developed in all of them. That most of them had formed rootlets at the extremity of the leaf-stalk much earlier, proves that they possessed to the full the power of forming them. That the presence of rootlets at the leaf-stalk was no impediment for the development of new rootlets elsewhere, appeared also from the fact that, with respect to these latter, no difference could be noticed between leaves with and without rootlets at the stalk.

If now these leaves were planted in mud with their apical rootlets (which, however, were hardly ever placed exactly at the top, but at a smaller or greater distance from it) the prolifications grew on or, if they had not been present beforehand, they always appeared after this. A connection was generally formed between the stream-bundle issuing from them and the rootlets and so a plant was obtained in which, under the impulse proceeding from the prolification, the nutritive current had developed in a direction opposed to the impulse existing in the leaf.

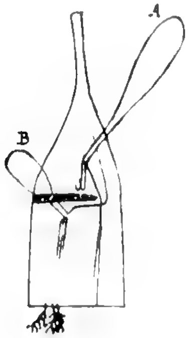

Fig. 2.

Here also it could be proved in the same way, as before by means of a cross-wound (as in fig. 2, in which the basal half of a leaf was planted upside down), that this bundle in the leaf obeyed indeed the impulse of the prolification *A*, since from this side the thrust occurred.

Yet here also the reversion appeared to be only local. A small prolification *B* had namely been formed below the cross-wound, after this had been made (consequently at the side of the apical rootlets). This new leaflet in its turn formed a small stream-bundle of which some thinner currents went in the direction of these rootlets; one thicker current however took his course athwart alongside the wound, turned at the end with a sharp bend and went to the old base of the leaf. In doing so this current crossed [1]) the bundle going from the other prolification to the apical rootlets, but even this did not cause it to change its direction.

So here also a reversion was obtained, this time by the influence of gravity, but it also was proved to have a very local character.

The inverted leaves gave me material for still another experiment.

These leaves, as has been remarked, had at last for the greater part formed prolifications and rootlets towards the apical side. Now in some of them a prolification and a rootlet were found at about the same height, but the one on the left side of the leaf, the other on the right.

What would happen now if this piece of the leaf, isolated from the other basal rootlets and prolifications by a cross-wound, were planted separately? Since a manifold direct, but feeble communication actually existed between the two organs by means of the numerous fine protoplasmic currents, it was possible that the direct communication would be strengthened and so a cross-current would arise, in the same way as above a large cross-wound. But it was also possible that the basipetal impulse of the prolification and of the piece of the leaf would not admit a communication or not one in that direction.

The three experiments for which suitable material was obtained, were not entirely at an end at my departure. Yet it then appeared already with perfect distinctness that nowhere a strengthening of the cross-communication had taken place. On the contrary, the currents everywhere went from the prolifications straight to the basal wound; currents communicating with the rootlet showed the same. Even an indirect communication between the two, via the basel wound, was not established.

In one of the leaves a young rhizome was formed beside the prolification at a distance of $1^1/_2$ millimetre from it; a communication between the two was established, but by a very roundabout way, viz. via the basal wound, which lay at a distance of $6^1/_2$ mm.

In another leaf a rhizome was developed near the rootlet and another a little above the prolification. In both cases the communication between each of the two groups was again established via the basal wound, but none between prolification and rootlet. The complete physiological separation between prolification and rootlet

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[1]) The current seemed to intersect the bundle, but as the currents proceed from beam to beam and often two currents are attached to one beam at different heights, these currents must have crossed each other. The same often happens with stream-loops.

finally appeared from the fact that in a small spot at the wound, exactly in the place where the currents from the prolification reached it, a number of small rootlets were formed.

Hence the basipetal impulse was so strong that it entirely prevented a cross-communication, as a consequence of which each of the parts of the leaf formed two individuals, cohering in a morphological sense but scarcely in a physiological sense.

We spoke above of currents that were reflected by the wound; this expression was chosen because the direction of the wound evidently influences the direction which the current assumes afterwards and this in a similar way in which a solid wall affects an impinging wave-front.

This influence is most clearly seen when of three leaves the top part is cut off, (this latter being taken as large as possible) following in the first leaf a transverse line, in the second a V-shaped one, the point of the V being downward, and in the last leaf an inverted V-shaped line. After a few days the currents are seen to bend near the wound in such a way that the lines bisecting these current arches, are in the first case parallel to the longitudinal axis of the leaf, in the second converge and in the third diverge. These currents are often so strong that one can follow them over long distances with the naked eye.

However, only those parts of the currents that lie near the wound must be taken into account, firstly because the reflection is not sudden but gradual, so that the currents assume a more or less sharp bend with a radius of $^1/_4$ to 2 mm, secondly because the leaves are rather narrow and so the reflected currents cannot, for a long distance, freely continue their new course.

That in the formation of wound-cork in higher plants the new cross-walls in the phellogen are always parallel to the direction of the wound in the nearest place, suggests a similar influence of the wound in these plants.

The basipetal impulse, indicated by the experiments mentioned, shows itself no less distinctly in the formation of new organs in cut leaves.[1] .

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[1] I never saw rootlets or rhizomes arise on intact leaves, attached to the rhizome: cut rootlets die off at once, while loose rhizomes, when they are strong enough, form new organs, but always in an entirely normal way.

WAKKER[1]) already pointed out that in these the young rhizomes and rootlets always arise above the basal wound.

Investigation has shown that immediately after the lesion the formation of these organs is prepared, namely by a division in the protoplasm. This I could only observe in leaves which were in very good condition of life; in these, however, the changes were well visible with the naked eye or else with the hand-magnifier.

Above the basal wound a clear white spot is gradually seen to arise, often several millimetres in size. In these places only the rootlets are later formed, while in the immediate vicinity of them the rhizomes appear.

Where it was mentioned above (pag. 425) that the wounded leaves showed an inclination for forming rootlets, the arising of such a white spot was meant.

The first question now was: what causes this white spot?

In vigorous cut leaves one sees often already one day after the cutting whitish streaks occur, of which no trace can be detected in the intact plant. As far as they are rendered visible by a strong hand-magnifier they begin at some distance from the top as well as from the edges of the leaf, but become soon thicker and proceed in a feeble curve (which is concave towards the edge) towards the middle and there assemble and proceed together to the leafstalk; here and there they are connected among each other. So their mode of proceeding is exactly the same as that of the green currents.

But also in other respects they behave like these latter: if the cut leaf bears a prolification, from the stalk of this latter a bundle of these currents passes into the leaf; when the currents meet a cross-wound they proceed as far as this, move sideways and when they have arrived at the corner of the wound, continue their way straight to the leaf-stalk.

These currents, which sometimes appear light greenish because they are seen through the peripheral layer of chlorophyl, consist of a very fine-granulated and therefore milky white protoplasm, very different from the much clearer protoplasm of the green currents, in which the chlorophyl-grains are moved along. The white currents partly originate from the green ones: these latter are namely seen to become feebler when the latter arise, while at the disappearance of the white currents the green ones gradually become more distinct again.

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[1]) Die Neubildungen an abgeschnittenen Blättern von *Caulerpa prolifera*: Versl. en Meded. der Kon. Akad. van Wetenschappen te Amsterdam, 1886, 3d series, part 2, p. 252.

From all points of the wounded leaf consequently fine-granulated protoplasm flows together; it gathers immediately above the wound, replaces the chlorophyl-containing peripheral layer and currents and so causes the leaf locally to assume a white colour.

When the white currents are observed microscopically, also in them a distinct streaming is observed, mostly in the two opposite directions at the same time or otherwise alternately, while a number of uncoloured granules are dragged along. But chlorophyl grains are entirely lacking. Yet after the lesion the quantity of plasm above the wound, "white" as well as "green", increases, while in the top it diminishes, occasionally to such an extent even that the top becomes empty and dies. From this follows that the mass of plasm, conveyed downward by the currents is greater than the mass which is taken back upward, so that the resultant of the two motions is equivalent to a current going to the organic base.

So the white currents behave exactly like the green ones; yet there is a difference between them, although only a quantitative one: while both groups of currents obey the same basipetal impulse, this latter appears to exert a somewhat greater influence on the white currents than on the green, for the green protoplasm is always observed to be pushed aside by the white.

Now, when it had appeared that the white currents move towards the basal wound, the question arose whether they only strove to reach this wound or, perhaps not contented with this, would also try to occupy the very lowest (most basal) place near this wound.

Experiments showed this latter to be indeed the case.

If a wound be made in a slanting direction with regard to the diameter of the leaf, the white plasm flows down along the wound and assembles in the sharp point; if the wound be V-shaped all gathers in the middle, while with a Λ-shaped impediment the white currents flow off to the two points near the edges of the leaf. With these lesions the green currents behave exactly as the white ones, but again their terminal point is left a few millimetres behind that of the uncoloured currents. From this it appears more clearly still that these latter feel the basipetal impulse more strongly.

Especially the current of uncoloured protoplasm which flows off along the wound is seen to follow a wavy course, since it consists of very short pieces of current, which go longitudinally downward, are then reflected by the wound and soon afterwards bend down again. Not unfrequently two currents run close to each other and in doing so cross each other repeatedly. The height of these waves is small, no more than $^1/_4$ to $^1/_2$ mm.

The basal part of the so wounded leaves underwent no change when it remained in connection with the rhizome. If, however, shortly before, it had been separated from it, the lower piece behaved like a cut entire leaf. White currents here also appear; they however only begin at some distance below the lesion as fine lines and, growing thicker, pass all into the leaf-stalk. At the lower end of this latter the accumulation of white protoplasm then takes place.

The very sharp antithesis between the phenomena below and above the wound, again furnishes a striking proof of the existence of the basipetal impulse and of its influence on the white plasm.

With regard to the origin of this plasm it must be remembered that all organs during their growth always contain a large quantity of such plasm at their top. Behind it, when growth has been completed, it is clear and contains in leaves and rhizomes a very great number of chlorophylgrains. When an organ stops growing, the white top soon disappears.

For this reason and on account of its appearance, I compared already formerly [1]) this fine-granulated, turbid protoplasm to that which fills the meristem-cells in higher plants.

Hence *Caulerpa* possesses, notwithstanding its being unicellular, a "meristem-plasm" which, however, is only to be found during growth and in the growing tops. After the growth has ceased it disappears, which disappeareance must be regarded as a mixing up with the remaining protoplasm [2]).

The experiments now showed that after serious lesion this meristem-plasm is secreted again (which can take place evidently in all points of the leaf), after which it unites to currents of increasing thickness and flows together at the organic base.

On the thus formed white spots the rootlets are produced, while the rhizomes take their origin in the immediate vicinity of them, mostly on the transition of the white spot to the dark green part, but still within reach of the white currents. So both arise in consequence of the resulting descending current after the lesion.

Hence the rootlets and rhizomes derive their meristem-plasm from the same confluent, turbid protoplasm and therefore this latter may in itself be regarded as meristem-plasm.

Although the source of the meristem-plasm of rootlets and rhizomes

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[1]) l. c. p. 203.

[2]) Such a secretion of meristem-plasm from the protoplasm of the cell and its re-solution in it, has recently been described by Noll for a closely related plant (*Bryopsis*); cf.: Beobachtungen und Betrachtungen über embryonale Substanz; Biologisches Centralblatt, 1903, No 8.

is the same, yet there exists a sort of antagonism between the two.

So, for example, it is not unfrequently seen that when somewhere on a leaf a rootlet has been formed, immediately behind it a rhizome arises, or the reverse.

The most striking case in this respect I observed with a leaf which had formed two rhizomes laterally of the leafstalk (which is a rare occurrence) one close above the other: at the other side of the leafstalk, exactly behind each of the rhizomes, a well-developed rootlet was found.

Properly speaking this antagonism is already observed when a rootlet is formed on a rhizome in the ordinary way; it namely does not arise at some distance from the top, but quite close to it, so that sometimes the impression is given as if the top, of the rhizome would divide dichotomically, i. e. into two equivalent branches, whereas later one point develops into a rhizome, the other into a rootlet.

So the two meristem-plasms are very nearly equal, until at a certain moment a division takes place. The principal cause of this division is, in my opinion, light.

The rootlets can very well form and develop in light, but, if possible, they seek the shaded side or turn away from the light. Rhizomes, on the other hand, as well as prolifications, generally are formed at the bright side.

Now taking into account that Noll [1]) has shown that a rhizome of *Caulerpa* forms rootlets at the upper side if this is shaded above and only illuminated from below, I think we have every reason to look upon the difference in the intensity of the light on both sides of the rhizome as the principal cause of the separation, which takes place in the at first homogeneous meristem-plasm, and hence also of the antagonism between rhizome and rootlet.

That also internal causes play a part here, follows already from the fact that the rootlets as well as the leaves, are formed on the rhizome at distances which for each of them are pretty regular.

A rhizome-top is even occasionally seen to dissolve entirely into rootlets, which proves that there can be no considerable difference of origin between them.

So we are naturally led to the question: how do the leaves arise?

In this respect I must restrict myself to a few hints, since the investigation of this point has not been completed yet.

In the intact plant they arise either on the rhizome or as prolifi-

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[1]) Einfluss der Lage, u. s. w.; Arbeiten aus dem botanischen Institut in Würzburg, Bd. III, 1888, S. 470.

cations on the leaves. On the rhizome they arise on the upper side but, in opposition with the rootlets, always at a great distance (a few centimetres) from the top and consequently quite out of reach of the meristem-plasm there. I presume that their formation on the upper side is also determined by light, although this has not been proved yet.

In unwounded leaves, and hence in the normal life of the plant, they are formed on full-grown leaves and then generally near the top, in cut leaves they very rarely occur near the top; in these they as a rule arise on the lower two thirds of the leaf, preferably even on the lowest third part, but hardly ever immediately above the wound. So here also they arise out of reach of the meristem-plasm.

The formation of the leaf begins with the appearance of a very small white spot on the dark green organ. This rapidly grows out into a cylindrical, soon broadening appendix, which often remains entirely white until it has reached a length of one centimetre, after which it becomes green from below during further growth. The top remains white as long as the leaf increases in length, but turns green when growth is arrested, either by the leaf having reached maturity or by unfavourable external circumstances.

In no case the formation of a leaf was preceded by the appearance of a large white spot with affluent streams of meristem-plasm. This leads to the conclusion that the young leaf derives its meristem-plasm evidently from the protoplasm of the whole neighbourhood; so a preferred direction of motion, as a consequence of a basipetal or acropetal impulse, cannot be detected. As a consequence of this each of these currents is so feeble, that it could not be observed with the hand-magnifier. So the formation of leaves appears to be independent of the descending current of meristem-plasm.

In one case only I have seen white currents in connection with a young leaf; in a cut leaf I observed that a strong white bundle had differentiated itself, running close to the base of a young leaflet (prolification) that had arisen after the cutting. This was a little over a centimetre long and still as white as ivory. From its stalk six white streams passed into the leaf; they all ran in a basal direction and soon became absorbed in the white principal bundle.

So these also obeyed the basipetal impulse; they had gradually formed during the development of the leaflet and so had not appeared as preliminaries to the formation of it, as is the case with the rootlets. Also the large white spot was absent here.

Since the white currents in this cut leaf also flowed together at the base in order to prepare there the formation of a rhizome and of rootlets, we may infer from this that there is no essential difference between the meristem-plasm of leaves on one hand and that of rhizomes and rootlets on the other.

Hence there must be causes which in the cut leaf or in the rhizome bring about a division in the plasm for the formation of new prolifications and leaves, and since in cultures it is regularly observed that new prolifications arise on the lighted side of the leaf, light certainly plays a part here. Undoubtedly, however, there are still other, internal, at present unknown, factors which cooperate in determining the origin and place of origin of the prolifications.

From the here briefly described observations we may infer that in the leaves of *Caulerpa* a basipetal impulse is active, proceeding from every point of the leaf and revealing itself in two ways:

1. in leaves, connected with rhizomes and rootlets, in the course of the "green" currents of protoplasm in the unwounded leaf as well as in the severely wounded leaves.

2. in cut, vigorous leaves in the occurrence and course of the "white" currents of meristem-plasm which partly assemble at the most basally situated place. It is this descending current which prepares the formation in that place of new rhizomes and rootlets.

None of the observations, on the other hand, gave reason for assuming also the existence of a contrary, acropetal impulse, thus even not with the formation of leaves and prolifications.

It proved possible, by certain lesions and by planting invertedly, to cause the formation of currents which developed contrary to the currents in the normal leaf. It could be proved however that this was not an inversion of the impulse itself, but that gravity or reflection by a wound caused a change in the direction of the current, whereas the basipetal impulse underwent no or hardly any change, and even then in any case only a very local one.

The chief phenomena observed with *Caulerpa* remind us of observations which have been known for a long time in higher plants.

The consequences of annular wounds or of large transverse wounds in the bark-tissue of trees, the formation of much plasm-containing tissue (callus) above the wound, the frequent mortification of the tissue below the wound, the formation or sprouting of adventitious roots exclusively above the wound and in the very lowest place of the living bark-tissue, are, mutatis mutandis, evidently analogous. The same may be said of the formation of adventitious roots exclusively at the base of cut leaves of very many plants, of the regenerative phenomena of the fruit-stalks of *Marchantia*, etc.

The former phenomena were explained by the older physiologists by means of the hypothetical descending "sap-current", by the newer physiologists they were, as a rule, not explained at all. Now that the existence of a resulting descending current could be proved with *Caulerpa*, which shows so many analogous phenomena, it seems to me to be probable that on closer investigation it will also be found with higher plants, although perhaps in an entirely different form than was originally thought.

Physics. — *"Double refraction near the components of absorption lines magnetically split into several components"*, according to experiments made by Mr. J. Geest. By Prof. P. Zeeman.

It has already appeared from experiments which I had the honour to communicate to the Academy on a former occasion that the magneto-optic theory of Voigt[1]), who established a simple and rational connexion between the magnetic splitting up of the spectral lines and dispersion, accounts extremely well for all the phenomena observed in the region of the absorption lines.

If light traverses parallel to the lines of force very attenuated sodium vapour placed in the magnetic field, the plane of polarization is rotated in the positive direction for all periods lying outside the components of the doublet, but in the negative direction, and very strongly[2]), for periods intermediate between those of the components.

If light traverses the vapour normally to the field, there is double refraction as predicted by Voigt from theory. When placed in a magnetic field, all isotropic bodies should show double refraction, but to a measurable degree only in the neighbourhood of the absorption lines. Voigt in collaboration with Wiechert experimentally verified this result, using a small grating and a flame with relatively much sodium vapour.

I have extended these results[3]) by working with sodium vapour so dilute that, in a strong magnetic field, there were seen the four absorption lines corresponding to the components of the quartet into which the line D_1 is split by the magnetic field. The mode of dependency of double refraction on the period could, in this special case with some reserve, be predicted from Voigt's theory. Observations, in which Mr. Geest took part, confirmed the theoretical result. Mr.

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[1]) Voigt, Wiedemann's Annalen. Bd 67, p. 359, 1899.

[2]) Zeeman, Proc. Acad. Amsterdam, May 1902, see also Hallo, Thesis for the doctorate, Amsterdam, 1902.

[3]) Zeeman en Geest, Proc. Acad. Amsterdam, May 1903.

Geest has now extended these observations and will give a more detailed exposition of his results elsewhere[1]); I intend to give here a short explanation of them.

The arrangement of the apparatus was for the most part the same as in our former experiments. Plane polarized light, under azimuth 45° to the vertical, falls on a **Babinet**'s Compensator with horizontal edges. The light then traverses a second Nicol with its plane of polarization perpendicular to that of the first. An image of the system of parallel interference bands in the compensator, is thrown on the slit of the spectroscope. The light is then analysed by means of a large **Rowland** grating mounted for parallel light. The greater part of the experiments were made with a compensator of which the prisms had angles of about 50′, but for the study of some details compensators were used with angles of 10′ or of 3°. In the spectroscope a few dark horizontal interference bands are observed as long as the magnetic field is off. The fine absorption lines of the vapour are then coincident with the reversed sodium lines due to the arc light. As soon as the field is on, the bands become distorted. Their vertical displacements are, with the method used, proportional to the difference of phase between vibrations respectively parallel and normal to the field.

For the simplest case of a line split by the field into a triplet, **Voigt** deduced a formula giving the difference of phase as a function of the wave length[2]). The sodium lines D_1 and D_2 being split, however, by the magnetic field into a quartet and a sextet, it was, in order to compare theory with observation, necessary to deduce the formulae for these cases. Mr. **Geest** has made these calculations according to the method already indicated by **Voigt**[3]) on another occasion. According to his calculation, the difference of phase between vibrations normal and parallel to the field, the light having traversed a layer l of the absorbing vapour, is given by:

$$\Delta = \frac{\omega_0 \varepsilon l}{V^2} \left\{ \frac{4\delta^2 - d'^2 \vartheta_0^2}{(4\delta^2 - d'^2 \vartheta_0^2)^2 - 4c^2 R^2 \delta^2} - \frac{1}{4\delta^2 - d^2 \vartheta_0^2} \right\} .$$

In this formula V indicates the velocity of light in the aether, R the strength of the field, ε, d, d' and c being constants characteristic of the medium. Moreover $2\pi\vartheta_0 = \tau_0$ is the period of vibration and $\delta = \partial\vartheta$. The formula given applies to the case of the sextet; for the quartet, $d' = o$ and for the triplet, moreover $d = o$. Figs. 1—3

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[1]) **Geest**, Thesis for the doctorate, Amsterdam, 1904.

[2]) **Voigt** l. c.

[3]) **Voigt** Wied. Ann. 68 p. 352. 1899.

give the graphical representation of $\angle$ as a function of d for each of these three cases.

The result of the observations is represented in figs. 4–8. These drawings are made with the aid of photographic negatives. We have not yet succeeded in getting negatives that showed all details simultaneously and equally well. Hence ocular observations had to supply the imperfections of the photographic records.

Figs. 1, 4, 5 refer to the triplet (type line D_2 in feeble fields); figs. 2, 6, 7 to the quartet (type line D_1); figs. 3, 8 to the sextet (type line D_2).

When comparing the results of observation with theory, it should be taken into account that the theoretical curve indicates the distortion which one single interference band would undergo. With the method of observation used, the central part of the field of view contained also parts originating from bands lying higher and lower than the one considered. The theoretical figure must therefore be completed with parts of theoretical curves lying above and below the one represented.

We will first of all consider the quartet. We indicate the bands by *a*, *b*, *c*, *a* being the superior one, and by 1, 2, 3, 4, we indicate the positions in the spectrum which would be occupied by the components. The double curved line between 2 and 3 shows entirely the same character in both figures. This sinuous line (figs. 6 and 7) thickens out at the extremities into more intense parts (where the double refraction is at a maximum or at a minimum) turning their concave side towards band *b*. These intense parts correspond to the loop of the theoretical curve, the loop between 1 and 2 belonging to band *c*, and the one between 3 and 4 to band *a*. It was not to be expected that the two branches which asymptotically approach the components, would be seen separated from the loops. The distance is too small by far to allow that. The vertical central line in the figure is the reversed sodium line due to the arc. With increased vapour density the loops increase their distance from their band. Fig. 7 relates to this case, which is also in accordance with theory. As the vapour density increases, fewer details become visible, but we will not go further into this point now.

The observations concerning the sextet are very difficult on account of the extremely small distance of the components. It is already difficult to observe the inverse sextet, and hence so much the more to observe phenomena occurring between its components. Only under very favourable circumstances could the phenomenon be observed as it is represented in fig. 8. The other phenomena observed with

D_2 are most readily interpreted by considering them as originating from a triplet and not from a sextet.

It seems rather superfluous to give any further explanation of figs. 8, 4, 5; in the case relating to fig. 5, the vapour density is again greater than in fig. 4. All the phenomena we have considered are qualitatively in excellent accordance with VOIGT's theory.

The phenomena described for D_1 and D_2 again demonstrate the existence of very characteristic differences between different spectral lines, differences no less striking here than in the case of the related phenomena of the magnetic separation of the spectral lines and of the rotation of the plane of polarization in the interior [1]) of, and close to, the absorption line. It is certainly very interesting that the theory explains the entirely different behaviour of D_1 and D_2 in the case now considered by differences between the velocities of propagation of vibrations normal and parallel to the field, assuming, of course, the magnetic division of the lines.

Physics. — "*The motion of electrons in metallic bodies*". I. By Prof. H. A. LORENTZ.

It has been shown by RIECKE [2]), DRUDE [3]) and J. J. THOMSON [4]) that the conductivity of metals for electricity and heat, the thermo-electric currents, the THOMSON-effect, the HALL-effect and phenomena connected with these may be explained on the hypothesis that a metal contains a very large number of free electrons and that these particles, taking part in the heat-motion of the body, move to and fro with a speed depending on the temperature. In this paper the problems to which we are led in theories on these subjects will be treated in a way somewhat different from the methods that have been used by the above physicists.

§ 1. I shall begin by assuming that the metal contains but one

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[1]) ZEEMAN, Proc. Acad. Amsterdam May 1902, see also the description of another phenomenon in VOIGT, Göttinger Nachrichten, Heft 5, 1902.

[2]) E. RIECKE, Zur Theorie des Galvanismus und der Wärme, Ann. Phys. Chem. 66 (1898), p. 353, 545, 1199; Ueber das Verhältnis der Leitfähigkeiten der Metalle für Wärme und für Elektrizität, Ann. Phys. 2 (1900), p. 835.

[3]) P. DRUDE, Zur Elektronentheorie der Metalle, Ann. Phys. 1 (1900), p. 566; 3 (1900), p. 369.

[4]) J. J. THOMSON, Indications relatives à la constitution de la matière fournies par les recherches récentes sur le passage de l'électricité à travers les gaz, Rapports du Congrès de physique de 1900, Paris, 3, p. 138

kind of free electrons, having all the same charge e and the same mass m; the number of these particles per unit volume will be represented by N, and I shall suppose their heat-motion to have such velocities that, at a definite temperature, the mean kinetic energy of an electron is equal to that of a molecule of a gas. Denoting by T the absolute temperature, I shall write for this mean kinetic energy αT, where α is a constant.

We shall further consider a cylindrical bar, unequally heated in its different parts, so that, if x is reckoned along its length, T is a function of this coordinate. We shall also suppose each electron to be acted on, in the direction of OX, by a force mX, whose intensity is a function of x. Such a force may be due either to an electric field or, in the case of a non-homogeneous metal, to a molecular attraction exerted by the atoms of the metal. Our first purpose will be to calculate the number of electrons ν and the amount of energy W crossing an element of surface perpendicular to the axis of x in the positive direction, or rather the difference between the numbers of particles in one case and the quantities of energy in the other that travel towards the positive and towards the negative side. Both quantities ν and W will be referred to unit area and unit time.

This problem is very similar to those which occur in the kinetic theory of gases and, just like these, can only be solved in a rigourous way by the statistical method of MAXWELL and BOLTZMANN.

In forming our fundamental equation, we shall not confine ourselves to the cylindric bar, but take a somewhat wider view of the subject. At the same time, we shall introduce a simplification, by which it becomes possible to go further in this theory of a swarm of electrons than in that of a system of molecules. It relates to the encounters experienced by the particles and limiting the lengths of their free paths. Of course, in the theory of gases we have to do with the *mutual* encounters between the molecules. In the present case, on the contrary, we shall suppose the collisions with the metallic atoms to preponderate; the number of these encounters will be taken so far to exceed that of the collisions between electrons mutually, that these latter may be altogether neglected. Moreover, in calculating the effect of an impact, we shall treat both the atoms and the electrons as perfectly rigid elastic spheres, and we shall suppose the atoms to be immovable. Of course, these assumptions depart more or less from reality; I believe however that we may safely assume the general character of the phenomena not to be affected by them.

§ 2. Let dS be an element of volume at the point (x, y, z). At the time t, this element will contain a certain number (in fact, a very large number) of electrons moving in different ways.

Now, we can always imagine a piece of metal of finite dimensions, say of unit volume, in which the "concentration", as we may call it, of the electrons and the distribution of the different velocities among them are exactly the same as in the element dS. In studying the said distribution for the N electrons, with which we are then concerned, we shall find a diagram representing their velocities to be very useful. This is got by drawing, from a fixed point O, N vectors, agreeing in direction and magnitude with the velocities of the electrons. The ends of these vectors may be called the velocity-points of the electrons and if, through the point O of the diagram, we draw axes parallel to those used in the metal itself, the coordinates of a velocity-point will be equal to the components ξ, η, ζ of the velocity of the corresponding electron.

Writing now

$$f(\xi, \eta, \zeta)\, d\lambda$$

for the number of velocity-points within the element $d\lambda$ at the point (ξ, η, ζ), we make the exact solution of all problems relating to the system of electrons depend on the determination of the function $f(\xi, \eta, \zeta)$.

We may also say that

$$f(\xi, \eta, \zeta)\, dS\, d\lambda \quad \ldots\ldots\ldots \quad (1)$$

is the number of electrons in the element dS, whose velocity-points lie in $d\lambda$; in particular

$$f(\xi, \eta, \zeta)\, dS\, d\xi\, d\eta\, d\zeta \quad \ldots\ldots\ldots \quad (2)$$

is the number of electrons for which the values of the components of velocity are included between ξ and $\xi + d\xi$, η and $\eta + d\eta$, ζ and $\zeta + d\zeta$. The expression (2) is got from (1) by a proper choice of the element $d\lambda$.

If the function in (1) were known, we could deduce from it the total number of electrons and the quantities ν and W mentioned in § 1. Integrating over the full extent of the diagram of velocities, we have

$$N = \int f(\xi, \eta, \zeta)\, d\lambda, \quad \ldots\ldots\ldots \quad (3)$$

$$\nu = \int \xi f(\xi, \eta, \zeta)\, d\lambda, \quad \ldots\ldots\ldots \quad (4)$$

and if, in treating of the flux of energy, we confine ourselves to the kinetic energy of the particles,

$$W = \tfrac{1}{2}\, m \int \xi\, r^2 f(\xi, \eta, \zeta)\, d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the latter formula, r denotes the magnitude of the velocity.

It ought to be observed that, in general, the state of the metal will change from point to point and from one instant to another. If such be the case, the function $f(\xi, \eta, \zeta)$ will depend on x, y, z and t, so that the symbol may be replaced by $f(\xi, \eta, \zeta, x, y, z, t)$. We shall, however, often abbreviate it to f.

As to the integrations in (3), (4) and (5), in performing these, we must treat x, y, z and t as constants.

§ 3. We shall now seek an equation proper for the determination of the function f. For this purpose we fix our attention on the electrons present, at the time t, in the element dS at the point (x, y, z), and having their velocity-points within the element $d\lambda$; we shall follow these particles, the number of which is

$$f(\xi, \eta, \zeta, x, y, z, t)\, dS\, d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in their course during the infinitely short time dt. At the end of this interval those particles of the group which have escaped a collision with an atom will be found in an element dS', which we may get by shifting dS in the directions of the axes over the distances ξdt, ηdt, ζdt. At the same time, if there are external forces, the velocities will have changed. I shall suppose each electron to be acted on by the same force (mX, mY, mZ). Then, for each of them, the components of the velocity will have increased by Xdt, Ydt, Zdt and, at the end of the interval dt, the velocity-points will be found in the element $d\lambda'$, which may be considered as the original element $d\lambda$, displaced over those distances.

We must further keep in mind that, while travelling from dS to dS', the group (6) loses a certain number of electrons and gains others. Indeed, all particles of the group that strike against an atom have their velocities changed, so that they do not any longer belong to the group, and, on the other hand, there are a certain number of encounters by which electrons having initially different velocities, are made to move in such a way, that their velocity-points lie within $d\lambda$. Writing

$$a\, d\, S\, d\, \lambda\, d\, t$$

for the number of electrons leaving the group and

$$b\, d\, S\, d\, \lambda\, d\, t$$

for the number entering it, we may say:

If, to the number (6), we add $(b - a)\, d\, S\, d\, \lambda\, d\, t$, we shall get the number of electrons which, at the time $t + dt$, satisfy the conditions that they themselves shall be found in the element dS' at the point $(x + \xi\, dt, y + \eta\, dt, z + \zeta\, dt)$ and their velocity-points in the element $d\lambda'$ at the point $(\xi + X dt, \eta + Y dt, \zeta + Z dt)$. Hence, since $dS' = dS$ and $d\lambda' = d\lambda$,

$$f(\xi, \eta, \zeta, x, y, z, t) + (b - a)\, dt =$$
$$= f(\xi + X dt, \eta + Y dt, \zeta + Z dt, x + \xi dt, y + \eta dt, z + \zeta dt, t + dt),$$

or

$$b - a = \frac{\partial f}{\partial \xi} X + \frac{\partial f}{\partial \eta} Y + \frac{\partial f}{\partial \zeta} Z + \frac{\partial f}{\partial x} \xi + \frac{\partial f}{\partial y} \eta + \frac{\partial f}{\partial z} \zeta + \frac{\partial f}{\partial t}. \quad . \quad (7)$$

This is the equation we wanted to establish [1]).

It is easily seen that, in calculating the numbers of collisions $a\, dS\, d\lambda\, dt$ and $b\, dS\, d\lambda\, dt$, we need not trouble ourselves about the state of the metal varying from one point to another; we may therefore understand by $a\, d\lambda\, dt$ the decrease, and by $b\, d\lambda\, dt$ the increase which the group of electrons characterized by $d\lambda$ would undergo, if we had to do with a piece of metal occupying a unit of volume and being, in all its parts, in the state that exists in the element dS.

§ 4. We are now prepared to calculate the values of a and b. Let R be the sum of the radii of an atom and an electron, n the number of atoms in unit space, and let us in the first place confine ourselves to encounters of a definite kind. I shall suppose that in these the line joining the centres falls within a cone of the infinitely small solid angle $d\omega$.

Taking as axis of this cone one of the straight lines that may be drawn in it, and denoting by ϑ the *acute* angle between the axis and the direction of motion of the group (6), I find for the number of electrons in this group undergoing an encounter of the kind chosen,

$$n R^2 f(\xi, \eta, \zeta)\, r \cos \vartheta\, d\lambda\, d\omega \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

per unit time, a result which leads to the value

$$a = n \pi R^2 f(\xi, \eta, \zeta)\, r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

if we take into account *all* encounters, whatever be the direction of the line joining the centres.

Now, if we ascribe to a metallic atom so large a mass, that it is not sensibly put in motion by an electron flying against it, the velocity of the latter after the encounter is given by a very simple rule. We have only to decompose the initial velocity into one

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[1]) See LORENTZ, Les équations du mouvement des gaz et la propagation du son suivant la théorie cinétique des gaz, Arch. néerl. 16, p. 9.

component along the line of the centres and another perpendicular to it; the latter of these components will remain unchanged and the former will have its direction reversed.

In applying this to the encounters of the particular kind specified at the beginning of this §, we may take for all of them the line of centres to coincide with the axis of the cone $d\omega$. Our conclusion may therefore be expressed as follows: Let V be a plane through the origin in the diagram of velocities, perpendicular to the axis of the cone. Then, the velocity-point of the electron after impact will be the geometrical image of the original point with respect to this plane. It is thus seen that all electrons whose velocity-points before the encounters are found in the element $d\lambda$ will afterwards have their representative points in $d\lambda_r$, the image of $d\lambda$ with respect to the plane V.

By this it becomes also clear, in what way the number b can be calculated; indeed, in encounters taking place under the circumstances considered, velocity-points may as well jump from $d\lambda_r$ to $d\lambda$ as from $d\lambda$ to $d\lambda_r$. The number of cases in which the first takes place is found from (8), if in this expression we replace ζ, η, ξ by the coordinates ξ', η', ζ' of the image of the point (ξ, η, ζ) with respect to the plane V. It is to be remarked that the factor $r \cos\vartheta\, d\lambda$ may be left unchanged, because the lines drawn from the origin of the diagram to the points (ζ, η, ξ) and (ξ', η', ζ') have equal lengths and are equally inclined to the axis of the cone. Also $d\lambda_r = d\lambda$. The increase per unit volume of the number of electrons in the group (6), insofar as it is due to encounters in which the line of centres lies within the cone $d\omega$, is thus found to be

$$n R^2 f(\xi', \eta', \zeta')\, r \cos\vartheta\, d\lambda\, d\omega$$

and, in order to find b, it remains only to divide this by $d\lambda$ and to integrate with respect to all cones that have to be taken into account.

Using the formula (8) we may as well calculate directly the difference $b-a$. By this the equation (7) becomes

$$n R^2 r \int \{ f(\xi', \eta', \zeta') - f(\xi, \eta, \zeta) \} \cos\vartheta\, d\omega =$$

$$= \frac{\partial f}{\partial \xi} X + \frac{\partial f}{\partial \eta} Y + \frac{\partial f}{\partial \zeta} Z + \frac{\partial f}{\partial x} \xi + \frac{\partial f}{\partial y} \eta + \frac{\partial f}{\partial z} \zeta + \frac{\partial f}{\partial t} \quad . \quad . \quad (10)$$

We must now express ξ', η', ζ' in ξ, η, ζ. Let f, g, h be the angles between the axes of coordinates and the axis of the cone $d\omega$, this last line being taken in such a direction that it makes the *acute* angle ϑ with the velocity (ξ, η, ζ). Then

$$\xi' = \xi - 2r \cos\vartheta \cos f, \quad \eta' = \eta - 2r \cos\vartheta \cos g, \quad \zeta' = \zeta - 2r \cos\vartheta \cos h, \quad (11)$$

These formulae show that, as we know already, the magnitude of the velocity (ξ', η', ζ'), which I shall call r', is equal to the magnitude r of the velocity (ξ, η, ζ).

As to the integration in (10), it may be understood to extend to the half of a sphere. Indeed, if in the diagram of velocities, we describe a sphere with centre O and radius 1, and if P and Q are the points of this surface, corresponding to the directions (ξ, η, ζ) and (f, g, h), we must give to the point Q all positions in which its spherical distance from P is less than $\frac{1}{2}\pi$. For $d\omega$ we may take a surface-element situated at the point Q.

§ 5. At the time t and the point (x, y, z) the metal will have a certain temperature T and the number N, the concentration of the swarm of electrons, a definite value.

Now the assumption naturally presents itself, that, if T and N had these values continually and in all points, the different velocities would be distributed according to MAXWELL's law

$$f(\xi, \eta, \zeta) = Ae^{-hr^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Here, the constants A and h are related to the number N and the mean square of velocity $\overline{r^2}$ in the following way

$$A = N\sqrt{\frac{h^3}{\pi^3}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\overline{r^2} = \frac{3}{2h}.$$

Since $\frac{1}{2} m \overline{r^2} = \alpha T$, the latter relation may also be put in the form

$$h = \frac{3m}{4\alpha T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

It appears from this that the way in which the phenomena depend on the temperature will be known as soon as we have learned in what way they depend on the value of h.

§ 6. The function f takes a less simple form if the state of the metal changes from point to point, so that A and h are functions of x, y, z. In this case we shall put

$$f(\xi, \eta, \zeta) = Ae^{-hr^2} + \varphi(\xi, \eta, \zeta), \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where φ is a function that has yet to be determined by means of the equation (10). We shall take for granted, and it will be confirmed by our result, that the value of $\varphi(\xi, \eta, \zeta)$ is very small in comparison with that of Ae^{-hr^2}. In virtue of this, we may neglect the terms depending on $\varphi(\xi, \eta, \zeta)$ in the second member of (10), this having already a value different from 0, if we put $f = Ae^{-hr^2}$. For a stationary state and for the case of the bar mentioned in § 1, the member in question becomes

$$\left(-2\,h\,A\,X + \frac{dA}{dx} - r^2\,A\,\frac{dh}{dx}\right)\xi\,e^{-hr^2} \quad . \quad . \quad . \quad . \quad (16)$$

As to the left hand side of the equation (10), it would become 0, if we were to substitute $f = Ae^{-hr^2}$. Here, we must therefore use the complete value (15), the deviation from MAXWELL's law being precisely the means by which this member may be made to become equal to (16).

The occurrence of the factor ξ in this last expression makes it probable that the same factor will also appear in the function φ. We shall therefore try to satisfy our equation by putting

$$\varphi\,(\xi, \eta, \zeta) = \xi\,\chi\,(r) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

This leads to

$$f\,(\xi, \eta, \zeta) = A\,e^{-hr^2} + \xi\,\chi\,(r)$$

and

$$f\,(\xi', \eta', \zeta') = A\,e^{-hr'^2} + \xi'\,\chi\,(r'),$$

consequently, since $r' = r$, if we use (11),

$$f\,(\xi', \eta', \zeta') - f\,(\xi, \eta, \zeta) = -\,2\,r\cos\vartheta\cos f\,\chi\,(r),$$

so that the first member of (10) becomes

$$-\,2\,n\,R^2\,r^2\,\chi\,(r)\int\cos^2\vartheta\cos f\,d\,\omega. \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Denoting by μ the angle between the velocity (ξ, η, ζ), i. e. the line OP, and the axis of x, and by ψ the angle between the planes QOP and XOP, I find for (18)

$$-\,2nR^2r^2\,\chi\,(r)\int_0^{\frac{1}{2}\pi}\int_0^{2\pi}\cos^2\vartheta\,(\cos\vartheta\cos\mu + \sin\vartheta\sin\mu\cos\psi)\sin\vartheta\,d\,\vartheta\,d\,\psi =$$

$$= -\,\pi\,n\,R^2r^2\,\chi\,(r)\cos\mu = -\,\pi\,n\,R^2\,\xi\,r\,\chi\,(r).$$

If this is equated to (16), the factor ξ disappears, so that $\chi\,(r)$ may really be determined as a function of r. Finally, putting

$$\frac{1}{\pi\,n\,R^2} = l, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

we draw from (15) and (17)

$$f\,(\xi, \eta, \zeta) = A\,e^{-hr^2} + l\left(2h\,A\,X - \frac{dA}{dx} + r^2\,A\frac{dh}{dx}\right)\frac{\xi}{r}\,e^{-hr^2}\,. \quad (20)$$

I must add that, as is easily deduced from (9), the quantity l defined by (19) may be called the mean length of the free paths of the electrons, and that, in the equation (20), the terms in $\frac{dA}{dx}$ and

$\frac{dh}{dx}$ are very small in comparison with $A\,e^{-hr^2}$, provided only the state of the metal differ very little in two points whose mutual distance is l. This is seen by remarking that the ratios of the terms in question to $A\,e^{-hr^2}$ are of the order of magnitude

$$\frac{l\,\frac{dA}{dx}}{A} \quad \text{and} \quad l\,r^2\,\frac{dh}{dx},$$

and that, in the second of these expressions, $\overline{r^2}$ is of the same order as $\frac{1}{h}$.

If the term in (20) which contains X, is likewise divided by $A\,e^{-hr^2}$, we get

$$2\,h\,l\,X.$$

Now, $2\,l\,X$ is the square of the velocity an electron would acquire if, without having an initial motion, it were acted on by the external force $m\,X$ over a distance l. If this velocity is very small as compared with that of the heat-motion, the term in X in our equation may also be taken to be much smaller than the term $A\,e^{-hr^2}$.

It appears in this way that there are many cases in which, as we have done, the function $q\,(\xi, \eta, \zeta)$ may be neglected in the second member of the equation (7).

The above reasoning would not hold however, if, in the case of two metals in contact with one another, there were a real discontinuity at the surface of separation. In order to avoid this difficulty, I shall suppose the bodies to be separated by a layer in which the properties gradually change. I shall further assume that the thickness of this layer is many times larger than the length l, and that the forces existing in the layer can give to an electron that is initially at rest, a velocity comparable with that of the heat-motion, only if they act over a distance of the same order of magnitude as the thickness. Then, the last terms in (20) are again very small in comparison with the first.

As yet, a theory of the kind here developed cannot show that the values we shall find for certain quantities relating to the contact of two metals (difference of potential and PELTIER-effect) would still hold in the limit, if the thickness of the layer of transition were indefinitely diminished. This may, however, be inferred from thermodynamical considerations.

§ 7. Having found in (20) the law of distribution of the velocities[1]), we are in a position to calculate the quantities ν and W (§ 1) with which we are principally concerned. If the value (20) is substituted in (4) and (5), the term $A\, e^{-hr^2}$ leads to an integral containing the factor ξ; this integral vanishes, if taken over the full extent of the diagram of velocities. In the remaining integrals the factor ξ^2 occurs; these are easily found, if we replace ξ^2 by $\frac{1}{3}\, r^2$, the element $d\lambda$ by $4\, \pi\, r^2\, d\, r$, and if then we integrate from $r = 0$ to $r = \infty$. Taking $r^2 = s$ as a new variable, we are led to the integrals

$$\int_0^\infty s\, e^{-h\, s}\, d\, s,\quad \int_0^\infty s^2\, e^{-h\, s}\, d\, s \text{ and} \int_0^\infty s^3\, e^{-h\, s}\, d\, s,$$

whose values are

$$\frac{1}{h^2},\quad \frac{2}{h^3}\quad \text{and}\quad \frac{6}{h^4}.$$

Finally, the "stream of electrons" and the flux of heat are given by

$$\nu = \frac{2}{3}\, \pi\, l \left[\frac{1}{h^2} \left(2\, h\, A\, X - \frac{d\, A}{d\, x} \right) + 2 \frac{A}{h^3} \frac{dh}{dx} \right] . \quad . \quad . \quad (21)$$

$$W = \frac{2}{3}\, \pi\, m\, l \left[\frac{1}{h^3} \left(2\, h\, A\, X - \frac{dA}{dx} \right) + 3 \frac{A}{h^4} \frac{dh}{dx} \right] \quad . \quad . \quad (22)$$

These are the equations that will be used in all that follows. For the sake of generality, I shall suppose (though, of course, this is not strictly true) that, if only a proper value be assigned to l, the formulae may still be applied even if we make other assumptions concerning the metallic atoms and their action on the electrons. From this point of view, we may also admit the possibility of different kinds of electrons, if such there are, having unequal mean lengths of free paths, and of, for each kind, l varying with the temperature.

Provisionally, we shall have to do with only one kind of electrons, reserving the discussion of the more general case for a future communication.

§ 8 From the equation (21) we may in the first place deduce a formula for the *electric conductivity* σ of the metal.

Let a homogeneous bar, which is kept in all its parts at the same temperature, be acted on by an electric force E in the direction of its length. Then, the force on each electron being $e\, E$, we have to put

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[1]) It may be observed that, as must be the case, the value (20) gives N for the number of electrons per unit volume and $\frac{3}{2h}$ for the mean square of velocity.

$$X = \frac{eE}{m}.$$

Also,

$$\frac{dA}{dx} = 0 \text{ and } \frac{dh}{dx} = 0,$$

so that (21) becomes

$$\nu = \frac{4\pi l A e}{3hm} E.$$

Multiplying this by e, we find an expression for the electric current per unit area, and in order to find the coefficient of conductivity, we must finally divide by E. The result is

$$\sigma = \frac{4\pi l A e^2}{3hm}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (23)$$

or, taking into account the relations (13) and (14) and denoting by u a velocity whose square is the mean square $\frac{3}{2h}$ of the velocity of heat-motion,

$$\sigma = \sqrt{\frac{2}{3\pi}} \cdot \frac{lNe^2u}{\alpha T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (24)$$

Drude gives the value

$$\sigma = \frac{1}{4} \frac{lNe^2u}{\alpha T}.$$

§ 9. The determination of the coefficient of *conductivity for heat*, which we shall call k (expressing quantities of heat in mechanical units) is rather more difficult. This is due to the circumstance that, if initially $X = 0$, the equation (21) implies the existence of an electric current in a bar whose parts are unequally heated. This current will produce a certain distribution of electric charges and will ultimately cease if the metal is surrounded on all sides by non-conductors. The final state will be reached when the difference of potential and the electric force arising from the charges have increased to such a degree that everywhere $\nu = 0$.

Since it is this final state, with which one has to do in experiments on the conduction of heat, we shall calculate the flux of heat in the assumption that it has been established.

In the first place we have then by (21), putting $\nu = 0$,

$$2hAX - \frac{dA}{dx} = -2\frac{A}{h}\frac{dh}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

and next, substituting this in (22) and again using the formula (14),

$$W = -\frac{8\pi l A a}{9h^2}\frac{dT}{dx}.$$

Consequently, the coefficient of conductivity has the value

$$k = \frac{8\pi l A a}{9h^2}, \quad \ldots\ldots\ldots\ldots \quad (26)$$

or

$$k = \frac{8}{9}\sqrt{\frac{2}{3\pi}}\, l\, N\, a\, u\,, \quad \ldots\ldots\ldots\ldots \quad (27)$$

Drude's result for this case is

$$k = \frac{1}{3}\, l\, N\, a\, u\,.$$

The ratio of the two conductivities is by my formulae

$$\frac{k}{\sigma} = \frac{8}{9}\left(\frac{a}{e}\right)^2 T \quad \ldots\ldots\ldots\ldots \quad (28)$$

and by those of Drude

$$\frac{k}{\sigma} = \frac{4}{3}\left(\frac{a}{e}\right)^2 T.$$

Here again, the difference between the two formulae consists merely in the numerical coefficients.

Just like Drude we may therefore conclude that the value of $\frac{k}{\sigma}$ does not depend on the nature of the metal and that it varies proportionately to the absolute temperature, consequences that have been verified with a certain approximation in the case of many metals.

It need hardly be observed that these conclusions could only be arrived at because we have neglected the mutual encounters between electrons [1]). In fact, these would tend to diminish the conductivity for heat, but not that for electricity, since they cannot have an influence in a phenomenon in which all electrons move in the same way. It is clear that, under these circumstances, a value of $\frac{k}{\sigma}$ independent of the nature of the metal could hardly be expected.

Let us next consider the absolute values.

The value of $\frac{aT}{e}$ that can be deduced from those of k and σ and for which, using (28), I find

$$\frac{aT}{e} = \sqrt{\frac{9}{8}\frac{k}{\sigma}T}, \quad \ldots\ldots\ldots\ldots \quad (29)$$

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[1]) See Thomson, l. c., p. 146.

may be compared, as has been observed by **Drude** and **Reinganum**[1]), to a value of the same expression that is obtained from other data. I shall suppose that the charge e of an electron is equal to that of an ion of hydrogen in an electrolytic solution and I shall represent by p the pressure that would be exerted, at the temperature T, by gaseous hydrogen, if a unit of volume contained one electrochemical equivalent. Then

$$\frac{\alpha T}{e} = 3p.$$

The proof of this formula is as follows. We may write for the number of atoms in unit volume of the gas considered $\frac{1}{e}$, for the number of molecules $\frac{1}{2e}$, and, since the mean kinetic energy of a molecule amounts to αT, for the total kinetic energy $\frac{\alpha T}{2e}$. As is well known, the numerical value of the pressure per unit area is two thirds of this.

Using the C. G. S. system and electromagnetic units, we have for the electrochemical equivalent of hydrogen 0,000104 and, putting, $T = 273^\circ + 18^\circ$,

$$3p = 38.$$

On the other hand, the measurements of **Jaeger** and **Diesselhorst** have given for silver at 18° C.

$$\frac{k}{\sigma} = 6{,}85 \times 10^{10},$$

whence, by (29),

$$\frac{\alpha T}{e} = 47.$$

The agreement between the results of the two calculations, for which the data have been furnished by widely different phenomena, though not quite satisfactory, is close enough to make us feel confident that **Drude**'s theory rests on a sound basis[2]).

§ 10. We might now return to the formula (25) and, denoting by φ the electric potential, so that

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[1]) **Reinganum**, Theoretische Bestimmung des Verhältnisses von Wärme- und Elektrizitätsleitung der Metalle aus der **Drude**'schen Elektronentheorie, Ann. Phys., 2 (1900), p. 398.

[2]) A better agreement is found if, instead of (28), we use **Drude**'s formula.

$$X = -\frac{e}{m}\frac{d\varphi}{dx}.$$

we might deduce from it expressions for the fall of potential in each point and for the difference of potential between the ends of the bar.

It is more interesting, however, to make a calculation of this kind for a more general case. Before doing so, we may observe that the equations (21) and (22) may be applied to a thin curved wire or bar and that we may as well suppose the normal section slowly to change from one point to another. The line passing through the centres of gravity of the normal sections may be called the axis of the conductor and we shall understand by x the distance from a fixed point, measured along this axis. We shall also assume that in all points of one and the same normal section the properties of the bar and the temperature are the same, but that, generally speaking, both depend on x, changing from one section to the next. By making different assumptions in this respect, we come to consider *circuits* of different kinds, composed of one or more metals and with any distribution of temperature we like.

For the sake of generality we shall introduce the notion of "molecular" forces of one kind or another exerted by the atoms of the metal on the electrons and producing for each electron a resulting force along the circuit in all points where the metal is not homogeneous. Actions of this nature have been imagined long ago by HELMHOLTZ for the purpose of explaining the phenomena of contact-electricity. We may judge of their effect in the simplest way by introducing the corresponding potential energy V of an electron relatively to the metallic atoms. This quantity, variable with x wherever the metal is not homogeneous, will be a constant in any homogeneous part of the circuit; we shall suppose this even to be so in case such a part is not uniformly heated. If, as before, we write φ for the electric potential, the force X divides into two parts

$$\left.\begin{aligned} X &= X_m + X_e, \\ X_m = -\frac{1}{m}\frac{dV}{dx}&,\quad X_e = -\frac{e}{m}\frac{d\varphi}{dx} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

We shall now consider an *open* circuit, calling the ends P and Q, and reckoning x from the former end towards the latter. Putting in (21) $\boldsymbol{v} = 0$ and attending to (30), we obtain for the stationary state

$$\frac{d\varphi}{dx} = -\frac{1}{e}\frac{dV}{dx} - \frac{m}{e}\frac{d}{dx}\left(\frac{1}{h}\right) - \frac{m}{2eh}\frac{d\,log\,A}{dx}, \quad . \quad . \quad . \quad (31)$$

whence by integration

$$\varphi_Q - \varphi_P = \frac{1}{e}\left(V_P - V_Q\right) + \frac{m}{e}\left(\frac{1}{h_P} - \frac{1}{h_Q}\right) - \\ - \frac{m}{2e}\int_P^Q \frac{1}{h}\frac{d \log A}{d x} d x , \quad . \quad . \quad (32)$$

a formula which may now be applied to some particular cases.

a. Let all parts of the circuit be kept at the same temperature. Then, h is a constant, and

$$\varphi_Q - \varphi_P = \frac{1}{e}\left(V_P - V_Q\right) + \frac{m}{2\,e\,h}\left(\log A_P - \log A_Q\right) \quad . \quad (33)$$

The potential-difference will now have a positive or negative value, if the ends of the circuit are made of different metals. It appears in this way that the differences that have been observed in this case may be attributed either to an inequality of V_P and V_Q, i. e. to "molecular" forces acting at the places of junction (HELMHOLTZ), or to an inequality of A_P and A_Q, i. e. to a difference in the "concentrations" proper to the metals (DRUDE).

It need hardly be added that (33) becomes 0 whenever the ends are made of the same metal and that the law expressed in VOLTA's tension-series is implied by the equation.

b. Let the metal be the same everywhere. Then A is a function of h and (32) will always be 0, if the *ends* P and Q are kept at the same temperature, whatever be the distribution of temperature in the intermediate parts.

c. Let us next examine the potential-difference between the ends of an open thermo-electric circuit, a difference that may be regarded as the measure for the electromotive force F existing in it. Starting from P. and proceeding towards Q, the state of things I shall consider is as follows: 1st. Between P and a section R', the metal I maintained at a temperature varying from T_P to T' in R'. 2nd Between R' and S', a gradual transition (§ 6) from the metal I to the metal II, at the uniform temperature T'. 3rd From S' to S'', the metal II with temperatures varying from T' to T''. 4th Between S'' and R'', a gradual transition from the metal II to the metal I, the temperature being T'' in every point of this part of the circuit. 5th Finally, between R'' and Q, the metal I with a temperature changing from T'' to $T_Q = T_P$. It being here implied that the ends of the circuit consist of the same metal and have the same temperature, the equation (32) reduces to the last term, and we find, after integration by parts,

$$F = \frac{m}{2e} \int\limits_{P}^{Q} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

This integral may be divided into five parts, corresponding to the above parts of the circuit.

Distinguishing by appropriate indices the different values of h and A that have to be considered and keeping in mind that h is a constant both in the second and the fourth part, we have

$$\int\limits_{R'}^{S'} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx = 0, \quad \int\limits_{S''}^{R''} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx = 0,$$

$$\int\limits_{P}^{R'} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx + \int\limits_{R''}^{Q} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx = \int\limits_{h''}^{h'} \log A_I \frac{d}{dh}\left(\frac{1}{h}\right) dh,$$

h' and h'' being the values corresponding to T' and T'', the temperatures in R' and R''. Similarly

$$\int\limits_{S'}^{S''} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx = \int\limits_{h'}^{h''} \log A_{II} \frac{d}{dh}\left(\frac{1}{h}\right) dh.$$

If we combine these results, the formula (34) for the electromotive force becomes

$$F = \frac{m}{2e} \int\limits_{h'}^{h''} \log \frac{A_I}{A_{II}} \frac{1}{h^2} dh,$$

or, if we use (13) and (14),

$$F = \frac{2a}{3e} \int\limits_{T'}^{T''} \log \frac{N_{II}}{N_I} dT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Geodesy. — *"The connection between the primary triangulation of South-Sumatra and that of the West Coast of Sumatra."* By Mr. S. Blok. (Communicated by Prof. J. A. C. Oudemans).

I. *Short description of the triangulations of South-Sumatra and the West Coast of Sumatra* [1]).

Towards the end of 1896 the measurements for the primary triangulation, which will serve as a basis for the topographical sur-

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[1]) For a more detailed description I refer to the papers of Dr. J. J. A. Muller, occurring in the proceedings of the International Geodetic Association of 1892, 1896 and 1903.

vey of South-Sumatra, were begun at the station Langeiland *P* 68. These measurements were carried from the West Coast of Java over the Strait of Sunda and are lately completed at the station B^t^ Gadang *P* 39, situated in the Government of the West Coast of Sumatra.

The triangulation consists of one continuous chain of triangles, which, beginning at the side Langeiland *P* 68 — G^g^ Radja Basa *P* 67, is connected with the side G^g^ Talang *P* 38 — B^t^ Gadang *P* 39 of the triangulation of the West Coast of Sumatra.

It is true that this side does not exceed the length of 17120 meters, but a connection with the longer side B^t^ Poenggoeng Parang *P* 45 — G^g^ Talang *P* 38 had to be abandoned after it was found that the pillar, erected at B^t^ Poenggoeng Parang during the triangulation of the West Coast, was so damaged that it no longer could be used for this purpose.

The experience made during the measurements of the base at Padang for the triangulation of the West Coast of Sumatra, executed by means of a 20 meters steel tape, did not tempt us to measure also the base line for South Sumatra with this comparatively unreliable apparatus; and as an instrument admitting of a high degree of accuracy was not available, no special base was measured, but the length of the first side of the chain was based upon the two sides Batoe Hideung *P* 15 — G^g^ Karang *P* 35 and G^g^ Karang *P* 35 — G^g^ Gede *P* 36 of the Java triangulation. For the Java triangulation 3 base lines had been measured with an apparatus of Repsold, which had been sent back to Europe in 1882.

For the orientation of the South-Sumatra chain, determinations of latitude and azimuth were made at the station G^g^ Dempoe *P* 71 in the Lampong Districts in 1897. The geographical longitudes were reckoned from the meridian of 3° 15′ West of Batavia. This meridian, which nearly passes over the middle of South-Sumatra, is determined by the geographical longitude of the Java station G^g^ Karang *P* 35, as given in Abtheilung V der Triangulation von Java, p. 207.

To obtain a zero mark for the determinations of altitude, tidal observations were made during a year at Telok Betong in 1897 and 1898. From these the mean height of the sea level in Lampong Bay, the Lampong-zero, was derived. This was transferred to the pillar *T* 1559 at Telok Betong by levelling, and thence by reciprocal but not simultaneous zenith distances measurements to the primary point G^g^ Betoeng *P* 70 ¹).

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¹) In 1902 and 1903 tidal observations were also made at Benkoelen and from them the Benkoelen-zero (the mean height of the sea level at that place) was derived, which will be used afterwards, when the secondary measurements will be so far advanced.

With respect to the triangulation of the West coast, I have remarked above that the steel tape, with which a base line near Padang of 4860 M. was measured in 1883, did not admit of a high degree of accuracy. The length of the steel tape was determined before and after the operation by measuring with it under the necessary precautions a line of 200 M., of which the true length was accurately known from measurements with the base apparatus of Repsold.

Determinations of latitude and azimuth for the orientation of the chain were made at the West end of the base in 1883 [1]).

The geographical longitudes were reckoned from the meridian of Padang, which passes through the West end of the base, for which meridian 6° 26′ 42″ West of Batavia has been preliminarily accepted, a difference in longitude formerly determined by chronometers.

As zero mark for the altitudes was taken the Padang-zero, the mean sea level at Padang, formerly determined by observations during some months of 1874 [2]).

For the astronomical determinations, the measurements of the horizontal angles and those of the altitudes, the 10-inch Universal instruments of Pistor and Martins and of Wegener were used in both triangulations.

The telescopes of these instruments are placed excentrically; each circle is read with two micrometer microscopes.

With the exception of the Padang base-net, where directions were measured, the triangulation was made according to Schreiber's method; the measurements of all combinations of angles were repeated so often that the weight of a direction adjusted at the station was about 24, the weight of one observation of a direction being adopted as unit.

For the trigonometrical determinations of altitude, reciprocal but not simultaneous measurements were made; at each station, whenever possible, 6 zenith distances were measured for each point, under conditions as favourable as possible. With the exception of the first measurements on the West Coast, where signals were employed, all observations were taken on heliotropes.

As to the adjustments and computations I remark that, for the South-Sumatra chain, exclusive of the connecting pentagon with Java, which was adjusted according to the method of least squares, the

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[1]) In 1896 determinations of azimuth and latitude were also made at the station Tor Batoe na Goelang, *P* 62.

[2]) In 1889 the mean sea level at Siboga, about 350 kilometers off Padang, was determined by tidal observations; the connection of the two marks showed a difference of 0,85 M.

adjustment was effected by equally distributing the error of closure of each triangle over the 3 angles. The computation was made in a plane by transference by means of a Mercator's projection according to the method of Schols.

The adjustments of the triangulation of the West Coast of Sumatra were made in portions; only for the base-net and for the Northern part the method of least squares was applied; in most cases an approximation method was used. The computations were made on the ellipsoid.

The following remarks may be useful for a judgment of the accuracy which may be expected in the different connections.

(1). The distance between the base of Simplak, on which the triangulation of South-Sumatra rests, and that of Padang is about 850 kilometers; the least number of triangles, necessary for the transference of the length of the side Poetri-Dago of the Simplak base-net to the first side Gs Gadoet $P1$ — Poelau Satoe $P2$ of the triangulation of the West Coast of Sumatra, is 49.

(2). The distance between the stations Gs Dempoe and the West extremity of the base at Padang, used for the orientation of the net, is about 700 kilometers; the least number of triangles, by means of which the azimuth of the line Gs Dempoe — Gs Tenggamoes can be transferred to the first side of the triangulation of the West Coast, is 40.

(3). The distance between Telok Betong and Padang, where the tidal observations were made, is over 700 kilometers; the least number of steps, necessary for the transference of the altitude of the pillar at Telok Betong to the zero mark of Padang, is 24.

The difference between the two values of the logarithm of the length of the connecting side is expressed in units of the 7th decimal and corresponds to about $\frac{1}{23000}$ of the length of the side or to 43.2 mms. per kilometer.

The differences found are comparatively so small that their origin may be easily explained by the accumulation of errors of observation and by the irregularities of refraction. The difference between the values found for the latitudes does not indicate a local deviation at Gs Dempoe with respect to Padang.

For the length of the connecting side a better result might have been expected, if for the base measurement at Padang a more suitable apparatus had been available.

For the rest, the differences are such that for the purpose of the triangulation, namely, to afford a basis for the topographical work, they do not come into consideration.

II. Mean Errors.

Nature of the errors.	South-Sumatra	West Coast of Sumatra	Remarks.
In the determination of the geographical latitude (1)	0″.21	0″.35	(1) For the orientation of the nets.
In the determination of the azimuth of a night signal (1)	0″.25	0″.46	
In the azimuth of the 1st side, in so far as they arise from errors of the base-net.	—	0″.85	(2) Determination derived from 37 closing errors (see appendix).
In the angles adjusted at the station (weight 12);			(3) Determination derived from 73 closing errors.
a from the results of the adjustments at the station;	0″.34	0″.52 (4)	(4) If we consider only the 10 triangles*), which in the shortest way connect the first side with the connecting side, we find: *a* 0.″59, *b* 0″.86.
b from the errors of closure of the triangles according to the formula: $m = \sqrt{\frac{[xx]}{3n}}$	0″.64 (2)	0″.96 (3) (4)	

III. Differences found in the adjustments.

Nature of the determination.	South Sumatra	West Coast of Sumatra	Difference.
Logarithm of the connecting side	4,2335135.7	4,2334948.0	187.7
Length » » »	17120.39 M	17119.65 M.	0.74 M.
Azimuth » » »	247°26′18″.07	247°26′13″.13	4″.94
Geogr. latitude Gg. Talang	2°6′9″.312 S	2°6′8″.699 S.	0″.613
» » Bt. Gadang	2°9′43″.465 S	2°9′42″.555 S.	0″.610
Altitude above the sea level Gg. Talang	1375.5 M	1376.7 M.	1.2 M.
» » » Bt. Gadang	281.8 M.	284.1 M.	2.3 M.

From the triangulation of South Sumatra we derive:

the geographical longitude of Gg. Talang 5° 32′ 48″,525 } West of
" " " " Bt. Gadang 5° 41′ 20″,236 } Batavia

and from that of the West Coast of Sumatra:

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*) These triangles occur under the numbers 1, 2, 16, 17, 35, 36, 43, 50, 51 and 52 on pp. 603 and 604 of Comptes Rendus des séances de la dixième conférence générale de l'Association Géodésique Internationale.

Appendix.

Errors of closure of the triangles in the South Sumatra chain.

No. of the triangle	Instruments used, and diameter of the horizontal circle.	Readings of the microscope in seconds.	Number of microscopes.	Number of observations taken for each direction.	Closing errors for each triangle Δ +	−	Δ²
1	Pistor and Martins, 27 cm.	1″	2	24	0.44	—	0.1936
2	»	1″	2	24.25	1.82	—	3.3124
3	»	1″	2	24.25	0.44	—	0.1936
4	»	1″	2	24.25	—	0.63	0.3969
5	»	1″	2	24.25	0.31	—	0.0961
6	Wegener, Pistor and Martins, 27 cm.	2″.1″	2	24.25	—	0.65	0.4225
7	» »	2″.1″	2	24.25	0.58	—	0.3364
8	» »	2″.1″	2	24.25	—	0.93	0.8649
9	» »	2″.1″	2	24.25	0.21	—	0.0441
10	» »	2″.1″	2	24	—	1.74	3.0276
11	» »	2″.1″	2	24	—	0.29	0.0841
12	» »	2″.1″	2	24	0.04	—	0.0016
13	» »	2″.1″	2	24	1.20	—	1.4400
14	Pistor and Martins, 27 cm.	1″	2	24	—	0.73	0.5329
15	Pistor and Martins, Wegener, 27 cm.	1″.2″	2	24	—	1.33	1.7689
16	» »	1″.2″	2	24	1.93	—	3.7249
17	» »	1″.2″	2	24	—	1.11	1.2321
18	» »	1″.2″	2	24	—	1.76	3.0976
19	Pistor and Martins, 27 cm.	1″	2	24	2.36	—	5.5696
20	»	1″	2	24	—	1.70	2.8900
21	» Wegener, 27 cm.	1″.2″	2	24	—	1.06	1.1236
22	» »	1″.2″	2	24	0.38	—	0.1444
23	Wegener, 27 cm.	2″	2	24	—	0.03	0.0009
24	»	2″	2	24	—	1.41	1.9881
25	»	2″	2	24	—	1.36	1.8496
26	»	2″	2	24	—	0.66	0.4356
27	»	2″	2	24	—	0.55	0.3025
28	»	2″	2	24.25	1.83	—	3.3489
29	»	2″	2	24.25	—	1.05	1.1025
30	»	2″	2	24.25	—	0.12	0.0144
31	»	2″	2	24.25	0.75	—	0.5625
32	»	2″	2	24	—	0.56	0.3136
33	»	2″	2	24	1.12	—	1.2544
34	»	2″	2	24	0.81	—	0.6561
35	»	2″	2	24	1.56	—	2.4336
36	»	2″	2	24	0.40	—	0.1600
37	»	2″	2	24	0.43	—	0.1849

the geographical longitude of G^{t} Talang 0° 53′ 37″,833 } East of
„ „ „ „ B^{t} Gadang 0° 45′ 6″,151 } Padang,

whence for the longitude of the West end of the base of Padang respectively: 6° 26′ 26″,358 and 6° 26′ 26″,387, of which the mean value is 6° 26′ 26″,373 West of Batavia, corresponding to 100° 22′ 10″,68 East of Greenwich.

Hence follows that the difference in longitude between Padang and Batavia, as determined by geodetic measures, is less by 16″ or over 1^{s} than that found by chronometers.

Probably the difference is due for a small part only to the accumulation of errors of observation in the triangulation and almost exclusively to the method of determination by means of chronometers.

Physics. — *"On the melting of floating ice"*, by Dr. CH. M. VAN DEVENTER. (Communicated by Prof. VAN DER WAALS).

In what follows I shall discuss a physical fact, which though one of the simplest and most important of phenomena, seems to have escaped the attention of physicists up to now. The author asked at least some twenty men versed in physics after it, and not one of them had heard about it: many of them and specially the most experienced in this branch of science were not a little astonished at it. It is therefore not devoid of interest to discuss the fact in question, though the explanation can be followed even by beginners in physics.

§ 1. In order to show how surprising the fact is, we put the following

Problem.

Given a tray of a certain dimension, in which water is up to a certain level, and in which floats a piece of ice of a certain weight, everything at 0°. Required to find: in what way will the level of the water be changed, when the ice melts?

Solution: the level of the water does *not* change.

§ 2. This answer may be derived as a simple application of the law of ARCHIMEDES.[1])

If the piece of ice weighs A kg., the upward pressure is also A kg., and so the weight of the displaced water also A kg. As now the melted ice weighs also A kg., the melted mass will occupy

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[1]) The weight of the air is neglected in this discussion.

exactly the place of the immerged part, and accordingly leave the position of the surrounding water intact.

In short: the ice when melting contracts into the volume of the immerged piece.

§ 3. A more elaborate, but perhaps more graphical demonstration is the following.

Let the piece of ice have the volume of A liter. Then the volume of the free part is 83 A cm. and of the immerged volume 917 A cm. The immerged part gives, when melting, 841 A cm. of water, the free piece 76 A cm. of water. The water of the free piece supplies therefore what the immerged piece had lost in volume when melting, and there is no reason for change in the level of the surrounding water.

In this the specific gravity of ice is put at 0,917.

§ 4. It is obvious, that the same reasoning applies to other substances, so that the following general rule may be drawn up: when a substance, floating in its own melting-liquid, melts, the level of the liquid will not change.

§ 5. An application of everyday interest is this: if a glass is filled to the brim with water, in which ice floats, the water will not flow over when the ice melts.

We should, however, take care, when making the experiment with a full glass, not to mistake water that is condensed on the cold outside wall, and runs down, for water flowing over. A better proof is furnished by a glass which is not quite full of water, and on which the first level is indicated: after melting we must find the same level.

§ 6. Attention may be called to the fact that not only *after*, but also *during* the melting the level is the same as before.

For if one gramme of ice (or a given part of it) melts and gives one cm. (or an equally large part of it) of water, the weight of the floating piece and so also the upward pressure will be diminished by one gramme (or an equally large part of it), and consequently the volume of the immerged piece will be decreased by one cm. (or an equally large part of it). For the additional water room has been made by the decrease in displacement.

§ 7. The law of the permanent level holds also when the floating ice has *empty cavities*.

This is obvious for cavities which are in the piece rising above the surface, as these cavities have no influence on the upward pressure.

If the immerged piece has a cavity of A cm., the upward pressure is equally large as for a solid piece of ice of the same weight, but there are A grammes of ice more above the water. When melting, these A grammes of ice form A grammes of water, just sufficient for filling up this cavity.

The law of the permanent level holds also when the ice contains *air bubbles,* at least by the same degree of approximation, with which we may neglect the weight of the air.

§ 8. When fresh water ice floats and melts in salt water, the level does rise, though slightly, the immerged part now being smaller than before, and so the melted ice cannot be contained in the volume of the immerged part.

Here and in what follows the change of volume, caused by the *mixing* of *salt water* and *fresh water,* is neglected, which is certainly permissible when the proportion of the salt is slight.

For A liters of ice, which weigh 917 A grammes and float in salt water of 1,03 specific gravity, the volume of the immerged piece is 890 A cm.; the available space can therefore hold 890 A cm. of the melted water, but the remaining 27 A cm. raise the level.

This remaining part is about one fourth of the piece which rises above the surface of the water (110 A cm.).

§ 9. If in *salt water* a piece of one liter of ice floats, which has a cavity under water of B cm., then there are $(1000\text{-}B)$ cm. of solid ice of a weight of $0{,}917(1000\text{-}B)$ grammes.

The upward pressure is therefore $0{,}917\ (1000\text{-}B)$ gramme, and with a specific gravity of the salt water of 1,03, the immerged volume is $0{,}89(1000\text{-}B)$ cm. When melting, we get $0{,}917(1000\text{-}B)$ cm. and so there is a surplus of $0{,}027(1000\text{-}B)$ cm. of water to the volume yielded by the immerged piece, which raises the level.

The piece of ice rising above the surface was $1000\text{-}0{,}89(1000\text{-}B)$ cm. or $(110 + 0{,}89B)$ cm., and the ratio of the remaining piece mentioned to this volume is as one to $\left(4{,}1 + \dfrac{B}{27-0{,}027\,B}\right)$.

The smaller B is, the more this relation approaches to about a fourth.

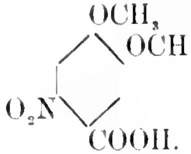
§ 10. *History.* A remark made two years ago by a pupil of the third year of the "Gymnasium Willem III" at Batavia to the writer suggested this paper. This pupil, called van Erpecum, said that he had observed that a glass filled to the brim with water and floating ice, does not flow over, when the ice melts.

This fact leading easily to the law of the permanent level and this law — as the writer is bound to believe — having up to now escaped the attention of physicists, physical science owes the discovery of a remarkable fact and the addition of a paragraph to this pupil.

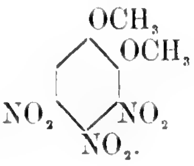
Amsterdam, Dec. 1904.

Chemistry. — "*On trinitroveratrol*". By Dr. J. J. Blanksma. (Communicated by Prof. H. W. Bakhuis Roozeboom).

It has been previously stated [1] that the dimethylether of trinitropyrocatechin is formed by the nitration of the dimethylether of 3.5 dinitropyrocatechin. As the nitro-group might have been introduced either in the position 4 or 6, it was still necessary to ascertain the constitution of this compound. The substance which melts at 146°—147° is identical with trinitroveratrol, which has already been described by Tiemann and Matsmoto [2] and is obtained by nitration of veratrol (the dimethylether of pyrocatechin) or of veratric acid. Tiemann and Matsmoto have shown that veratric acid on nitration yields nitroveratrol and nitroveratric acid. Afterwards, Zincke and Francke [3]) have proved that nitroveratric acid formed by nitration of veratric acid has the following constitution:



Now, on further nitration with fuming nitric acid this nitroveratric acid yields trinitroveratrol so that the constitution of trinitroveratrol is



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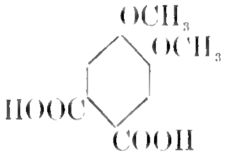
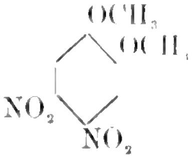
[1] Recueil **23**, 114.

[2] Ber. **9**, 937.

[3] Ann. der. Chem. **293**, 175.

Dinitroveratrol prepared by nitration of veratrol [1]) and of metahemipinic acid [2]) and which is consequently formed as follows:



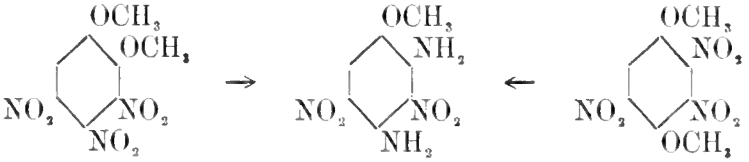


also gives on subsequent nitration the same trinitroveratrol, again showing that the constitution of that substance may be expressed by $C_6\,H(OCH_3)_2\,(NO_2)_3$ 1, 2, 3, 4, 5.

Now, trinitroveratrol obtained from veratrol is identical with that from the dimethylether of 3.5 dinitropyrocatechin; the melting points of both substances are the same; a mixture of the two substances shows no lowering of the melting point, whilst the same reaction products are obtained from both substances by the action of alcoholic ammonia or methyl-alcoholic sodium methoxide. We therefore see that in the nitration of 3.5 dinitroveratrol, the nitro-group is introduced between the two existing nitro-groups.

Tiemann and Matsmoto [3]) have already demonstrated that trinitroveratrol reacts readily with alcoholic ammonia. As they thought that the two OCH_3 groups were replaced by NH_2, they have not been able to identify the product formed in this reaction.

On repeating the experiment, I noticed that ammonium nitrite is formed so that also one of the NO_2 groups is replaced by NH_2. The substance formed melts at 247° and is identical with the compound afterwards obtained by Nietzki and Kurtenbacher [4]) which is formed by the action of alcoholic ammonia on trinitrohydroquinonedimethylether.



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[1]) Brüggemann, Journ. f. prakt. Chem. (2). **53**, 252.

[2]) Rossin, Monatsh. f. Chem. **12**, 491. Heinisch, ibid. **15**, 229.

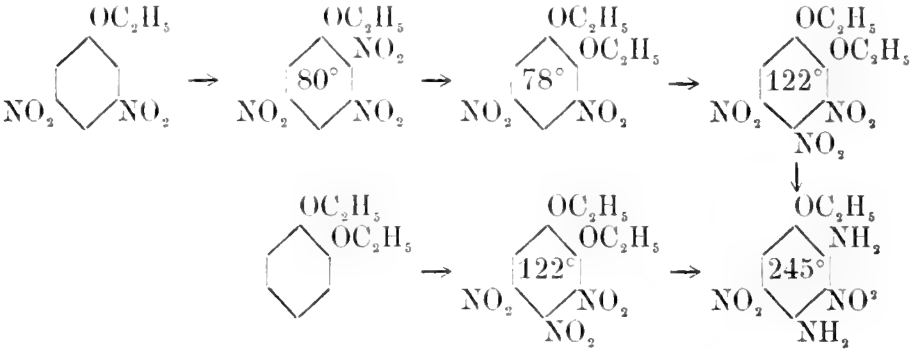
[3]) Ber. **9**, 937; **11**, 131.

[4]) Ber. **25**, 282.

This also shows that the NO_2 groups in trinitroveratrol are situated in the positions 3, 4 and 5.

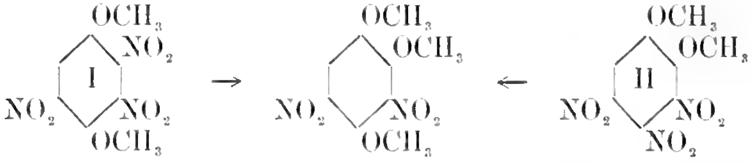
If this dinitrodiamidoanisol is treated with KOH we obtain the monomethylether of dinitrotrioxybenzene, a substance already obtained by Nietzki and Kurtenbacher from the said reaction-product of trinitrohydroquinonedimethylether and ammonia.

In quite an analogous manner the same result was obtained for the oxyethyl compound:

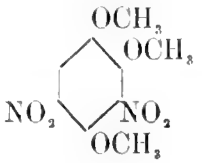


This latter substance has been formerly obtained by Nietzki [1]) by treating trinitrohydroquinonediethylether with alcoholic ammonia.

Although now the constitution of trinitroveratrol and of trinitropyrocatechindiethylether seemed to be satisfactorily determined, I have tried to furnish additional evidence by treating these substances with sodium ethoxide or methoxide; then it was to be expected that the following changes might occur:



If now trinitrohydroquinonedimethylether (I) is treated with a solution of sodium methoxide in absolute methylalcohol the addition of each drop causes a brownish coloration which nearly instantly disappears. After a partial evaporation of the solvent, crystals are formed which melt at 92°; according to an analysis this is the trimethylether of dinitro-oxyhydroquinone.



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[1]) Ann. der Chem. **215**, 153.

When we treat this substance with alcoholic ammonia two OCH_3's are readily replaced by NH_2 and we obtain the same dinitrodiamidoanisol as that obtained from trinitrohydroquinonedimethylether.

Trinitroveratrol (II) however behaves quite differently from $Na\,OCH_3$. If to the methyl-alcoholic solution is added sodium methoxide a purple-red coloration is obtained, which only disappears after heating for a few minutes on the waterbath, after which the liquid turns yellow. On cooling, fine yellow crystals are deposited (m.p. 152°) which are not affected by alcoholic ammonia or by potassium hydroxide.

The motherliquor contains besides $Na\,NO_2$ a small quantity of a substance which is perhaps identical with that from trinitrohydroquinonedimethylether.

Fine crystalline compounds are also obtained by the action of potassium cyanide on trinitroveratrol in alcoholic or methyl-alcoholic solutions; in either case two different substances are produced.

It is probable that trinitroveratrol (in common with other nitro-compounds) first forms an additive product with $Na\,OCH_3$ or KCN [1]), which then suffers decomposition and causes the formation of the said products.

The fact that the course of the reaction is a somewhat unusual one is most likely to be attributed to the presence of three adjacent nitro-groups in the benzenecore. I hope a further study will throw some more light on the subject.

Amsterdam, Dec. 1904.

Chemistry. — "*On* W. Marckwald*'s asymmetric synthesis of optically active valeric acid.*" By Dr. S. Tijmstra Bz. (Communicated by Prof. Bakhuis Roozeboom).

Some time ago, Marckwald [2]) prepared active valeric acid in a manner which according to his opinion entitled him to look upon this synthesis as the first purely asymmetric one. Shortly afterwards this opinion was challenged in an article from Messrs. Cohen and Patterson [3]), who denied that the synthesis could be an asymmetric one as being opposed to the theory of electrolytic dissociation. After-

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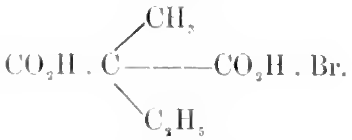
[1]) Loring Jackson. Amer. Chem. Journ. **29**, 89, (1903).
Lobry de Bruyn. Rec. **23**. 47.

[2]) Ber. 37, 349.

[3]) Ber. 37, 1012.

wards, **Marckwald**[1]) defended his standpoint in such a manner that no further controversyhas taken place.

Although the theoretical aspect of the question might be considered as solved, it still occurred to me that from an experimental point of view, the synthesis might be capable of some improvement. **Marckwald** starts from methylethylmalonic acid; of this the acid brucine salt is made in which now occurs an asymmetric carbon atom in the residue of the methylethylmalonic acid:



$$CO_2H\,.\,C(CH_3)(C_2H_5)\text{——}CO_2H\,.\,Br.$$

Owing to the influence of the active brucine, the two possible forms will not be produced in equal quantities and as a transformation between the two forms is possibly owing to the ionisation, the solution, on evaporation, will only deposit one salt, as during the crystallisation the equilibrium between the two forms is constantly being restored. The active brucine salt is now heated at 170° when carbon dioxide is eliminated and the brucine salt of methylethylacetic acid is formed. As this elimination of carbon dioxide will take place exclusively, or nearly so, at the free carboxyl group, the result will be a brucine salt of active methylethyl acetic or in other words *l*-valeric acid. By acidification with dilute sulphuric acid, distillation in steam and rectification, **Marckwald** obtained a product which in a 10 c.m. tube showed a rotation of $[\alpha]_D = -1^\circ.7$ which corresponds with not quite 10% of *l*-valeric acid. **Marckwald** attributes this low yield of active material to the high temperature employed (170°), which may have caused atomic shiftings.

The problem appeared to me of too great importance not to try and obtain a better yield of active valeric acid by altering the *modus operandi*. The idea struck me that it ought to be possible to considerably lower the temperature at which carbon dioxide is eliminated and thus remove one cause of atomic shifting.

In my preliminary experiments I used the methylethylmalonic acid itself which melts at 118° and of which it is stated in the literature that it rapidly loses its carbon dioxide at 180°. As a rule the acids, which possess two carboxyl groups attached to one carbon atom, lose carbon dioxide when heated above their melting point; we rarely find, however, in the literature cases where this temperature is correctly indicated and very often, at least in the case of substances melting at low temperature, the uniform temperature of 170°—180° is accepted.

The methylethylmalonic acid was now heated in vacuo at 130° in

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[1]) Ber. 37, 1368.

a tube connected with a mercury barometer and also with a mercury airpump, which caused a fairly rapid decomposition; the pressure rose beyond 1 atmosphere. Even at 100°, decomposition takes place if we only take care to continually evacuate; the mass first becomes partially liquid owing to the valeric acid formed and now we can plainly see the evolution of carbon dioxide from the solid particles of methylethylmalonic acid still suspended in the liquid. We cannot, therefore, speak of a definite decomposition point of acids with two carboxyl groups attached to one carbon atom. The statement that these substances lose carbon dioxide by heating above their melting point is consequently not only very vague but to some extent also incorrect as methylaethylmalonic acid already loses CO_2 when still in the solid condition.

Whilst, however, it takes days before the methylethylmalonic acid is decomposed at 100° at the ordinary pressure, this process is finished in a few hours if we continually evacuate. This would be most readily explained by assuming that this decomposition is a dissociation phenomenon. At each temperature, there would then exist a definite dissociation tension and if now by a continual evacuation care is taken that one of the decomposition products is always being removed, it is obvious that finally all must be decomposed. The only difference between this phenomenon and the classical example of $Ca\,CO_3$ is this that one has never succeeded in obtaining an acid with two carboxyl groups by heating an acid, containing one carboxyl group, in carbon dioxide. This may be explained either by assuming false equilibria, or by supposing that the velocity of reunion of the decomposition products is exceedingly small. I intend to further investigate this point.

As it had now been proved that the temperature of decomposition of acids with two carboxylgroups to one carbon atom could be greatly decreased by diminution of pressure, it was obvious that the synthesis of l-valeric acid might also be improved by allowing the CO_2-elimination to take place in vacuo at least if MARCKWALD's idea was correct that the bad yield of active material was due to atomic shiftings [1]).

I have now heated the acid brucine salt of methylethylmalonic acid with continual evacuation at 120°, therefore far below its melting

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[1]) It is easy to understand that a decrease of the temperature at which carbon dioxide is expelled is in itself not capable of improving the synthesis. The velocity of the atomic shiftings would no doubt have much diminished but then also the velocity of the carbon dioxide elimination, and the complete decomposition of the substance would take a much longer time. The evacuation, therefore, merely serves to accelerate the decomposition process.

point (155°), and after the whole mass had turned to a thick liquid and no more carbon dioxide was evolved the product was dissolved in boiling water. The solution was acidified with sulphuric acid and distilled in a current steam. The distillate was shaken with ether, the etheral solution was dried and after the ether was evaporated, the residual valeric acid was rectified and its boiling point found to be 174°—176°. The rotation of this was determined at $[\alpha]_D = -4°.3$ which corresponds with 25,8°/₀ *l*-valeric acid. It made no difference whether the first or last fraction of the distillate was taken.

The synthesis of *l*-valeric acid has, therefore, been much improved and it is possible to still further increase the yield of active acid by operating at still lower temperature as I have observed that the acid salt of methylethylmalonic acid possesses even at 100° a fairly large decomposition tension.

Amsterdam, Org. Chem. Lab.

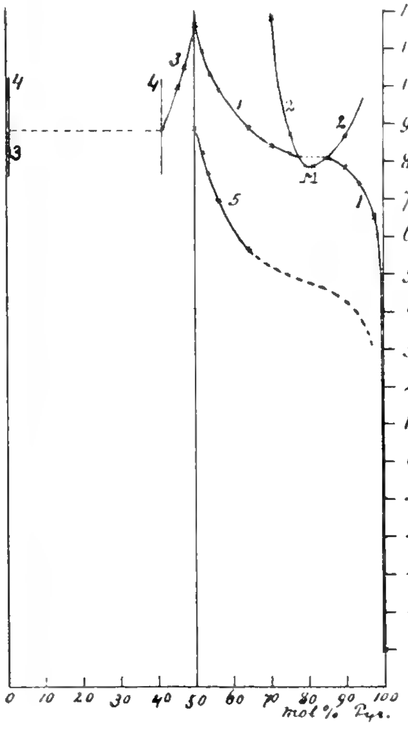
Chemistry. — "*On the system pyridine and methyl iodide.*" By Dr. A. H. W. Aten. (Communicated by Prof. Bakhuis Roozeboom).

Among the binary systems which have been studied up to the present in the gaseous, liquid and solid condition there are many in which occur chemical compounds formed from the two components. In most of those cases, those compounds possessed but little stability so that the conditions of formation and decomposition were situated within an easily attainable range of temperatures.

In the case of the more stable chemical compounds, however, those conditions of gradual formation and decomposition are less easy to attain. Still, their study promises a clearer insight into the changes which a system undergoes when a chemical compound is formed therein, and in the systems which form very stable compounds; such a comparison can be made all the more readily at a lower temperature because the reaction velocities are then generally so reduced that the system can be studied at will in the presence or absence of the compound so that these two cases may be compared.

A first example in which this could be at least partially attained is given by the system pyridine and methyl iodide. These two substances are capable of forming a quaternary ammonium compound $C_5H_5N.CH_3I$ which possesses a fairly great stability. At 60° and higher temperatures this compound is rapidly formed in the mixtures of the two liquids; at the ordinary temperature this formation takes place rather slowly and exceedingly slowly on cooling. On cooling rapidly, we should therefore undoubtedly get from the liquid mixtures solid pyridine (m.p. —50°) and solid methyl iodide (m.p. below —80°). Moreover, all those liquid mixtures in which no compound has formed as yet are homogeneous.

If, however, the liquid mixtures are kept for some time, the compound is formed with a considerable evolution of heat and it separates at the ordinary temperature in the solid condition, the amount depending on the temperature and the proportion of the mixture. At higher temperatures, however, it may cause the formation of two liquid layers. The peculiar behaviour shown is elucidated in the annexed figure in which the composition of the mixtures is expressed in molecule-percents of pyridine.



Let us first glance at the right side of the figure. In this 1 is the melting- or solubility-line of the compound, commencing with the melting point of the compound (117°) and extending to a eutectic point very close to the melting point of pyridine, because at lower temperatures the compound is but little soluble in pyridine. At 81°, from 77.5—85.5 mol. % of pyridine, the line 1 is however interrupted as no homogeneous liquid can exist between the two concentrations. The line 2 incloses with its two branches, which meet in M, an immiscibility-region which becomes enlarged at higher temperatures. The fused compound is therefore miscible with pyridine to a limited extent only. The point M, however, can only be reached when there is no separation of solid compound which may be easily prevented for some time.

At the left side of the figure we meet with nearly the same series of phenomena: 3 is here the solubility line, 4 the two branches of the immiscibility line. The immiscibility region is here very great, at 88° from about 0.5 to 41 mol. % of pyridine, whilst no change could be observed at higher temperatures and consequently no critical mixing point is known.

The line 5 is the solubility line of a metastable form of the solid compound; this line, however, can only be partially determined in the presence of an excess of pyridine. With a large excess the stable form was formed too readily. If the line could have been continued, it would have been continuous, in distinction from 1, as it is situated entirely below the mixing point M.

It could not be determined at the side of the mixtures which are richer in CH_3I as these crystallise very slowly and then we always obtain the stable form.

The most noteworthy result of this research is, however, that two liquids which are miscible in all proportions, may yield two sets of coexisting liquids owing to the formation of a chemical compound. In the formation of less stable compounds such has never as yet been observed and the better known stable compounds have not as yet been studied from this point of view chiefly because the comparison of combined and uncombined liquids is so often rendered difficult by the great differences in the melting points of the components.

The sharp intersection of the melting point lines 1 and 3 at 117° and the strong elevation of the boiling point after the combination (pyridine 116°, CH_3I 42°, combined liquid 270°) show that even in the liquid state, the compound is certainly for the greater part undissociated.

Probably the partial miscibility of this combined liquid with its components is connected with the fact that the chemical nature of the compound differs so greatly from those of the components. On this point also we possess but very little knowledge at present.

Chemistry, — "*The reaction of* FRIEDEL *and* CRAFTS". By Dr. J. BÖESEKEN. (Communicated by Prof. A. F. HOLLEMAN).

As is well known, the reaction of FRIEDEL and CRAFTS does not always proceed uniformly. Sometimes traces only of the catalyzer seem to suffice for the preparation of large quantities of the desired product; in other cases equimolecular quantities of the products to be condensed require from $^1/_{20}$ to $^1/_{10}$ mol. of the reagent. In a great many condensations it has been shown that at least 1 mol. of $AlCl_3$ is required in order to obtain the highest possible yield.

The reaction is also dependent on a number of circumstances which are either connected with a secondary action of aluminium chloride (Rec. XXII p. 302) on one of the substances present during the reaction, or else depend on the nature of these substances themselves.

It strikes me that the number of different syntheses made since the discovery of the catalytic action of aluminium chloride is large enough to enable us to explain the cause of this different conduct by a somewhat systematic consideration.

It must be well remembered that aluminium chloride can only then exert its power when it is capable of rendering the chloride (or anhydride) active; that is to say it must be present in the mass either in a free or loosely-combined state.

This mass contains besides the catalyzer (and eventually some diluent, such as CS_2): A the chloride (or anhydride), B the benzene derivative, C the formed product. If now we disregard the above-mentioned secondary decomposition phenomena the following cases may occur.:

I. The aluminium chloride combines with *none* of these substances or the compounds are completely dissociated at the reaction-temperature.

We are then dealing with the catalytic action in the truest form. A trace of aluminium chloride will suffice to convert unlimited quantities of A and B into C. This is for instance the case in the chlorination (bromination) of benzene at the ordinary temperature. If the substances used have been carefully dried more than 1 kilo of chloro-(bromo) benzene may be prepared with the aid of 0.5 gram of aluminium chloride without a visible diminution of the quantity of the catalyzer. When preparing diphenylmethane from benzyl chloride and benzene we can also work with very small quantities of the catalyzer if the strongly diluted benzyl chloride is poured into a large excess of benzene and the reaction-mass is from time to time replaced by new benzene; yet the decomposition of the benzyl chloride by the catalyzer cannot be entirely prevented (Recueil XXIII p. 98).

II. The aluminium chloride combines with the chloride (A) to a more or less strong additive product. When these compounds are very stable, the reaction may not take place at all: the phosphorus oxychloride combines with strong evolution of heat with a mol. of aluminium chloride (CASSELMANN, Ann. 98 p. 220), and this product is *not* attacked by benzene or toluene. In the other cases the reaction proceeds, however, very favourably. As aluminium chloride also combines with the formed product (C) only one mol. of the catalyzer is required for equimolecular quantities of the components.

Here we must still distinguish between the following categories:

a. the catalyzer is situated closely to the place where the condensation takes place, which is the case in all syntheses of ketones, sulphones etc from the corresponding acid chlorides, where it is linked to the carbonyl (sulphuryl) group, for instance:

$$CH_3COClAlCl_3 + C_6H_6 = CH_3COC_6H_5AlCl_3 + HCl$$

(Recueil XIX p. 20).

Presumably, this ought to include the syntheses of GATTERMANN, B 1897 p. 1622, where the aromatic aldehydes are constructed from CO and HCl and the amides of the aromatic carboxylic acids are obtained from carbamine chloride (Cl CO NH$_2$) B. 1899 p. 1117.

b. the aluminium chloride is combined to the chloride but not near the place where the condensation occurs, for instance:

$$AlCl_3 p.NO_2C_6H_4CH_2Cl + C_6H_6 = AlCl_3 p.NO_2C_6H_4CH_2C_6H_5 + HCl$$

(Recueil XXIII p. 103),

the catalyzer is here combined to the nitro-group.

III. The aluminium chloride combines with the benzene derivative (B) and not or with great difficulty, with the chloride (A).

In this case, the benzene-group which has combined with the catalyzer may increase (*a*) or diminish (*b*) the activity of the other H-atoms.

a. In the first case although the reaction may take place it will be much retarded.

Anisole, for instance, which yields a well-defined additive product with aluminium chloride hardly reacts at the ordinary temperature with carbon tetrachloride; the chlorine atoms of this chloride do not, apparently, get under the influence of the combined catalyzer.

Benzyl chloride, which acts very violently on benzene, attacks anisole so slowly that the velocity of the reaction could be measured at the ordinary temperature. (H. GOLDSCHMIDT, Central-Blatt 1903 II p. 820).

b. In the second case, the reaction does not take place. Nitrobenzene, aceto- and benzophenone, sulphobenzide etc. do not suffer condensation with carbon tetrachloride, chloroform, methylene chloride, sulphur chloride etc. by means of aluminium chloride.

IV. The aluminium chloride unites both with the chloride (A) and the benzene derivative (B). In this case it will depend chiefly on the influence of the groups present in the benzene whether the condensation takes place or not.

Whilst nitrobenzene cannot be acetylised or benzoylised, the nitroanisoles may be converted into the corresponding acetyl compounds.

One does not succeed in introducing a second acetyl group into acetophenone, but on the other hand *m*-xylene, mesytilene, *sym.*

triethylbenzene, and *sym.* durene appear to be *di*acetylised; from the experiments it appears that at least two mols. of the catalyzer are wanted (V. Meyer, B. 1895 p. 3212; B. 1896 p. 846; B. 1896 p. 2564; H. Weil, B 1897 p. 1285).

V. The catalyzer combines but little or not at all with the chloride (A) or the benzene derivative (B) combines only with the formed product. When this is a molecular compound (as in the cases known up to the present) at least one mol. will be required for one mol. of the chloride.

I have found that one mol. of carbon tetrachloride exactly requires the molecular quantity of aluminium chloride for the formation of triphenylmethane chloride

$$CCl_4 + 3C_6H_6 + AlCl_3 = 3HCl + (C_6H_5)_3CCl.AlCl_3.$$

S_2Cl_2 and SCl_2 also require one mol. of the catalyzer when being condensing with benzene.

The behaviour of sulphur itself towards benzene is very interesting in this respect; from an investigation, the details of which will be published elsewhere, it appears that this condensation must be represented by the following scheme:

$$S_8 + 6C_6H_6 + 3AlCl_3 = \underset{\text{diphenylsulphide}}{2(C_6H_5)_2S.\,AlCl_3} + \underset{\text{thianthrene}}{(C_6H_4)S_2.\,AlCl_3} + 4H_2S$$

For one mol. of sulphur, three mols. of the catalyzer are absorbed: the element itself does not combine with aluminium chloride.

As stated above we have only mentioned the cases where no secondary actions occur or where these may be greatly prevented. In a number of syntheses this is very difficult to realise particularly where we start from chlorides where the carbon atom which carries the chlorine atom is also combined with hydrogen atoms (Recueil XXII p. 306), or where hydrogen and chlorine occur near adjacent carbon atoms. ((Mouneyrat, Bull. Soc. chim [3] 17 p. 797; [3] 19 p. 179, p. 407 and p. 554).

To this belong all the syntheses of the homologues of benzene where we also have the circumstance that the more alkyl groups enter into the benzene, the more readily it will be decomposed by aluminium chloride; the quantities of aluminium chloride required therefore become larger and vary in each individual case. In order to get a better insight in the *actual catalytic* action of aluminium chloride these last reactions will furnish in my opinion, a less suitable material than the first five categories which I have mentioned. These will have to be submitted to a systematic and, if possible, also quantitative research.

I have been engaged for some time in experiments in this direction, which will be published from time to time.

Assen, Dec. 1904. *Chem. Lab. H. B. S.*

Physics. — *"The influence of admixtures on the critical phenomena of simple substances and the explanation of* TEICHNER'S *experiments."* By J. E. VERSCHAFFELT. Supplement N°. 10 to the Communications from the Physical Laboratory at Leiden by Prof. KAMERLINGH ONNES.

§ 1. *Introduction.* That small proportions of any admixture cannot but have a great influence on the critical phenomena of a simple substance has repeatedly been demonstrated by KAMERLINGH ONNES and his pupils. This conviction led them to look for an explanation of the abnormal phenomena at the critical point — on which some observers base their doubts of the validity of the theories of ANDREWS and VAN DER WAALS — by preference in small quantities of admixture, and gave rise in the Leiden laboratory to several researches in which the greatest care was bestowed upon the cleaning of the substances investigated.

As early as Oct. '93, in Comm. N°. 8, p. 15, KUENEN has demonstrated the importance of phenomena of retardation, due to the irregular distribution of admixtures. In Comm. N°. 11 (Proc. May '94) he proved experimentally that, when pure substances were used, the deviations found by GALITZINE were not observed. The subject of Comm. N°. 68, p. 4 (Proc. April '01, p. 629) was a difference in opinion between DE HEEN and KAMERLINGH ONNES about the significance of the former's well-known experiments, of which the results were ascribed by the latter to admixtures. I have taken part in some preliminary experiments undertaken in consequence of this difference of opinion. They gave us the conviction that DE HEEN'S observations required systematic corrections and that, if these were applied, the observations would agree with the theories of ANDREWS and VAN DER WAALS[1]).

Indeed, according to KAMERLINGH ONNES' opinion, maintained by him in Comm. N°. 68, p. 13 (Proceedings, April '01, p. 637), the deviations found should be ascribed for a good deal to impurities, and should be explained by means of VAN DER WAALS' theory of mixtures[2]), l. c. p. 6 (Proc. p. 631). Moreover, if attention were paid to the variation of the molecular pressure the deviations to be expected in consequence of admixtures would show exactly the same nature as those observed by DE HEEN, while the variation of the molecular pressure owing to impurities, however small it may be for a small quantity of admixture, would yet cause considerable differences of density owing

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[1]) A more careful repetition of those preliminary researches is begun at Leiden soon after the controversy with DE HEEN.

[2])Cf. also HARTMAN, Suppl. N°. 3 to the Comms. from the Phys. Lab. at Leiden, p. 47.

to the high degree of compressibility of the substance in the critical state; l. c. p. 13 (Proc. p. 637).

At the time it was not possible to form a true judgment about the influence of admixtures and the required corrections. While other corrections, which had probably to be applied and which might have the same influence, were fully discussed, about the correction for admixtures, nothing could be said but that (l. c. p. 6, Proc. p. 631) measurements were being made at the laboratory, which would spread the desired light on the influence of small admixtures.

Since that time have been published those measurements by myself on mixtures of carbon dioxide and hydrogen (Comms. N°. 45, Jan. '99 and N°. 47, Febr. '99) and those by Keesom on carbon dioxide and oxygen (Comm. N°. 88, Jan. '04). In the series of "Contributions to the knowledge of van der Waals' ψ-surface" occur several calculations of Keesom (Comms. N°. 75, Dec. '01 and N°. 79, April '02) and of myself (Comm. N°. 81, Oct. '02 and Suppl. N°. 6, May and June '03). These calculations in which the law of corresponding states has been applied according to Kamerlingh Onnes for substances with admixtures, reduce all the deviations from the properties of the pure substances to the knowledge of the two quantities $\alpha = \frac{1}{T_k}\left(\frac{dT_{xk}}{dx}\right)_{x=0}$ and $\beta = \frac{1}{p_k}\left(\frac{dp_{xk}}{dx}\right)_{x=0}$ and of the empirical equation of state.

I have availed myself of the obtained results to investigate what differences of density will be observed in a tube of Cagniard de la Tour, containing carbon dioxide mixed with a small molecular composition of oxygen, if in the manner indicated by Teichner [1]) floats are placed into it to determine the density. I found it confirmed that the nature of the deviations which would be observed in Teichner's experiments in consequence of small admixtures (if pressure and temperature are in equilibrium), corresponds entirely to that of the deviations observed.

It seems to me an important result that, on the strength of the knowledge of the behaviour of the mixtures of carbon dioxide and oxygen, we can calculate that even very small quantities of oxygen in carbon dioxide (a few 0.001 mol.) are sufficient to produce the

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[1]) Drude's Ann., 13, 595, 1904. The explanation of Teichner's experiments covers that of Galitzine's experiments, where the density was determined at different heights by an optical method. In tubes filled with carbon dioxide, Gouy (C. R. 116 p. 1289, June 1893) has observed a slow displacement of the meniscus a little below the critical temperature, and has ascribed this phenomenon, and rightly I hold, to impurities.

differences of density which DE HEEN observed in carbon dioxide. Small admixtures of the same kind as those by which DE HEEN's experiments can be explained, may, until we have a proof to the contrary, also be assumed in the carbon tetrachloride with which TEICHNER experimented. I therefore hold that TEICHNER's researches, which from an experimental point of view leave less to be desired than those of DE HEEN's, must be explained in the same way.

They are now being repeated at the Leiden laboratory with carbon dioxide of the greatest possible purity, while in order to omit all doubts of temperature equilibrium [1]), thermoelements are sealed in the tube.

§ 2. *Difference in density between two phases with slightly differing proportions of admixture, when equilibrium of pressure and of temperature exists.* We imagine that in a tube, at a temperature T, which differs only little from the critical T_k of the pure substance, there are two layers of which the one contains per gramme molecule x_1 mol. of the admixture, the other x_2 mol.; the pressure is supposed to be the same [2]), i. e. equal to p, and also to differ little from the critical pressure p_k of the pure substance. In order to determine the density of a mixture with an (infinitely small) composition x, we may proceed as follows. The quantities α, β, and $\gamma = \alpha - \beta$ determine the critical elements T_{xk}, p_{xk}, v_{xk} of the point which for the mixture corresponds to the critical point of the pure substance, in first approximation (Comm. N°. 81 equation (14)) by the equations:

$$T_{xk} = T_k (1 + \alpha x),\quad p_{xk} = p_k (1 + \beta x),\quad v_{xk} = v_k (1 + \gamma x).$$

Hence to the temperature of observation T, i. e. the temperature of the mixture, a temperature T' of the pure substance corresponds in such a way that $\dfrac{T'}{T} = \dfrac{T_k}{T_{xk}}$; and we may therefore write in first approximation: $T' = T(1 - \alpha x)$. In the same way the pressure $p' = p(1 - \beta x)$ of the pure substance corresponds to the observed pressure p (pressure of the mixture). Suppose that at the temperature T' and the pressure p' the pure substance occupies the molecular volume v', a volume which may be derived from the empirical equation of state or which may be read on a diagram of isothermals, then, under the circumstances observed (T, p), we have for the molecular volume of the mixture considered $v = v' \ (1 + \gamma x)$.

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[1]) Cf. VILLARD, C. R. 118 and Comm. N°. 68 (April '01).

[2]) Doing so, we neglect the influence of gravitation, which is much smaller than at of the admixtures, and moreover increases the differences of density.

Determining the value of v, either by calculation or by means of a diagram, we find that, if the proportion $\frac{\beta}{\alpha}$ differs much from $\frac{T_k}{p_k}\left(\frac{\partial p}{\partial T}\right)_{v_k} = \left(\frac{\partial \pi}{\partial t}\right)_k = 7.3$ [1]) (cf. Suppl. N°. 6, p. 14; Proc. June '03, p. 121) owing to the particular shape of the isothermals near the critical point, the difference $v' - v_k$ is much larger (of lower order, viz. $\frac{1}{3}$) than the correction term $v' \gamma x$. For that reason and also because of the uncertainty about the volumes which belong to a definite pressure, again owing to the shape of the isothermals, we need not distinguish between v and v', in other words, we may neglect the correction term $v' \gamma x$ [2]). As, however, we intend to determine the density of the mixture, we must bear in mind that v is the volume occupied by $M_1(1-x) + M_2 x$ gr., M_1 and M_2 representing the molecular weights of the pure substance and the admixture. Thence follows the density $\frac{M_1(1-x)+M_2 x}{v}$, for which, for the same reason as above, we may put $\frac{M_1}{v'}$, i. e. the density of the pure substance itself at the temperature T' and the pressure p'.

On the strength of this consideration we may conclude that the densities of the two mixtures x_1 and x_2, at a temperature which is about the critical temperature of the pure substance T_k, may be read approximately on a p, ϱ diagram of the isothermals of the pure substance; on the isothermals of the temperatures $T_1' = T_k(1-\alpha x_1)$ and $T_2' = T_k(1-\alpha x_2)$ we seek two points for which the pressures are $p_1' = p_k(1-\beta x_1)$ and $p_2' = p_k(1-\beta x_2)$ respectively.

Besides these two layers, however, the tube really contains still several others of different composition, because the composition varies gradually [3]). If for different compositions we determine the densities

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[1]) Further on we shall see that, in the cases known thus far, this condition is satisfied.

[2]) The circumstance that we must determine the difference between the v's for two mixtures, does not alter this conclusion in the least. For also the difference between v_1' and v_2' is found to be of a lower order $\left(\frac{1}{3}\right)$ than the first.

[3]) What has been said here about accidental impurities, holds also for the experiments of Cailletet and Colardeau (C. R. 108, 1280, 1889) where jodine, which had been dissolved in liquid carbon dioxide, was not diffused equally through the tube at the temperature at which the meniscus disappeared; it also holds for similar experiments of Hagenbach (*Drude's Ann.*, 5, 276, 1901), who dissolved

at the same temperature and pressure, we obtain points which all lie in one curve, this curve therefore represents the variation of the density in the tube; from the shape of this curve, which very much resembles that of an isothermal in the neighbourhood of the critical point, it is evident that the substance in the tube cannot but show considerable differences of density.

I assume that between the two ends of the tube there is a certain difference in composition; then the greatest difference in density depends not only on the α and the β of the substances considered, and on the difference in composition, but also on the temperature, on the mean density and on the mean composition. For those mixtures of which the α and the β are known, I now shall give the difference in density which corresponds to $x_2 - x_1 = 0.001$, if the temperature is about the critical temperature of the pure substance and the mean density is also the critical density:

CO_2 with 0.001 mol. CH_3Cl, $\alpha = 0.378$, $\beta = 0.088$, $\Delta = 34\%$
CH_3Cl „ „ „ CO_2, $\alpha = -0.221$, $\beta = 0.281$, $\Delta = 31\%$
CO_2 „ „ „ H_2, $\alpha = -1.17$, $\beta = -1.62$, $\Delta = 42\%$
CO_2 „ „ „ O_2, $\alpha = -0.66$, $\beta = -1.09$, $\Delta = 36\%$
of the critical density.

The following differences in density would be observed in carbon dioxide with small quantities of oxygen, with different temperatures and differences of concentration, the mean density being still the critical one:

t	$x_2 - x_1 = 0.001$	$x_2 - x_1 = 0.0005$	$x_2 - x_1 = 0.0001$
31°.0	$\angle = 36\%$	$\angle = 30\%$	$\angle = 17\%$
31°.5	24	17	6
32°	17	10	2.5
33°	12	5	$\pm \frac{1}{2}$
34°	6	3	$\pm \frac{1}{2}$

How the difference in density depends on the mean density of the substance may be seen from the following table, which relate to carbon dioxide with oxygen at a temperature of about 31° C. and for $x_2 - x_1 = 0.001$.

Mean density	
$1.3\varrho_k$	$\Delta = 3\%$
1.2	8
1.1	24
1.0	36
0.9	24
0.8	6
$0.7\varrho_k$	1.5%

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salts in liquid sulphur dioxide. These experiments, therefore, where an admixture had intentionally been added, have been erroneously adduced as arguments against the theory of ANDREWS and VAN DER WAALS; for the rest HAGENBACH himself has understood the cause of the deviation he had found.

Dr. J. E VERSCHAFFELT. "The influence of admixtures on the critical phenomena of simple substances and the explanation of Teichner's experiments."

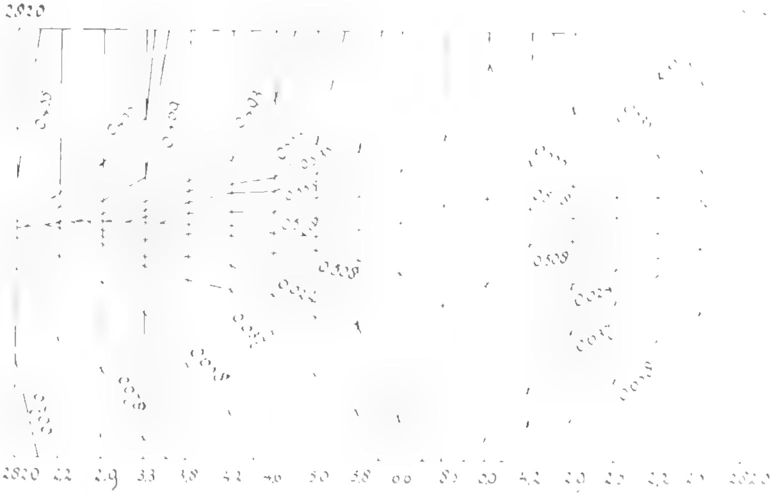

Fig. 1.

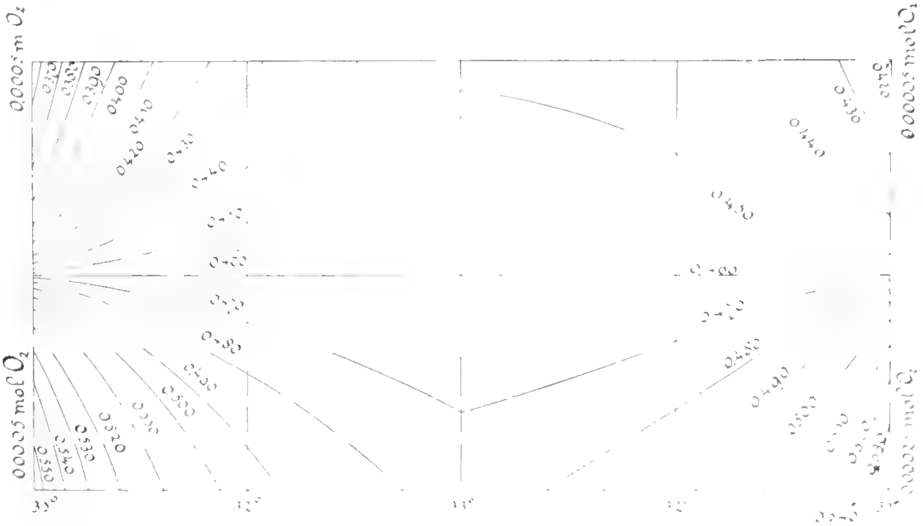

Fig. 2.

The next table shows how for carbon dioxide with oxygen, at a temperature of about 31° C., the mean density being the critical density and $x_2 - x_1 = 0.001$, the difference in density depends on the mean composition.

$\frac{1}{2}(x_2 + x_1) = 0.0005$	$\Delta = 36\,{}^0/_0$.
0.005	17
0.01	12
0.015	6

All these numbers relate to carbon dioxide with oxygen as admixture; it is probable that these results will also be more or less applicable to carbon dioxide with nitrogen, hence also with air, and as in carbon dioxide, which had been purified with great care, KEESOM detected about 0.00025 mol. of air, the possibility is not excluded of explaining the anomalies observed with carbon dioxide, by impurities of air.

The variation of the difference in density with the mean density reminds of a diagram concerning DE HEEN's experiments, formerly made by me (cf. Comm. N°. 68, Appendix p. 26; Proc. April 1901, p. 695); in Comm. N°. 68, Appendix p. 22 (Proc. April 1901 p. 691) KAMERLINGH ONNES has derived the same diagram for the course of the differences in density that would result from differences of temperature; therefore part of the deviations observed by DE HEEN are perhaps due to differences of temperature.

§ 3. *Survey of the experiments of* TEICHNER. In the influence of impurities we have a complete qualitative explanation of TEICHNER's observations. The results of his second series of observations, of which I have used only those above the critical temperature, are represented in fig. 1. The positions of the floats are indicated on vertical lines and the points occupied by the same bulb at different temperatures are combined by lines. In this manner curves of equal densities are obtained; for each curve I have given the corresponding density. In this series of experiments TEICHNER has first made observations at gradually increasing, and then at decreasing temperatures; after each variation of temperature the observer waited till the temperature had become the same throughout. As abscissae I have not taken the temperatures themselves, but I have placed the different observations at equal distances, that is to say, I have taken time as abscissa, thus assuming that between two observations there is always the same interval of time, which will not probably be far wrong. The temperature 282°.0 C. (uncorrected) is that at which the meniscus with increase of temperature was seen last and reappeared when the temperature was lowered; hence very nearly the critical temperature. It will be seen that most of the curves of equal density, when the temperature is raised, leave the point where the meniscus was seen last, bend away from that point more and more rapidly, turn round at about the highest temperature observed and return to the same point, which only few, however, reach when the temperature is fallen to the critical temperature.

From this last circumstance we conclude that the course of the curves of equal density is not only governed by the variation of the temperature but also by diffusion. Both through increase of temperature and also through diffusion, the distribution of the substance becomes more regular, and hence the curves of equal density ascend and would finally project beyond the drawing, if not the decrease of temperature in the second part of the experiment caused the withdrawing curves, partly at least, to return. But the very fact that the curves of equal density in the second part lie higher than those at equal temperatures in the first, is a proof that the progressing diffusion opposes the influence of the temperature; the following numbers may show which is about the course of the greatest difference of density in the tube throughout the series of experiment:

$t =$	282°	283°	284°	285°	286°	288°	286°	284°	283°	282°
$\Delta =$	50 %	40 %	30 %	25 %	20 %	15 %	15 %	20 %	25 %	30 %

It will be seen that the difference in density first decreases, then increases, but the values at equal temperatures are lower in the second part than in the first and the deviation increases; from this appears the influence of diffusion.

The value of Δ is not even smallest at the highest temperatures; the smallest value is not reached until the temperature is falling, in harmony with which is the fact that the bulbs 0.555 and 0.578 have reached their highest position not at 281°.1 C. but at 286°.0 C., hence during the period of decreasing temperature. This proves that, at least at the beginning of the decrease of temperature, the diffusion has a preponderating influence. That the heaviest bulbs did not show this peculiarity must probably be ascribed to the circumstance that in the lower part of the tube, where the substance is much denser, the diffusion takes place much more slowly; in those lower curves of density, however, we can clearly distinguish a point of inflection, which also, though less striking, points at the progressing diffusion.

That these circumstances can actually be explained by the diffusion of impurities I have tried to demonstrate by calculating and by representing graphically in the same way as in fig. 1 how the density of a substance is distributed in a tube which is filled with carbon dioxide, mixed with a small proportion of oxygen, if that admixture increases in concentration from the bottom upwards. I also suppose that the temperature first rises from the critical temperature of 31° C. to 33° C., and then falls again to 31° C. Further I assume that the concentration of the oxygen which at first decreased regularly from the top downwards, so that the greatest difference of concentration was 0.001 mol., at last, owing to a more rapid diffusion in the upper space, varies there less rapidly with the height than in the lower space[1]). Fig. 2 thus obtained, may really be looked upon as a diagrammatical reproduction of fig. 1; in the falling period the density curves, as in fig. 1, show a point of inflection; in the upper half no maximum has yet been reached by the curve 0.450, but by adopting a more rapid diffusion in that space I might have brought about also this circumstance.

§ 4. *Conclusion.* On the strength of what precedes we can therefore firmly deny that TEICHNER's observations[2]), at least with respect to the nature of the phenomena, are incompatible with the theory of ANDREWS and VAN DER WAALS. Down to details these phenomena can be explained by the presence of admixtures, which are slowly diffusing through the substance; and calculations based on existent data have shown that in order to reach a quantitative agreement, we must assume a proportion of the admixture of the same order as that which actually was present in other experiments with so-called pure substances. Whether in the carbon tetrachloride, used by TEICHNER, the required proportion of any admixture, of which neither the nature nor the α and β are known with certainty, has occurred, is a question that cannot be answered. It does not seem impossible, however, because carbon tetrachloride is a substance which, owing to the manner in which it is prepared, might contain many foreign components, and the constancy of the boiling point (to within 0°.1 C?) is not deemed by us a guarantee for sufficient chemical purity. We are even inclined to consider the existence of the deviations as a proof to the contrary, and the non-existence of the deviations (other

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[1]) Starting from a given condition, I might evidently have worked out this problem in perfect harmony with reality; it appeared to me, however, that this would have been useless trouble, and that the scheme, I have given of it, does at any rate represent the phenomena qualitatively.

[2]) The same conclusion holds for similar observations (DE HEEN, GALITZINE, etc.) about the so-called abnormal phenomena near the critical point.

causes taken into account) as the only certain *physical* criterium of purity.

As long as it has not been proved that existing impurities *cannot* account for the phenomena *quantitatively*, I see no reason to abandon the thesis that each substance shows a critical point at which the two coexisting phases become identical, so that one single critical density belongs to the critical temperature and the critical pressure.

Geodesy. — "*Determinations of latitude and azimuth, made in* 1896—99 *by* Dr. A. PANNEKOEK *and* Mr. R. POSTHUMUS MEYJES *at Oirschot, Utrecht, Sambeek, Wolberg, Harikerberg, Sleen, Schoorl, Zierikzee, Terschelling (the lighthouse Brandaris), Ameland, Leeuwarden, Urk and Groningen.*" Short account of the report published under this title by Prof. J. A. C. OUDEMANS.

Besides the stations mentioned in the title, the programme, as drawn by the Dutch Geodetic Committee, contained also the stations Leyden and Ubagsberg, where the observations were made under superintendence of Prof. H. G. VAN DE SANDE BAKHUYZEN, who himself will publish them.

The observations of Messrs. PANNEKOEK and POSTHUMUS MEYJES at the above named thirteen stations, have been made under my superintendence, and in an introduction I have given an account and a criticism of them. Here the following details may suffice:

The mean latitude of the four northernmost stations, Terschelling, Ameland, Leeuwarden and Groningen is 53°18′39″, that of Schoorl, Urk and Sleen 52°42′45″, that of Leyden, Utrecht, Wolberg and Harikerberg 52°10′40″, that of Zierikzee, Oirschot and Sambeek 51°35′51″, while the latitude of the southernmost station Ubagsberg is 50°50′53″.

The entire arc of meridian, of which the length will be computed as soon as the results of the entire triangulation will be known, amounts therefore to 2°27′46″ and may be considered to consist of four parts of 35′54″, 32′5″, 34′49″ and 44′58″ respectively. Thus it will appear afterwards whether the curvature of the meridian, as found here, agrees with the form adopted.

The Universal instruments used for the observations were of REPSOLD; they were provided with a horizontal circle of 315 mms., and a vertical circle of 245 mms. in diameter, and belonged to the observatories of Leyden and Utrecht respectively. The circles were graduated to 4′, whereas the microscopes of the Utrecht instrument are read directly to 2″, those of the Leyden instrument to single seconds.

The micrometer screws, the levels and the differences in diameter of the pivots were accurately investigated and all irregularities were accounted for. For the illumination, electric lamps were always used, for which the current was supplied by accumulators.

The latitudes were determined by zenith distances of northern and of southern stars. For the northern stars only the two pole stars, *α* and *δ* Ursae Minoris were used; the southern stars were chosen so that they had a northern declination from 6 to 14°, and consequently culminated at zenith distances almost equal to that of the pole, i. e. equal to the co-latitude.

As a rule, for each determination 16 zenith distances of the pole stars were observed, without regard to the point on the parallel they occupied; of the southern stars, four in number, 8 zenith distances were observed, four before and four after culmination; so that each complete determination of latitude rests on 32 zenith distances north and 32 south of the zenith.

At each station four such determinations were made in four positions of the circle which differed by 45 degrees. If we bear in mind that the reading was always made by two opposite microscopes, the zenith distance of each star may be said to be determined by eight different arcs of the circle, hence the periodic error of the graduation may be considered as almost entirely eliminated.

The declinations of the stars used were taken from the *Berliner Jahrbuch,* while due account was taken of the latest corrections, published by AUWERS in nos. 3927 –29 of the *Astronomische Nachrichten.* Finally the latitudes found were corrected for the polar motion, according to the latest data furnished by ALBRECHT.

For the azimuth determinations only the Polar star was used at different points of its parallel. The horizontal distance between the Polar star and the object was measured four times in 12 positions of the circle, differing 15 degrees; this was done according to the following scheme:
Object, Polar star, Polar star, Object, reverse the instrument 180°; Object, Polar star, Polar star, Object, while for each pointing at the Polar star the level was read in two positions. Accordingly each determination of azimuth consisted generally of 12 series of 8 observations i.e. 2 complete determinations each; hence of 24 complete determinations.

As object was used either a lamp, or a heliotrope, in most cases a heliotrope. Its position with relation to the adopted centrum of the station was determined by the Triangulation Service.

The following may be remarked about the accuracy attained:

For the mean error of one result from two zenith distances ± 0″455[1]) was found as mean value; the mean error of each final result, derived from say 128 double observations, was then calculated in different manners to be ± 0″065.

For the determinations of azimuth the mean error

of a single determination was found to be ± 1″22,

hence that of the mean of 12 determinations ± 0,355.

The amount of all these mean errors can very well stand a comparison with the determinations of other observers.

To this criticism of the determinations executed for geodetic purposes two appendices are added, namely:

I. "A comparison between the latitude, determined at the station Utrecht, Cathedral tower (Domtoren), by Mr. Posthumus Meyjes, and the determinations made at the Observatory."

The final result of this investigation was the following: Latitude of the Universal instrument at the Observatory:

derived from observations of circummeridian zenith distances . . . . 52° 5′ 9″48

derived from the observations in the prime vertical 52 5 10,29,

„ „ „ result of Mr. Posthumus Meyjes, reduced from the "Domtoren" to the Observatory . . . 52 5 9,84.

This agreement is quite satisfactory, especially if we consider that the observations of the circummeridian zenith distances at the Observatory, which had been made for exercise, were executed in only one position of the vertical circle, which was also a motive for neglecting the polar motion.

II. "A comparison between the azimuth of Amersfoort, determined by the author in 1879 and '80, and the same azimuth determined by Mr. Posthumus Meyjes in 1896."

The final result of this comparison, after due regard was paid to all reductions, was: Azimuth Utrecht (Centre) — Amersfoort (Centre):

Determination of 1879,80: 68° 22′ 44″71 ± 0″31,

„ „ 1896: 45,59 ± 0,29.

Between these two determinations there is a difference of 0″88 ± 0″42 (mean error), which partly may be explained by the accidental errors of the observation and the graduation, and partly by the uncertainty in the different reductions which occur in this comparison. We should also bear in mind that in the results of Mr. Posthumus

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[1]) For Mr. Pannekoek ± 0″49, for Mr. P. Meyjes ± 0″42, two numbers that are nearly reciprocal to the magnifying powers of the telescopes of the two instruments (60 and 68 times).

MEYJES three out of twelve differences from the arithmetic mean exceed the negative quantity $-0''88$, whereas in the author's results five out of nineteen differences exceed the positive quantity $+0''.88$. Accordingly the difference between the two results may be considered as purely accidental.

(The last sentence does not occur in the original. It should be remarked that in the publication of 1880, the last difference from the arithmetic mean for 1879, must be $+0'',74$ instead of $+1'',74$).

ERRATA.

Page 238, line 5 from bottom, for "increases" read "decreases."
,, 240 ,, 12 ,, ,, ,, T' read T'''.
,, ,, ,, 10 ,, ,, ,, T' read T''' (twice).
,, 241, in the formula for X_{lpT}, X_1, X_{vpT} read x_{lpT}, x_1, x_{vpT}.

(January 25, 1905).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday January 28, 1905.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 28 Januari 1905, Dl. XIII).

CONTENTS.

The following papers were read:

Mathematics. — *"The formulae of* Guldin *in polydimensional space."* By Prof. P. H. Schoute.

(Communicated in the meeting of December 24, 1904).

We suppose in space S_n with n dimensions an axial space $S_p^{(a)}$ and in a space S_{p+1} through this $S_p^{(a)}$ a limited part with $p+1$ dimensions rotating round $S_p^{(a)}$. Then an arbitrary point P of this limited space, which may be called a polytope independent of the shape of its limitation and may be represented by the symbol $(Po)_{p+1}$, describes a spherical space of $n-p$ dimensions lying in the space S_{n-p} through P perpendicular to $S_p^{(a)}$ having the projection Q of P

on $S_p^{(a)}$ as centre, PQ as radius; so it can be represented by the symbol $Sp_{n-p}(Q, PQ)$.

The question with which we shall occupy ourselves is as follows: "How do we determine volume and surface of the figure of revolution generated by $(Po)_{p+1}$ rotating round $S_p^{(a)}$ if we assume that $(Po)_{p+1}$ and $S_p^{(a)}$ though lying in the same space S_{p+1} have no points in common?"

This theorem is solved with the aid of a simple extension of the well known formulae of GULDIN, which serve in our space to determine the volume and the surface of a figure of revolution. To prove these generalized formulae we have but to know that the surface of the above-mentioned spherical space $Sp_{n-p}(Q, PQ)$ is found by multiplying $\overline{PQ}^{n-p-1}$ by a coefficient s_{n-p} only dependent on $n-p$; for its application however it is desirable to know not only this coefficient of surface s_{n-p} but also the coefficient of volume v_{n-p} by which PQ^{n-p} must be multiplied to arrive at the volume of the same spherical space. To this end we mention beforehand — as is learned by direct integration — that between these coefficients the recurrent relations

$$v_n = \frac{2\pi}{n} v_{n-2} \quad , \quad s_n = \frac{2\pi}{n-2} s_{n-2} \quad . \quad . \quad . \quad . \quad (1)$$

exist, whilst the well known relation between volume and surface leads in a simpler way still to the equation

$$v_n = \frac{1}{n} s_n \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this way we find as far as and inclusive of $n = 12$ out of the well known values of v_2, v_3 and s_2, s_3

n	2	3	4	5	6	7	8	9	10	11	12
v_n	π	$\frac{4}{3}\pi$	$\frac{1}{2}\pi^2$	$\frac{8}{15}\pi^2$	$\frac{1}{6}\pi^3$	$\frac{16}{105}\pi^3$	$\frac{1}{24}\pi^4$	$\frac{32}{945}\pi^4$	$\frac{1}{120}\pi^5$	$\frac{64}{10395}\pi^5$	$\frac{1}{720}\pi^6$
s_n	2π	4π	$2\pi^2$	$\frac{8}{3}\pi^2$	π^3	$\frac{16}{15}\pi^3$	$\frac{1}{3}\pi^4$	$\frac{32}{105}\pi^4$	$\frac{1}{12}\pi^5$	$\frac{64}{945}\pi^5$	$\frac{1}{60}\pi^6$

1. Determination of volume. If x indicates the length of the radius PQ and the differential dv the $p+1$-dimensional volume-element, lying immediately round P, of the rotating polytope $(Po)_{p+1}$, then the demanded volume is

$$V = s_{n-p} \int x^{n-p-1}\, dv,$$

if the integral is extended to all the elements of volume of $(Po)_{p+1}$. If now V_{p+1} is the volume of $(Po)_{p+1}$, we can imagine a quantity $\bar{x}$ satisfying the equation

$$\int x^{n-p-1}\, dv = \bar{x}^{n-p-1} \int dv = \bar{x}^{n-p-1}\, V_{p+1}$$

and we can insert this quantity in the above formula. By this it passes into

$$V = V_{p+1} \cdot s_{n-p}\, \bar{x}^{n-p-1} .$$

If we call $\bar{x}$ the "radius of inertia of order $n-p-1$" of the volume V_{p+1} of the rotating figure $(Po)_{p+1}$ with relation to the axial space $S_p^{(a)}$ lying in its space S_{p+1}, we find this theorem:

We find the volume of the figure of revolution generated by the polytope $(Po)_{p+1}$ rotating round an axial space $S_p^{(a)}$ not cutting this polytope of its space S_{p+1}, if we multiply the volume V_{p+1} of $(Po)_{p+1}$ by the surface of a spherical space Sp_{n-p}, having the radius of inertia of order $n-p-1$ of V_{p+1} with relation to $S_p^{(a)}$ as radius."

2. Determination of surface. If in the above we substitute the p-dimensional element of surface for the $p+1$-dimensional element of volume and in accordance with this for the volume V_{p+1} and its radius of inertia the surface Su_{p+1} and its radius of inertia, we arrive in similar way at the theorem:

We find the surface of the figure of revolution generated as above if we multiply the surface Su_{p+1} of $(Po)_{p+1}$ by the surface of a spherical space Sp_{n-p}, having for radius the radius of inertia of order $n-p-1$ of Su_{p+1} with relation to $S_p^{(a)}$.

3. The segment of revolution. The opinions will differ greatly about the use of the n-dimensional extension of the GULDIN formulae proved above. Those regarding only their generality and their short enunciation may rate them too high, though reasonably they cannot go so far as to believe that these formulae allow the volume and the surface of a figure of revolution to be found when the common principles of the calculus leave us in the lurch, as the quadratures can be indicated but not effected in finite form.

Others, whose attention is drawn to the fact that these formulae displace the difficulties of the quadratures but apparently — in this case displace them from definition of volume and of surface to the definition of radii of inertia — will on the other hand perhaps fall into another extreme and will deny any practical use to the formulae in question. Here of course the truth lies in the mean. Though it remains true that the GULDIN formulae help us but apparently out of the difficulty in the case where the direct integration falls short, yet by the use of those formulae many an integration is avoided because the radii of inertia appearing in those formulae of volume and surface of the figure of revolution are known from another source, which latter circumstance appears in the first place when $p = n - 2$, thus each point P of the rotating figure describes the circumference of a circle and the radii of inertia relate therefore to the centre of gravity of volume and surface of that figure, whilst for $p = n - 3$ the knowledge of the common radius of inertia of mechanics gives rise to simplification.

As simplest example of the case $p = n - 2$ we think that a segment $Sp_{n-1}(r, \varrho)$ of a spherical space Sp_{n-1} with r and ϱ as radii of spherical and base boundary generates a segment of revolution $Sp(r, \varrho, \alpha)_n$ by rotation round a diametral space $S_{n-2}^{(\alpha)}$, situated in its space S_{n-1}, having no point in common with it and forming an angle α with the space S_{n-2} of the base boundary. For this we find the following theorems:

"We find the volume of the segment of revolution $Sp(r, \varrho, \alpha)_n$ by multiplying the volume of a spherical space Sp_n with ϱ for radius by $\cos \alpha$."

"We find the surface of the segment of revolution $Sp(r, \varrho, \alpha)_n$ which is described by the spherical boundary of $Sp_{n-1}(r, \varrho)$ when rotating, by multiplying the circumference of a circle with r for radius by the volume of the projection of the base boundary of $Sp_{n-1}(r, \varrho)$ on the axial space $S_{n-2}^{(\alpha)}$."

These theorems are simple polydimensional extensions of well known theorems of stereometry. They can be found by direct integration where the case $\alpha = 0$ is considerably simpler than that of an arbitrary angle α. And now the formulae of GULDIN teach us exactly to avoid the integration in the general case, showing us immediately that the theorems are true for the case of an arbitrary angle α, as soon as they are proved for $\alpha = 0$. If namely x_v and x_s are the distances from the centres of gravity of volume V_{n-1} and surface

Su_{n-1} of $Sp_{n-1}(r, \varrho)$ to $S^{(a)}_{n-2}$, where Su_{n-1} now again indicates exclusively the spherical boundary, then the formulae of GULDIN furnish us with

$$\left.\begin{array}{ll} V_\alpha = 2\pi\, x_v \cos\alpha & .\ V_{n-1} \\ V_o = 2\pi\, x_v & .\ V_{n-1} \end{array}\right\} , \quad \left.\begin{array}{ll} Su_\alpha = 2\pi\, x_s \cos\alpha & .\ Su_{n-1} \\ Su_o = 2\pi\, x_s & .\ Su_{n-1} \end{array}\right\}$$

and from this ensues immediately

$$V_\alpha = V_o \cos\alpha \qquad , \qquad Su_\alpha = Su_o \cos\alpha$$

and therefore what was assumed above, so that only for $\alpha = 0$ the proofs have yet to be given. We commence with the volume. If x is the distance from $S^{(a)}_{n-2}$ to a parallel space $S^{(x)}_{n-2}$ cutting $Sp_{n-1}(r, \varrho)$ in a spherical space $Sp^{(x)}_{n-2}$ with $y = \sqrt{r^2 - x^2}$ for radius, then the demanded volume is

$$V = 2\pi\, v_{n-2} \int_{x=\sqrt{r^2-\rho^2}}^{x=r} y^{n-2}\, x dx$$

and this passes, as $x^2 + y^2 = r^2$ and $xdx + ydy = 0$, into

$$V = 2\pi\, v_{n-2} \int_o^{\varrho} y^{n-1}\, dy = \frac{2\pi}{n}\, v_{n-2}\, \varrho^n = v_n\, \varrho^n,$$

with which the special case of the theorem for the volume has been proved.

In the special case of the theorem for the surface we regard the superficial element generated by the rotation of the surface $Su_{n-1}(r, \varrho)$ situated between the parallel spaces $S^{(x)}_{n-2}$ and $S^{(x+dx)}_{n-2}$. If ds is the apothema of this frustum the demanded surface is

$$Su = 2\pi\, s_{n-2} \int_{x=\sqrt{r^2-\varrho^2}}^{x=r} y^{n-3}\, x ds.$$

With the help of the relations $yds = rdx$ and $xdx + ydy = 0$ this passes into

$$Su = 2\pi r\, s_{n-2} \int_o^{\varrho} y^{n-3}\, dy = \frac{2\pi}{n-2}\, r\, s_{n-2}\, \varrho^{n-2} = 2\pi r\, .\, v_{n-2}\, \varrho^{n-2},$$

i. e. the desired result.

Of course we can represent to ourselves the more general segment of revolution $Sp(r, \varrho, \alpha)_{n,k}$ of order k generated by the rotation of a spherical segment $Sp_{n-k}(r,\varrho)$ round a diametral space $S^{(a)}_{n-k-1}$ of its space S_{n-k}: of the various possible cases

$$k = 1, 2, \ldots\ldots\ldots, n-2$$

the first is the one treated above extensively. As any point generates at the rotation the surface of a spherical space Sp_{k+1}, we find — if along the indicated way by means of the formulae of **Guldin** the general case of an arbitrary angle α is reduced to the special case $\alpha = 0$ — for volume $V_{n,k}$ and the surface $Su_{n,k}$ of $Sp(r,\varrho,\alpha)_{n,k}$ the formulae

$$\left.\begin{aligned} V_{n,k} &= v_{n-k-1}\, s_{k+1} \cos^k \alpha \int\limits_{x=\sqrt{r^2-\varrho^2}}^{x=r} y^{n-k-1}\, x^k\, dx \\ Su_{n,k} &= r s_{n-k-1}\, s_{k+1} \cos^k \alpha \int\limits_{x=\sqrt{r^2-\varrho^2}}^{x=r} y^{n-k-3}\, x^k\, dx \end{aligned}\right\}$$

and from this ensues the general relation

$$Su_{n,k} = 2\pi\, r \cos^2 \alpha\, V_{n-2,k},$$

by which all cases of determination of surface except $Su_{n,n-2}$ and $Su_{n,n-3}$ are deduced to simpler cases of the determination of volume.

When determining the volume the integral gives a rational result, an irrational one or a transcendental one according to k being odd, n odd and k even, or n even and k even. And this is evidently likewise the case for the determination of surface.

4. The torusgroup. By rotation of a spherical space $Sp_{n-k}(r)$ around a space $S^{(a)}_{n-k-1}$ of its space S_{n-k} at a distance $a > r$ from the centre a ring is generated in S_n, the ring or "torus" $T(r,a)_{n,k}$. For volume $V(r,a)_{n,k}$ and surface $Su(r,a)_{n,k}$ of this figure of revolution of order k we find

$$\left.\begin{aligned} V(r,a)_{n,k} &= s_{k+1}\, v_{n-k-1} \int\limits_{-a}^{a} \sqrt{r^2-x^2}^{\,n-k-1} (a+x)^k dx \\ Su(r,a)_{n,k} &= r\, s_{k+1}\, s_{n-k-1} \int\limits_{-a}^{a} \sqrt{r^2-x^2}^{\,n-k-3} (a+x)^k dx \end{aligned}\right\} \quad \ldots (3),$$

from which ensues again the formula of reduction

$$Su_{n,k} = 2\pi\, r\, V_{n-2,k} \quad \ldots\ldots\ldots\ldots (4)$$

For the case $k = 1$ and $k = 2$ the results are calculated more easily by means of the formulae of **Guldin**, if one makes use of the centre of gravity and of the oscillation centre of the rotating spherical space.

Case $k = 1$. The centre of gravity of volume and surface of the spherical space $Sp_{n-1}(r)$ lying in the centre, we find

$$V = 2\pi a . v_{n-1} r^{n-1} \quad , \quad Su = 2\pi a . s_{n-1} r^{n-2}.$$

Case $k = 2$. The radii of inertia of volume and surface of a spherical space $Sp_{n-2}(r)$ with respect to the centre are $r\sqrt{\frac{n-2}{n}}$ and r, those with respect to a diametral space S_{n-3} are thus $r\sqrt{\frac{1}{n}}$ and $r\sqrt{\frac{1}{n-2}}$. So we find

$$V = 4\pi\left(a^2 + \frac{1}{n}r^2\right) v_{n-2} r^{n-2} \quad , \quad Su = 4\pi\left(a^2 + \frac{1}{n-2}r^2\right) . s_{n-2} r^{n-3}.$$

If instead of a whole spherical space $Sp_{n-k}(r)$ we allow only half of it to rotate around a space $S^{(a)}_{n-k-1}$ in its space S_{n-k} parallel to its base at a distance a, then the limits $(-r, r)$ of the two integrals (1) change into $(0, r)$ or $(-r, 0)$ according to the half spherical space $Sp_{n-k}(r)$ turning its base or its spherical boundary to the axial space $S^{(a)}_{n-k-1}$. We shall occupy ourselves another moment with the former of these cases, namely for $k = 1$ and $k = 2$.

Case $(0, r)$, $k = 1$. We find immediately

$$V = \pi\left(a + \frac{2}{n}\frac{v_{n-2}}{v_{n-1}} r\right) . v_{n-1} r^{n-1} \quad , \quad Su = \pi\left(a + \frac{2}{n-2}\frac{s_{n-2}}{s_{n-1}} r\right) . s_{n-1} r^{n-2}.$$

Case $(0, r)$, $k = 2$. We determine the moments of inertia of volume and surface first with respect to the base $S^{(b)}_{n-3}$ and then successively with respect to the parallel space $S^{(z)}_{n-3}$ through the centre of gravity and with respect to the axial space $S^{(a)}_{n-3}$. Thus we finally find the formulae

$$V = 2\pi\left\{\frac{r^2}{n} - \left(\frac{2}{n}\frac{v_{n-2}}{v_{n-1}} r\right)^2 + \left(\frac{2}{n}\frac{v_{n-2}}{v_{n-1}} r + a\right)^2\right\} . v_{n-2} r^{n-2},$$

$$Su = 2\pi\left\{\frac{r^2}{n-2} - \left(\frac{2}{n-2}\frac{s_{n-2}}{s_{n-1}} r\right)^2 + \left(\frac{2}{n-2}\frac{s_{n-2}}{s_{n-1}} r + a\right)^2\right\} . s_{n-2} r^{n-3},$$

or

$$V = 2\pi\left(a^2 + \frac{4}{n}\frac{v_{n-2}}{v_{n-1}} ar + \frac{r^2}{n}\right) . v_{n-2} r^{n-2},$$

$$Su = 2\pi\left(a^2 + \frac{4}{n-2}\frac{s_{n-2}}{s_{n-1}} ar + \frac{r^2}{n-2}\right) . s_{n-2} r^{n-3},$$

which pass for $a = 0$ appropriately into volume and surface of the spherical space $Sp_n(r)$.

Mathematics. — *"On a series of Bessel functions."* By Prof. W. KAPTEYN.

(Communicated in the meeting of December 24, 1904).

In the following we shall try to determine the sum of the series

$$I_1(a)\, I_1(x) + 3\, I_3(a)\, I_3(x) + 5\, I_5(a)\, I_5(x) + \ldots = \sum_{1.3}^{\infty} n\, I_n(a)\, I_n(x).$$

To this end we begin to determine the sum of the simpler series

$$S = \sum_{1.3}^{\infty} I_n(x) \cos n\varphi .$$

If we introduce, n being an odd number, for the Bessel function the form

$$I_n(x) = - \mathcal{E}_0\, e^{\frac{x}{2}\left(t - \frac{1}{t}\right)} t^{n-1} .$$

then

$$S = - \mathcal{E}_0 \frac{e^{\frac{x}{2}\left(t - \frac{1}{t}\right)}}{t} (t \cos \varphi + t^3 \cos 3\varphi + \ldots),$$

and

$$t \cos \varphi + t^3 \cos 3\varphi + \ldots = \frac{t\,(1-t^2) \cos \varphi}{1 - 2\, t^2 \cos 2\varphi + t^4} \; (mod\; t < 1),$$

hence

$$S = - \mathcal{E}_0 \frac{e^{\frac{x}{2}\left(t - \frac{1}{t}\right)} (1-t^2) \cos \varphi}{1 - 2\, t^2 \cos 2\varphi + t^4} .$$

If we put

$$R = \frac{\cos \varphi}{1 - 2\, t^2 \cos 2\varphi + t^4},$$

then

$$S = - \mathcal{E}_0\, e^{\frac{x}{2}\left(t - \frac{1}{t}\right)} (1 - t^2)\, R,$$

or

$$\sum_{1.3}^{\infty} I_n \cos n\varphi = - \mathcal{E}_0\, e^{\frac{x}{2}\left(t - \frac{1}{t}\right)} (1 - t^2)\, R.$$

Differentiating this equation, we get

$$\sum_{1.3}^{\infty} n\, I_n(x) \sin n\varphi = \mathcal{E}_0\, e^{\frac{x}{2}\left(t - \frac{1}{t}\right)} (1 - t^2) \frac{dR}{d\varphi} .$$

If now we multiply this equation by $\frac{1}{\pi} \sin(\alpha \sin \varphi)\, d\varphi$ and if we integrate between the limits 0 and π we find

$$\sum_{1.3}^{\infty} n\, I_n(x)\, I_n(\alpha) = \frac{1}{\pi} \mathcal{E}_0\, e^{\frac{x}{2}\left(t - \frac{1}{t}\right)} (1 - t^2) \int_0^{\pi} \frac{dR}{d\varphi} \sin(\alpha \sin \varphi)\, d\varphi$$

$$= -\frac{\alpha}{\pi} \mathcal{E}_0\, e^{\frac{x}{2}\left(t - \frac{1}{t}\right)} (1 - t^2) \int_0^{\pi} R \cos(\alpha \sin \varphi) \cos \varphi\, d\varphi .$$

Putting for the further reduction

$$u = \int_0^{\pi} R \cos(\alpha \sin \varphi) \cos \varphi\, d\varphi$$

$$= \int_0^{\pi} \frac{\cos^2 \varphi \cos(\alpha \sin \varphi)}{1 - 2\, t^2 \cos 2\varphi + t^4}\, d\varphi$$

we arrive at

$$\frac{du}{d\alpha} = -\int_0^{\pi} \frac{\cos^2 \varphi \sin(\alpha \sin \varphi)}{1 - 2\, t^2 \cos 2\varphi + t^4} \sin \varphi\, d\varphi,$$

$$\frac{d^2 u}{d\alpha^2} = -\int_0^{\pi} \frac{\cos^2 \varphi \cos(\alpha \sin \varphi)}{1 - 2\, t^2 \cos 2\varphi + t^4} \sin^2 \varphi\, d\varphi$$

and because

$$\sin^2 \varphi = \frac{1 - 2\, t^2 \cos 2\varphi + t^4}{4\, t^2} - \frac{(1 - t^2)^2}{4\, t^2},$$

we find

$$\frac{d^2 u}{d\alpha^2} = m^2\, u - \frac{1}{4\, t^2} \int_0^{\pi} \cos^2 \varphi \cos(\alpha \sin \varphi)\, d\varphi,$$

where $m = \dfrac{1 - t^2}{2t}$.

If we replace $\cos^2 \varphi$ by $\dfrac{1 + \cos 2\varphi}{2}$, we can easily reduce this differential equation to

$$\frac{d^2 u}{d\alpha^2} - m^2\, u = -\frac{\pi}{8t^2} \left(I_0(\alpha) + I_2(\alpha)\right)$$

$$= -\frac{\pi}{4t^2} \frac{I_1(\alpha)}{\alpha} .$$

Let us now determine the integral of this equation satisfying the conditions that for $\alpha = 0$

$$u = \int_0^{\pi} \frac{\cos^2 \varphi \, d\varphi}{1 - 2t^2 \cos^2 \varphi + t^4} = \frac{\pi}{2(1-t^2)},$$

and

$$\frac{du}{d\alpha} = 0.$$

We then find

$$u = \frac{\pi}{4(1-t^2)} \left[e^{m\alpha} + e^{-m\alpha} \right] - \frac{\pi}{8t^2 m} \int_0^{\alpha} \frac{I_1(\beta)}{\beta} d\beta \left[e^{m(\alpha-\beta)} - e^{-m(\alpha-\beta)} \right]$$

and by this

$$\sum_{1.3}^{\infty} n \, I_n(\alpha) \, I_n(x) = -\frac{\alpha}{4} \mathcal{E}_0 \left[e^{\frac{x-\alpha}{2}\left(t-\frac{1}{t}\right)} + e^{\frac{x+\alpha}{2}\left(t-\frac{1}{t}\right)} \right] +$$

$$+ \frac{\alpha}{4} \int_0^{\pi} \frac{I_1(\beta)}{\beta} d\beta \, \mathcal{E}_0 \frac{1}{t} \left[e^{\frac{x-\alpha+\beta}{2}\left(t-\frac{1}{t}\right)} - e^{\frac{x+\alpha-\beta}{2}\left(t-\frac{1}{t}\right)} \right].$$

Remembering now that

$$e^{\frac{z}{2}\left(t-\frac{1}{t}\right)} = I_0(z) + t\, I_1(z) + t^2 I_2(z) + \dots$$
$$- \frac{1}{t} I_1(z) + \frac{1}{t^2} I_2(z) - \dots$$

we see that the residues are easily determined. We have

$$\sum_{1.3}^{\infty} n \, I_n(\alpha) \, I_n(x) = \frac{\alpha}{4} \left[I_1(x-\alpha) + I_1(x+\alpha) \right] +$$

$$+ \frac{\alpha}{4} \int_0^{\alpha} \frac{I_1(\beta)}{\beta} d\beta \left[I_0(x-\alpha+\beta) - I_0(x+\alpha-\beta) \right]. \quad (1)$$

From this result another important relation may be deduced. To show this, we shall again develop

$$I_1(x-\alpha) + I_1(x+\alpha)$$

into a series.

From

$$I_1(x-\alpha) = \frac{1}{\pi} \int_0^{\pi} \sin\varphi \sin(x \sin\varphi - \alpha \sin\varphi) \, d\varphi$$

and

$$I_1(x+a) = \frac{1}{\pi}\int_0^\pi \sin\varphi \sin(x\sin\varphi + a\sin\varphi)\,d\varphi$$

follows

$$I_1(x-a) + I_1(x+a) = \frac{2}{\pi}\int_0^\pi \sin\varphi \sin(x\sin\varphi)\cos(a\sin\varphi)\,d\varphi.$$

If we write

$$\sin(x\sin\varphi) = 2\,I_1\sin\varphi + 2\,I_3\sin 3\varphi + \dots$$

we obtain

$$\begin{aligned} I_1(x-a) + I_1(x+a) &= \frac{4}{\pi}\,I_1(x)\int_0^\pi \sin^2\varphi\cos(a\sin\varphi)\,d\varphi \\ &+ \frac{4}{\pi}\,I_3(x)\int_0^\pi \sin\varphi\sin 3\varphi\cos(a\sin\varphi)\,d\varphi \\ &+ \frac{4}{\pi}\,I_5(x)\int_0^\pi \sin\varphi\sin 5\varphi\cos(a\sin\varphi)\,d\varphi \\ &+ \dots \end{aligned}$$

or as

$$2\int_0^\pi \sin\varphi\sin(2n+1)\varphi\cos(a\sin\varphi)\,d\varphi =$$

$$\begin{aligned} &= \int_0^\pi [\cos 2n\varphi - \cos(2n+2)\varphi]\cos(a\sin\varphi)\,d\varphi \\ &= \pi\,[I_{2n}(a) - I_{2n+2}(a)] \\ &= 2\pi\,\frac{d\,I_{2n+1}(a)}{da} \end{aligned}$$

we get

$$I_1(x-a) + I_1(x+a) = 4\left[I_1(x)\frac{dI_1}{da} + I_3(x)\frac{dI_3}{da} + I_5(x)\frac{dI_5}{da}\dots\right].$$

Substituting here

$$a\frac{dI_n}{da} = n\,I_n(a) - a\,I_{n+1}(a)$$

we arrive finally at

$$I_1(x-a) + I_1(x+a) = \frac{4}{\pi}\sum_{1.3}^{\infty} n\,I_n(a)\,I_n(x) - 4\sum_{1.3}^{\infty} I_{n+1}(a)\,I_n(x).$$

With this equation the result (1) may be written

$$\sum_{1.3}^{\infty} I_{n+1}(\alpha)\, I_n(x) = \frac{1}{4}\int_0^{\alpha} \frac{I_1(\beta)}{\beta}\, d\beta\, [I_0(x-\alpha+\beta) - I_0(x+\alpha-\beta)] \quad (2)$$

If here we develop

$$I_0(x-\alpha+\beta) = I_0(x)\, I_0(\alpha-\beta) + 2I_1(x)\, I_1(\alpha-\beta) + 2I_2(x)\, I_2(\alpha-\beta) + \ldots$$

$$I_0(x+\alpha-\beta) = I_0(x)\, I_0(\alpha-\beta) - 2I_1(x)\, I_1(\alpha-\beta) + 2I_2(x)\, I_2(\alpha-\beta) - \ldots$$

we find

$$\sum_{1.3}^{\infty} I_{n+1}(\alpha)\, I_n(x) = \sum_{1.3}^{\infty} I_n(x) \int_0^{\alpha} I_n(\alpha-\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta$$

and consequently by comparing the coefficients of $I_n(x)$

$$I_{n+1}(\alpha) = \int_0^{\alpha} I_n(\alpha-\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

By means of this formula we can give equation (1) another form. For, according to (3),

$$I_1(x-\alpha) = \int_0^{x-\alpha} I_0(x-\alpha-\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta$$

$$= -\int_0^{\alpha-x} I_0(x-\alpha+\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta$$

$$I_1(x+\alpha) = \int_0^{x+\alpha} I_0(x+\alpha-\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta$$

hence the second member of (1) takes the form

$$\frac{\alpha}{4}\left[-\int_0^{\alpha-x} I_0(x-\alpha+\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta + \int_0^{x+\alpha} I_0(x+\alpha-\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta\right]$$

$$+\frac{\alpha}{4}\left[\int_0^{\alpha} I_0(x-\alpha+\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta - \int_0^{\alpha} I_0(x+\alpha-\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta\right]$$

or

$$\frac{\alpha}{4}\left[\int_{\alpha-x}^{\alpha} I_0(x-\alpha+\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta + \int_{\alpha}^{\alpha+x} I_0(x+\alpha-\beta)\, \frac{I_1(\beta)}{\beta}\, d\beta\right].$$

If we now put in the first integral $\beta = \alpha - \gamma$ and in the second one $\beta = \alpha + \gamma$ this becomes

$$\frac{\alpha}{4}\left[\int_0^x I_0(x-\gamma)\,\frac{I_1(\alpha-\gamma)}{\alpha-\gamma}\,d\gamma + \int_0^x I_0(x-\gamma)\,\frac{I_1(\alpha+\gamma)}{\alpha+\gamma}\,d\gamma\right],$$

with which equation (1) assumes the final form

$$\sum_{1.3}^{\infty} n\, I_n(\alpha)\, I_n(x) = \frac{\alpha}{4}\int_0^x I_0(x-\gamma)\left[\frac{I_1(\alpha-\gamma)}{\alpha-\gamma} + \frac{I_1(\alpha+\gamma)}{\alpha+\gamma}\right] d\gamma. \quad . \; . \; (4)$$

A closer investigation of formula (3) teaches us, that it holds good for even values of n too, also that many analogous relations exist. So we find inter alia, k being any integer,

$$\int_0^\alpha \frac{I_n(\alpha-\beta)}{\alpha-\beta}\, I_1(\beta)\, d\beta = \frac{I_{n+1}(\alpha)}{n},$$

$$\int_0^\alpha I_n(\alpha-\beta)\,\frac{I_k(\beta)}{\beta}\, d\beta = \frac{I_{n+k}(\alpha)}{k},$$

$$\int_0^\alpha \frac{I_n(\alpha-\beta)}{\alpha-\beta}\, I_k(\beta)\, d\beta = \frac{I_{n+k}(\alpha)}{n},$$

$$\int_0^\alpha \frac{I_n(\alpha-\beta)}{(\alpha-\beta)^2}\, I_1(\beta)\, d\beta = \frac{1}{2n}\left[\frac{I_n(\alpha)}{n-1} + \frac{I_{n+2}(\alpha)}{n+1}\right],$$

$$\int_0^\alpha I_0(\alpha-\beta)\, I_0(\beta)\, d\beta = \sin \alpha.$$

We shall not dwell upon this at present; we only remark, that when a very great positive value is assigned in (1) to x, so that

$$I_n(x) = \sqrt{\frac{2}{\pi x}}\cos\left(x - \frac{2n+1}{4}\,\pi\right),$$

we find

$$I_1(x-\alpha) + I_1(x-\alpha) = 2\sqrt{\frac{2}{\pi x}}\cos\left(x - \frac{3\pi}{4}\right)\cos \alpha,$$

$$I_0(x-\alpha+\beta) - I_0(x+\alpha-\beta) = 2\sqrt{\frac{2}{\pi x}}\sin\left(x - \frac{\pi}{4}\right)\sin(\alpha-\beta).$$

This changes (1) into

$$\sum_{1.3}^{\infty} n\, I_n(\alpha)\sin\frac{n\pi}{2} = \frac{\alpha}{2}\cos\alpha + \frac{\alpha}{2}\int_0^\alpha \frac{I_1(\beta)}{\beta}\sin(\alpha-\beta)\, d\beta$$

or, noticing that

$$\sum_{1.3}^{\infty} n\, I_n(\alpha) \sin\frac{n\pi}{2} = \frac{\alpha}{2}\, I_0(\alpha),$$

we have

$$I_0(\alpha) = \cos\alpha + \int_0^{\alpha} \frac{I_1(\beta)}{\beta} \sin(\alpha-\beta)\, d\beta$$

If we differentiate this equation, we find

$$I_1(\alpha) = \sin\alpha - \int_0^{\alpha} \frac{I_1(\beta)}{\beta} \cos(\alpha-\beta)\, d\beta$$

from which we conclude that

$$\int_0^{\alpha} \frac{I_1(\beta)}{\beta} \sin\beta\, d\beta = 1 - \cos\alpha\, I_0(\alpha) - \sin\alpha\, I_1(\alpha),$$

$$\int_0^{\alpha} \frac{I_1(\beta)}{\beta} \cos\beta\, d\beta = \sin\alpha\, I_0(\alpha) - \cos\alpha\, I_1(\alpha).$$

Geology. — *"Contributions to the knowledge of the sedimentary boulders in the Netherlands. 1. The Hondsrug in the province of Groningen. 2. Upper Silurian boulders. — First communication: Boulders of the age of the Eastern Baltic zone G."* By Dr. H. G. Jonker. (Communicated by Prof. K. Martin).

This communication introduces the description of the Upper Silurian boulders of Groningen and its surroundings, in which my contribution that treats of the Cambrian and Lower Silurian erratics and appeared in 1904, is continued (36). The circumstance that in the summer of last year I had an opportunity of getting more intimately acquainted with the Scandinavian-Baltic strata by investigations of my own has aided me considerably in the study of these younger rocks. Owing to nearly a month's stay in Gothland I managed to collect a great number of different species of rocks together with fossils characteristic to them in order to compare them with erratics that are found here. Much I owe to the kindness and assistance of Drs. O. W. Wennersten, who accompanied me on some excursions and whom I had very often reason to admire for his extensive knowledge of his native country, the classical ground for the study of the Upper Silurian formation. But I have as yet not been able to pay a visit to Scania and Oesel; the material for comparison from those regions (present in the Min.-Geol. Institution in this town, for the greater part collected by Mr. J. H. BONNEMA), however, will make up for it to a large extent, though not all questions can be solved.

Some days' stay at Upsala enabled me, thanks to the kindly assistance of Dr. C. WIMAN, to examine the collections present in the Geological Institution from the different Lower Silurian regions of Sweden. This examination, which of course had to be made in haste, obliges me to introduce some alterations into my former description which however are not very important. By this time the material has been increased by new finds, and as more recent publications always make some alterations or completions necessary, I have made up my mind not to introduce them now but to collect all these corrigenda and addenda in an appendix at the end of the treatise of the Groningen erratics.

The real description of the Upper Silurian species of boulders of which two have been dealt with in this communication, is preceded by some pages which, from an historical point of view, are not unimportant. After the appearance of my first contribution Dr. L. HOLMSTRÖM at Åkarp was so kind as to draw my attention to some parts of his lately published biography of OTTO TORELL. From this I learned that, in 1866, the latter had written a prize-essay on a subject suggested by the Dutch Society of Sciences at Harlem, and treating of the origin of the stones and fossils of the Groningen Hondsrug. His essay was rewarded, but was never published and not given up to the Dutch Society till after the author's death. Thanks to the kindness of its secretary, Prof. dr. J. BOSSCHA, I have been able to study TORELL's essay, and now comprehend his relation to the Groningen boulders which formerly really puzzled me. His ideas about our subject are a necessary completion of the historical outline.

Finally, it pleases me to state that this year as well as last year the support of the Groningen University Fund fell to my share, while the expenses of my investigations in Sweden have for the greater part been defrayed by a subsidy granted to me by the "Central Bureau for the promotion of the knowledge of the province of Groningen" after receiving the approval of "the Board of the Physical Society at Groningen." This obvious interest taken in the subject of my study has been a source of much delight to me.

Supplement to the Historical Outline.

O. Torell.

The prize-subject of the Dutch Society of Sciences at Harlem (1865) ran as follows:

"On sait, surtout par le travail de M. ROEMER à Breslau, que plusieurs des fossiles, que l'on trouve près de Groningue appartiennent aux mêmes espèces que ceux que l'on trouve dans les terrains siluriens de l'île de Gothland. Ce fait a conduit M. ROEMER à la conclusion, que le diluvium de Groningue a été transporté de cette île de Gothland; mais cette origine paraît peu conciliable avec la direction dans laquelle ce diluvium est déposé, direction qui indiquerait plutôt un transport de la partie méridionale de la Norvège. La Société désire voir décidée cette question par une comparaison exacte des fossiles de Groningue avec les minéraux et les fossiles des terrains siluriens et autres de cette partie de la Norvège, en ayant égard aussi aux modifications que le transport d'un pays éloigné et ses suites ont fait subir à ces minéraux et à ces fossiles."

TORELL's answer to this question consists of two parts. The first part deals with the essential question and is entitled: "Essai sur la question proposée de la Société Hollandaise des Sciences à Harlem." Here the author enumerates the Groningen fossils known to him with their geological occurrence and the literature on this subject. Hardly any new fossils are mentioned, so that this description is little more than a development of ROEMER's treatise of the Groningen fossils. Nor is this wonderful, because he, too, had received the greater part of this material from COHEN, whom he had paid a visit in 1865. No doubt there were among the collection sent to him by the museum of Natural History at Groningen, about which I have spoken in my first essay (36, p. XXXIII), various fossils unknown to ROEMER, but TORELL seems not to have paid much attention to the determination of new fossils. From his enumeration he arrives at the conclusion that the sedimentary boulders *might* originate in Norway, but that there is not the least proof for it and that most likely the origin from Oesel-Gothland is much more probable.

In the second part of this first essay, however, he deals with the rocks themselves. By a comparison with limestones from Norway and Gothland he is led to exclude the first region altogether and this result is further on supported by what the crystalline boulders teach, which are described next. The dispersion of the different erratics being examined, his conclusion with regard to the question which had been put runs:

"Le résultat de ces recherches tend ainsi à confirmer l'opinion déjà émise par M. **Ferd. Roemer**, que les blocs siluriens de Groningue proviennent de l'Esthonie et de l'île de Gothland, mais nullement de la Norvège".

This first essay was inserted by him in 1866; the next year followed a second, entitled:

"Recherches sur les phénomènes glaciaires de l'Europe du Nord", which for more than one reason is a remarkable treatise. As, however, its contents do not refer directly to the question we are discussing it be only said that this treatise is, in short, *a pleading in all its details for the glacial theory*, which is here for the first time consistently adopted and asserted, under a motto borrowed from **L. von Buch** (Ueber die Ursachen der Verbreitung grosser Alpengeschiebe, 1811, Abhandl. d. Berlin. Akad., p. 185, 186), too interesting not to be cited here:

"Wer sich etwas mit den Blöcken beschäftigt hat, welche in so zahlloser Menge die Ebenen des nördlichen Europa bedecken, wird nicht einen Augenblick zweifeln, dasz nicht auch in dieser Zerstreuung dasselbe Phänomen wiederholt ist, was in der Schweiz so auffallend wird. Wäre die Granitzone des Wallisausbruchs nicht von den Jurabergen zurückgehalten worden, so würde sie an den Ufern des Doux und der Saone eben so zerstreut über die Flächen gelagert sein, eben so dicht wie in soviel Gegenden der Mark Brandenburg, von Pommern, Meklenburg, Holstein . . . . . . Das nordische Phänomen ist daher wohl bei weitem grösser als das schweizerische, *allein von derselben Natur; und wahrscheinlich liegt ihm deswegen auch eine ähnliche Ursache zum Grunde*".

Torell gives here a compendium of his opinions, founded on insights acquired by many travels about the origin of diluvial deposits and the grounds which in his opinion argue a glacial covering. The older theories are amply criticised, and after describing the formation of ice in Greenland, where the inland-ice covers an extent of country of $^5/_8$ of the North-European erratic zone, he says:

"Serait-il donc absurde de supposer, qu'une couverture glaciaire semblable, mais plus grande des $^3/_8$, a existé aussi dans l'Europe du Nord pendant une époque, où la faune marine du Spitzberg vivait entre les 50° et 60° de Lat., où le Betula nana croissait dans le Devonshire et où le renne avait son domicile dans la France méridionale!"

This quotation sufficiently illustrates the importance of this essay. It has however never been printed. **Torell** did claim back his work from the Dutch Society to revise it for the press and various emendations and marginal notes have been introduced, but he did not get farther than that. This is much to be regretted as it was now not until 1875 that his insights and opinions found adherents among the German geologists: it was the year when TORELL on the memorable day of Nov. 3 by his lecture for the German geological society in connection with the glacial scratches once more discovered by him on the Muschelkalk of Rüdersdorf convinced different colleagues of the correctness of his theory. For, if the above-mentioned essay had been printed as early as 1867 it would have contributed in a high measure to propagate the novel ideas more rapidly.

The bulky manuscript written in French and provided with French, Swedish and Dutch annotations (the Dutch annotations are by STARING, who was a members of the jury, as well as BOSQUET and VAN BREDA) is at present again in possession of the Dutch Society of Sciences. The maps (2) and plate mentioned in the text are not wanting. For further details about the contents the reader is referred to TORELL's biography by HOLMSTRÖM (35, p. 18—25).

UPPER SILURIAN BOULDERS.

In the description of the Upper Silurian boulders various difficulties present themselves, which all may be reduced to the fact that the exact succession of strata in the Scandinavian-baltic zone is not known for certain. Especially with regard to the eastern balticum the structure has long ago been made out by SCHMIDT and never refuted by anybody that I know of. His division of the strata in Gothland, on the contrary, corresponding with MURCHISON's conceptions has found but few adherents, and is especially called in question by LINDSTRÖM, who has a quite different opinion. This discrepancy as to the structure of Gothland, which has already existed many years, has not yet been satisfactorily removed. It must be said, however, that well-nigh all other investigators who have pronounced their opinion about this question, have taken LINDSTRÖM's side; a. o. DAMES, who has made a division which differs but a little from LINDSTRÖM's; then STOLLEY, WIMAN, BATHER, KAYSER and others. I myself, owing to my short stay in Gothland, am not so fortunate as to be able to pronounce a decided opinion, though it does seem to me that, on the whole, SCHMIDT's arguments are stronger than LINDSTRÖM's, so that it appears scarcely possible to me that new investigations will confirm the opinions of the latter in every respect. In collecting fossils in Gothland, I frequently doubted of the correctness of LINDSTRÖM's division, and in some cases noticed certain contradictions. Anyhow for the present it is impossible to parallel the Upper Silurian strata of Gothland with those of Oesel, a question, indeed, which for a determination of boulders of that age can hardly be dispensed with. We may sincerely hope that the researches by HOLM, who has been engaged in this question, may not be long in coming, and that this solution may finally settle the question!

(The chief literature about this controverted question follows here: 4; 15; 21; 22; 27; 28, p. 16; etc.).

Nevertheless in enumerating the species of boulders we must adopt a certain succession of strata to arrive at the determination of their age. I select for this purpose SCHMIDT's division of the Eastern Baltic Upper Silurian (8, p. 41—54), corresponding to the method hitherto followed in the museum:

G. 1. Jörden Beds.
  2. Borealis bank.
  3. Raiküll Beds.
H. Pentamerus-esthonus zone.
I. Lower Oesel zone.
K. Upper Oesel zone.
  1. Northern yellow zone.
  2. Southern grey zone.

DAMES (22), STOLLEY (30), SIEGERT (32), and others have founded the determination of their erratics on the division of Gothland by LINDSTRÖM; as it seems to me, however, that our boulders approach the Eastern baltic rocks much more, I did not follow this example, the more so, as I have said before, the above-mentioned opinion, which is quoted below with the alteration introduced by DAMES, does not appear to me to be the right one in every respect.

a. Oldest red shale beds with *Arachnophyllum*.
b. *Stricklandinia*-shale.
c. Shale beds and sandstone.
d. Bands of limestone and shale, in some parts oolite.
e. *Pterygotus*-beds.
f. *Crinoid*- and *Coral*-limestones with intermediate *Stromatopora*-riffs, *Gastropoda*- and *Ascoceras*-limestones, together with *Megalomus*-banks.
g. Upper *Cephalopodan* strata.

The material may best be subdivided into four groups: I Boulders of the age G_1—G_3; II... *H*; III... *I*; IV... *K*. The last division will appear to be by far the most important. Besides there are some characteristic boulders, which cannot be placed in the Eastern baltic scheme: these, together with others whose age lies between limits too far apart to reduce them to one of these divisions, will be described at the end.

After these introductory remarks we may proceed to the description of the boulders of the first-mentioned group.

G_1—G_3.

The boulders belonging to the oldest zone G_1, those of the Jörden beds in Esthonia with *Leptocoelia Duboisii* DE VERN., which are occasionally mentioned by German geologists, are not found near Groningen. The two younger zones G_2 and G_3, however, have been met with.

29. Borealis-limestone.

These well-known and characteristic boulders consist of limestone or dolomite, and usually contain in large quantities remains of

Pentamerus borealis EICHW.,

while other fossils are absolutely wanting. As regards the kind of rock my material from Groningen may be divided into two varieties:

a. Limestone, as a rule distinctly crystalline but somewhat marly, as may be easily observed on its weathered surface. The slightly variegated colour of the ground-mass shades from gray to brownish-yellow at the fresh fracture; if weathered, however, it has mostly a sallow-yellowish-gray tinge. In this ground-mass the valves of the above-mentioned species of Pentamerus always occur in great numbers; they are invariably changed into crystalline calcite and this is very often of a bright white colour, so that the always very thick shells sometimes stand out very distinctly against the surface of the boulders, which is sometimes polished. Besides the ground-mass weathers more readily than this calcite, so that the fossils appear in relief. The number of these petrifactions has influenced the exterior appearance of the boulder. Though always numerous, the ground-mass may yet occur in sufficient quantities to give a compact character to the stone. These limestones which are rather hard when not partially weathered make up the majority of the stones found. The dimensions of some of them amount to about 17 c.M. In other pieces the ground-mass recedes much to the background and the stone consists almost exclusively of fragments of the valves of this species of brachiopoda and thus forms a real shell-breccia. The ground-mass then is commonly weathered to a more or less earthy yellow mass, which also covers the surface of the shells, by which the whole assumes a yellow colour. In other cases, however, the weathered ground-mass is almost white, sometimes also brown-ochre-yellow. Though they differ so much in exterior appearance, all specimens have in common that this *Pentamerus* occurs almost always only in single valves which themselves are, for the greater part broken into more fragments. I have never been able to produce a wholly preserved specimen, though some fragments actually show that parts of both valves occur in natural position. So this confirms in the main the results of Roemer's examination (13, p. 74), though I doubt of the truth of his opinion, according to which these boulders should contain only ventral valves of this species. This conception was supported by Eichwald's communication that also in the parent rocks both valves were never seen in connection. Nevertheless Eichwald did know the smaller dorsal valve and describes it as having half the length of the larger one, being much broader and much less vaulted. This can hardly be right, for afterwards Schmidt found complete specimens at Weissenfeld in the neighbourhood of Hapsal in Esthonia. Among my material for comparison there are three such specimens from the above-mentioned place, collected by Bonnema. These, however, show a dorsal valve, but little smaller than the ventral one, but much flatter and so comparatively wider. This causes the great difference between the two shells to disappear, and so there is no reason left for the inexplicable fact that in boulders only the ventral valve should occur. Meanwhile the interior structure of the small shell has to be examined still to confirm this. I have not been occupied with this work.

b. Dolomite, very fine-grained, sometimes even impalpable, of a light-gray or light-brownish-yellow colour. This dolomitic ground-mass also contains great numbers of nuclei of *Pentamerus borealis* Eichw., which are covered all over with little, graceful, dolomite-rhombohedra, which, however, are easily perceptible by the naked eye.

Of these boulders, which in literature is usually called "Pentamerenkalk" are found here:

Limestone:	Boteringesingel,	Groningen	2
	Behind the "Sterrebosch",	,,	1
	Helpman		1
	the "Huis de Wolf", near Haren		1
	"Old Collection"		9
Dolomite:	Boteringesingel, Groningen		2

So in all 16 pieces. From this list appears that at an early time already these boulders have attracted the attention. Quite in correspondence with this is the fact that as early as 1878 MARTIN mentioned 11 pieces from Groningen (6, p. 21, *a* and *c*), and even earlier still ROEMER observed such boulders from here (1, p. 387, n°. 16; 3, p. 269, n°. 27). Afterwards VAN CALKER also pointed out their occurrence in the Hondsrug (19, p. 357; 25, p. 363).

As regards the further spreading of this species of boulders, I refer to ROEMER's excellent treatise about everything known at the time about this subject (13, p. 75), and only wish to state here, that in Germany these boulders are found in a great many places, but nowhere in large quantities. So everywhere in East- and West-Prussia (20, p. 53), in Posen, Silesia and Brandenburg, near Sorau in the district of Frankfurt on the Oder, in South-Holstein in various localities (18, p. 45). Further north they seem not to occur, more westward, on the other hand, Lüneburg in Hannover and Jever in Oldenburg are still to be called as places where they are found. Afterwards WAHNSCHAFFE has made mention of a specimen found near Havelberg (14), and various observations attached to it as to the value of these boulders for the determination of the direction of the ice-flow and the age of the diluvial deposits, in which they are found. I hope afterwards to recur to this question. In Pomerania the Borealis-limestone is not (yet) known (31, p. 83), no more, it seems, in Mecklenburg. STOLLEY afterwards states that he has found it again in Sleswick-Holstein, but differs in this respect from all other notations known to me that he has come upon greater numbers of dolomites than of limestones (30, p. 98). Lastly, these boulders are neither rare in the regions south of the Russian Baltic provinces.

While, as we see, an enormous tract is taken up by the erratics, the Borealis-limestone occupies but a very small part as solid rock. In the eastern baltic (8, p. 43) it forms SCHMIDT's zone G_2, the Borealisbank, which stretches in E.-W.-direction throughout Esthonia, in the shape of a zone narrowing to the west, which also appears in the island of Dagö. The rock consists of limestone or dolomite, just like the boulders, and for a long time only single valves of *Pentamerus borealis* EICHW. have been found in it. Afterwards SCHMIDT has discovered also complete specimens of this species, in a marly variety of the rock from the neighbourhood of Hapsal, as already stated (27, p. 130).

Of this eastern-baltic occurrence I possess limestones for comparison from Risti in the extreme west of this zone on the mainland and dolomite from Pantifer in East-Esthonia. Our boulders correspond very well with those limestones as regards the principal features, though they are not interchangeable with the latter. More perfect still is the correspondence of our dolomites with the sample from Pantifer. From this it appears sufficiently that we have to look for the origin of our boulders in the eastern-baltic zone. Besides all authors agree about this question. Of course we do not mean to say that these Groningen erratics must of necessity originate in the zone now known. As the Borealis-bank is also found in Dagö, it may be surmised that it stretches, or formerly stretched, still farther westward under the sea, and the very uniform petrographical character of the rock throughout Esthonia leads us to adopt the opinion that this submarine continuation may also be considered as the possible place of origin of our boulders. Of course it is impossible to indicate a definite point in this zone.

30. Elegans-limestone.

With this term, referring to one of the most important fossils of this species of boulders, I denote a crystalline-limestone, generally fine-grained, sometimes almost impalpable, but still oftener rather coarse-grained. Calcite, bright as water often occurs rather regularly spread through the stone, but not in large quantities. The limestone is not perceptibly dolomitic nor marly, as in the solution in nitric acid only a small part is left and this solution produces no or hardly any reaction with magnesia. Its colour is bright-gray, sometimes rather yellowish-gray, rarely blewish-gray ; when weathered, however, the stone shades from white to yellowish white. Its surface is very often marked by distinctly visible glacial scratches. Layers are but seldom perceptible and moreover not very distinct. Fossils are by no means rare, but belong to a relatively small number of species, which are mentioned here :

Phacops elegans Sars and Boeck sp.
Leperditia Hisingeri Schmidt.
Strophomena pecten L.
Vincularia nodulosa Eichw.
Vincularia megastoma Eichw.
Encrinurus punctatus Wahlb.
Calymene sp.
Orthoceras sp.
Proetus sp.
Ptilodictya sp.
Beyrichia sp.
Murchisonia sp.

The first five species almost occur in every piece. Head-shields of the said *Phacops*-species are very common, pygidia occur as well, and an almost complete thorax (which has not been figured by SCHMIDT) has also been found. I have named these boulders after this characteristic species. Equally important is further the presence of the *Leperditia*-species, whose valves, both right and left, are occasionally present in large numbers in a single stone; in the unweathered rock they are bright brown, weathered nearly white. The mentioned *Strophomena*-species is very plentiful, while especially the two bryozoa-species, mentioned next, sometimes give the stone a peculiar appearance. Though occurring in each of these boulders they are hardly perceptible in the unweathered rock: they are together in great numbers at the fractured surface, split along the foliaceous "Mittelschicht", like graceful little white feathers. But the structure of this fossil may be more distinctly perceived at the weathered surface of the boulders. The other fossils mentioned are found but rarely and do not contribute in a great measure to the diagnosis of the rock.

Besides these fossils, however, remains of brachiopoda are very frequently met with, which no doubt are characteristic, though I have failed to determine them satisfactorily. Some *Rhynchonella*- and *Orthis*-species are undeniably present among them. One piece also contains white, globular and angular crinoid-stems. Also the presence of *graptolite*-remains is most interesting; these, however, have been preserved too incompletely to be specifically determined.

Of this species of boulders, thus petrographically and palaeontologically characterized there are among my material 33 pieces from the following places:

"Noorderbegraafplaats",	Groningen	2
"Boteringesingel",	,,	9
"Noorderbinnensingel",	,,	1
"Nieuwe Boteringestraat",	,,	1
Between "Parklaan" and "Heerebrug",	,,	1
"Nieuwe Veelading",	,,	3
Behind "het Sterrebosch",	,,	1
"Schietbaan",	,,	1
Café "de Passage",	Helpman	2
"Hilghestede",	,,	4
	,,	1
Between Helpman and	Haren	2
Villa "Edzes" near	,,	1
	,,	1
	Groningen	1
"Old Collection"		2

To determine the age of these boulders, which, as the above list shows, are by no means rare near Groningen, all that is known about the occurrence of the characteristic fossils is communicated below as completely as possible.

Phacops elegans Sars and Boeck sp.

Schmidt, 8, p. 72, T. I, f. 1; T. X, f. 10—12; T. XI, f. 17,

is said by Schmidt to occur in the Raiküll strata and the Estonus-zone in Esthonia. It was first found in the oldest of the two zones G_3, near Wahhoküll in the centre of East-Esthonia, together with *Strophomena pecten* L. and *Diplograpsus estonus* Schmidt; its locality in the H-zone is almost straight to the south of it near Törwe in the neighbourhood of Talkhof, on the border of Livonia. Complete specimens, however, have not been found; the thorax found here is there unknown.

Most probably *P. quadrilineata* Ang. Lindström, 12, p. 43; 17, p. 2; is identical with this species; it has been described by the latter from the oldest strata of the Upper Silurian formation *a* and *b*, near Wisby. Moreover Schmidt mentions Farö and Lau there, places which according to him belong to his middle and youngest zone in Gothland (8, p. 74); this notation borrowed from Lindström seems to me to want confirmation. In Sweden this fossil is also found in Dalarne (17, p. 27) and if *P. elliptifrons* Esmarck must be identified with this species (which I cannot state with perfect certainty), in Jemtland (29, p. 269) as well. The stage there argues a conclusion in the affirmative. This fossil is not known from Scania. On the other hand it is found together with *Leperditia Hisingeri* Schmidt in Malmö in the bay of Christiania, it seems in a corresponding stratum (8, p. 74).

This species is not known in the literature of German boulders, though Wigand makes mention of *Phacops Stokesi* Milne Edwards, the English fossil, which is most like our species (16, p. 40). The illustrations of this fossil found near Rostock in Phacites-sandstone prove, however, that this species certainly does not correspond in all respects with our specimens. *Phacops prussica* Pompeckj, may also be taken into consideration but neither the latter is completely corresponding with those from Groningen; the rock in which this species occurs in East-Prussia, "krystalliner, gelblich-grauer obersilurischer Kalk" would not argue against it (23, p. 19). Roemer does not mention our species.

Leperditia Hisingeri SCHMIDT.

SCHMIDT, 10, p. 14—16, T. I, f. 5—7.

identical with *Leperditia Schmidtii* KOLMODIN, has already been known for a long time from the neighbourhood of Wisby, where it frequently occurs in the *Stricklandinia*-shale; esp. near Snäckgärdet I found beautiful loose specimens. But it also occurs south of Wisby in LINDSTRÖM'S stage c_1; according to KOLMODIN moreover also in the shale of Westergarn (c_2) and Capellshamn (7, p. 133). In Esthonia this fossil belongs to the zones G_1 and G_2, and is found there in many places, also in Dagö. Our specimens are on an average much smaller than those of Gothland, but for the rest correspond very well in their relative dimensions with the description of the true form. As already stated, this species is also found near Christiania. LINDSTRÖM states moreover, that it is found in Scania (17, p. 25); I failed to find out on what grounds this notation is based, and have reasons to doubt of the truth of it.

KIESOW writes that he has found it in German boulders from Spengawsken in West-Prussia and in a limestone (not corresponding with ours) which curious enough also contains *Leperditia baltica* HIS. (11, p. 274). CHMIELEWSKI on the other hand has not come upon the true species in East-Prussia and Kowno (34). KRAUSE, again, has found it in Neubrandenburg (24, p. 7) and STOLLEY in a bright yellow, crypto-öolitic limestone from Sleswick-Holstein (30, p. 109).

Strophomena pecten L.

is a fossil generally occurring in the Jörden and Raiküll beds in Esthonia; in Gothland it is frequently found near Wisby and our specimens correspond most with this occurrence. LINDSTRÖM, however, mentions it from c-h; hence I should not be surprised if different varieties of this species were to be distinguished. WIMAN also states to have found it in Jemtland in the quartzite with *Phacops elliptifrons* ESM. (29, p. 270).

GAGEL has described it from boulders of Beyrichia-limestone (20, p. 47) from East- and West-Prussia; various authors moreover mention it in boulders of different age, which strengthens my opinion to draw no important conclusions from this species.

Vincularia nodulosa EICHW. and *V. megastoma* EICHW.

EICHWALD, 5, T. XXIV, f. 8 and 9.

are very characteristic of the Raiküll stratum in Esthonia and are found there everywhere, though they occur in the Estonus-zone as well (8, p. 43).

Encrinurus punctatus Wahlb.

is only present in a single piece and is a fossil found in all Upper Silurian regions throughout all zones so that this species is of no value for the determination of the age.

If we take these results together we get:

	Esthonia.	Gothland.
Phacops elegans Sars and Boeck.	G_3 H	a — b.
Leperditia Hisingeri Schmidt.	G_1 , G_3	b — c.
Strophomena pecten L.	G_1 , G_3	c — h.
Vincularia nodulosa Eichw.	G_3—H	
Vincularia megastoma Eichw.	G_3 - H	

It appears from this distinctly, that these boulders are remains of an equivalent of the Raiküll zone G_3 in Esthonia. As to Gothland, the comparison with Lindström's zone *b*, if a comparison is desired, is the most probable one.

Moreover this result is especially interesting, because boulders of this age are not known in literature that I know of. In the Groningen collection on the other hand some pieces have been brought to this zone long since. But once Noetling mentions a stone belonging to this stratum which, however, contained no determinable fossils and was only under reservation by reason of the great correspondence to a piece of limestone from Raiküll, counted as a representative of this zone (9, p. 291). Roemer doubts of this (13, p. 77).

As regards the origin of these boulders, it may first be stated, that none of the regions where only one or a few of the fossils characteristic of this occur, viz. Norway, (Scania), Dalarne and Jemtland, can be taken into account. Besides the petrographic nature of these deposits precludes this supposition altogether. In Gothland on the contrary these fossils, with the exception of the two bryozoa-species, are all found. But the rock occurring there (almost always shales) does not show petrographically the least correspondence with our limestone. In fact these boulders must not be considered to originate in Gothland.

Lastly as regards Esthonia: The Raiküll zone, G_3, (8, p. 43) extends from Laisholm in Livonia and Wahhoküll in East-Esthonia westward as far as Dagö; in the eastern part the zone is wider and narrows westward. It almost always consists of two systems, now limestone, then dolomite. In the above-mentioned passage SCHMIDT gives no further petrographical description of the rock; but afterwards he speaks once more (33, p. 308) of a "dichten, festen, etwas kieselhaltigen hellgelben Kalkstein, der demjenigen unsrer Raiküll'schen Schicht am meisten gleicht". For want of material for comparison I dare not conclude from this a great correspondence with our limestone. Further it is striking that SCHMIDT says that petrifactions are comparatively rare in the Raiküll stratum, except corals. Now our boulders contain a comparatively great number of fossils, whereas corals are altogether wanting. Just the reverse argues the fact that graptolites occur in both, which though shortly described as *Diplograptus estonus* SCHM. (2, p. 226), are not yet figured. Perhaps the same species may be found in our pieces.

By reason of the differences adduced above, I deem it little probable, that the Raiküll stratum in Esthonia itself can be considered as the place of origin. It is not impossible that the submarine continuation of this zone consists of a rock more corresponding with our boulders. For the present this question cannot be solved more completely though material for comparison esp. from G_3 in Dagö, may render valuable services.

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Acad. Proefschrift, Groningen, 1904.

GRONINGEN, Min.-Geol. Instit., 31 December 1904.

Chemistry. — "*On some phenomena, which can occur in the case of partial miscibility of two liquids, one of them being anomalous, specially water.*" By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. In the second part of his *Continuität* (1900)[1]) Prof. VAN DER WAALS has given the theory of the so called *longitudinal plait* on the ψ-surface, and in the last Chapter (§ 12, p. 175 sequ.) he gives moreover a special, ample discussion of this plait, in particular with regard to *anomalous* components. It is shown there, that for the appearance of certain complications, which can present themselves at this plait, one of the two components must be anomalous[2]).

In the following pages I shall try to explain the appearance of the different particular forms, which can present themselves, when one of the components is associative, specially when this anomalous component is *water*.

2. We begin to remember briefly the theory of the phenomenon of partial miscibility for binary mixtures of *normal* substances.

It is well known, that the total thermodynamic potential is represented by

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[1]) p. 41—45.

[2]) Also compare These Proceedings of Nov. 5, 1902.

$$Z = -\Sigma(n_1 k_1)\,T\,(log\,T - 1) + \Sigma(n_1 (e_1)_0) - T\,\Sigma(n_1 (\eta_1)_0) -$$
$$-\int p dv + pv + RT\,\Sigma(n_1\,log\,n_1).$$

or

$$Z = \Sigma(n_1 C_1) - \left[\int p dv - RT\,\Sigma n_1\,.\,log\,\Sigma n_1 - pv\right] + RT\,\Sigma\left(n_1\,log\,\frac{n_1}{\Sigma n_1}\right).$$

Differentiating subsequently at constant T and p with respect to n_1 and n_2, we get:

$$\left.\begin{aligned}\mu_1 &= \frac{\partial Z}{\partial n_1} = C_1 - \frac{\partial \omega}{\partial n_1} + RT\,log\,\frac{n_1}{\Sigma n_1}\\ \mu_2 &= \frac{\partial Z}{\partial n_2} = C_2 - \frac{\partial \omega}{\partial n_2} + RT\,log\,\frac{n_2}{\Sigma n_1}\end{aligned}\right\},$$

where C_1 and C_2 are pure functions of the temperature, represented by

$$\left.\begin{aligned}C_1 &= -k_1 T\,(log\,T - 1) + (e_1)_0 - T(\eta_1)_0\\ C_2 &= -k_2 T\,(log\,T - 1) + (e_2)_0 - T(\eta_2)_0\end{aligned}\right\},$$

whereas the quantity ω is given by

$$\omega = \int p dv - RT\,\Sigma n_1\,.\,log\,\Sigma n_1 - pv\,. \quad . \quad . \quad . \quad . \quad (1)$$

The meaning of the different quantities n_1, $(e_1)_0$, $(\eta_1)_0$, etc. etc. is supposed to be known.

We will substitute now the variables n_1 and n_2 by x, so that $n_1 = 1 - x$, $n_2 = x$ and $\Sigma n_1 = 1$. As ω is, just as Z, a *homogeneous* function of the *first* degree with respect to n_1 and n_2, we may write:

$$\left.\begin{aligned}\mu_1 &= C_1 - \left(\omega - x\frac{\partial \omega}{\partial x}\right) + RT\,log\,(1 - x)\\ \mu_2 &= C_2 - \left(\omega + (1 - x)\frac{\partial \omega}{\partial x}\right) + RT\,log\,x\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now, when there is a plait on the Z-surface, the spinodal-curve, that is to say its projection on the T,x-plane, will be given by the condition $\frac{\partial^2 Z}{\partial x^2} = 0$; or also, μ_1 being $= Z - x\frac{\partial Z}{\partial x}$, and $\mu_2 = Z + (1 - x)\frac{\partial Z}{\partial x}$, by $\frac{\partial \mu_1}{\partial x} = 0$ or $\frac{\partial \mu_2}{\partial x} = 0$.

We therefore find for the equation of this curve in the T,x-plane:

$$x\frac{\partial^2 \omega}{\partial x^2} - \frac{RT}{1 - x} = 0,$$

or

$$RT = x\,(1 - x)\frac{\partial^2 \omega}{\partial x^2}\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we use the equation of VAN DER WAALS:

$$p = \frac{\Sigma n_1 \,.\, RT}{v-b} - \frac{a}{v^2},$$

then we obtain:

$$\omega = \Sigma n_1 \,.\, RT \log (v-b) + \frac{a}{v} - RT\, \Sigma n_1 \,.\, \log \Sigma n_1 - pv \text{ }^{1})\text{.}$$

Supposing now, that in the case of liquids the external pressure p (or the vapour-tension) can be neglected with respect to the molecular pression $\frac{a}{v^2}$, the equation of VAN DER WAALS may be written:

$$\frac{a}{v^2} = \frac{\Sigma n_1 \,.\, RT}{v-b},$$

and the expression for ω, when in the same manner pv is omitted by the side of $\frac{a}{v}$, passes into

$$\omega = \Sigma n_1 \,.\, RT \log \frac{\Sigma n_1 \,.\, RT}{a/_{v^2}} + \frac{a}{v} - RT\, \Sigma n_1 \,.\, \log \Sigma n_1 \,,$$

or

$$\omega = \Sigma n_1 \,.\, RT \log \frac{RT}{a/_{v^2}} + \frac{a}{v},$$

that is to say into

$$\omega = RT \log \frac{RT}{a/_{v^2}} + \frac{a}{v},$$

when $\Sigma n_1 = 1$. For $\frac{\partial^2 \omega}{\partial x^2}$ we find consequently:

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right) - RT \frac{\partial^2}{\partial x^2} \log \frac{a}{v^2},$$

by which the equation (3) of the projection of the locus of the points of inflection on the T,x-plane passes into

$$RT = x\,(1-x)\left[\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right) - RT \frac{\partial^2}{\partial x^2} \log \frac{a}{v^2}\right],$$

or into

$$RT = \frac{x\,(1-x)\,\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right)}{1 + x\,(1-x)\,\frac{\partial^2}{\partial x^2} \log \frac{a}{v^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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[1] If $b = f(v)$, then $\int p\,dv$ still gives a term $RT \int \frac{db}{v-b}$. But this term may be regarded as independent of x, and so can be added to the temperature function C_1.

The term with $log\,\frac{a}{v^2}$ was introduced some time ago by VAN DER WAALS[1]; in the original theory this term was neglected, and so the equation (4) was simply $RT = x\,(1-x)\,\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right)$.

In consequence of the relations $\frac{a}{v} = fRT_c$, $\frac{a}{v^2} = \gamma p_c$, where according to the variability of the liquid-volume v, the coefficients f and γ will still vary slowly with the temperature (f is the well known factor of the vapour-tension, which may be put circa 7), we can also write for (4):

$$T = \frac{fx\,(1-x)\,\frac{\partial^2 T_c}{\partial x^2}}{1 + x\,(1-x)\,\frac{\partial^2\, log\, p_c}{\partial x^2}} \quad \ldots\ldots\ldots \quad (4a)$$

We see, that only in the case, that the *critical pressures* of the two components *differ little*, the term with $log\,p_c$ can be omitted. This will be also the case, when x is in the neighbourhood of 1 and 0. But in all other cases if would be inaccurate to omit à priori the designed term.

Further we write:

$$\left.\begin{array}{l} a = (1-x)^2\, a_1 + 2x\,(1-x)\, a_{12} + x^2\, a_2 \\ v = (1-x)\ \ v_1 + x v_2 \end{array}\right\} ,$$

since for liquids at low temperatures v can be supposed dependent on x in entirely the same manner as $b = (1-x)\, b_1 + x b_2$. The molecular volumes v_1 and v_2 must then be regarded, just as b_1 and b_2, as constant or as slowly varying with the temperature[2]. We then find after some reductions:

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[1] These Proceedings, in Ternary Systems, specially IV, p. 96—100. (June 12, 1902); see also July 13, 1904, p. 145 sequ.

[2] If we substitute in the case of liquids v by b, and then write $b = (1-x)\, b_1 + x b_2$, the difficulty arises, that in that way quantities of order $v - b$ are neglected against those of order v, and the question would present itself, if this is only upon very definite conditions *not* in contradiction with omitting p by the side of $\frac{a}{v^2}$. (This observation was kindly made to me by Prof. LORENTZ).

I hope to escape this difficulty by not substituting v by b, but by simply supposing the volume v *linearly* variable with x in the case of liquids at low temperatures: by writing therefore for v, analogous to the expression for b, $v = (1-x)\, v_1 + x v_2$. As I remarked, v_1 and v_2 still vary slowly with the temperature, whereas b_1 and b_2 of course would be perfectly constant. Now it

$$\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right)=\frac{2}{v^3}\left(a_1 v_2^{\,2}+a_2 v_1^{\,2}-2a_{12}v_1v_2\right),$$

or — when we suppose for *normal* components the relation of BERTHELOT, viz. $a_{12}=\sqrt{a_1a_2}$, as approximately exact:

$$\underline{\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right)=\frac{2}{v^3}\left(v_2\sqrt{a_1}-v_1\sqrt{a_2}\right)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As the second member will be always *positive*, even if a_{12} might be $<\sqrt{a_1a_2}$ [1]), the curve $T=f(x)$ will always turn its *convex* side to the x-axis.

We will now determine $\frac{\partial^2}{\partial x^2} log \frac{a}{v^2}$. With $a_{12}=\sqrt{a_1a_2}$ [2]) the expression for a becomes:

$$a=\left[(1-x)\sqrt{a_1}+x\sqrt{a_2}\right]^2,$$

so that

$$log\frac{a}{v^2}=2\,log\frac{(1-x)\sqrt{a_1}+x\sqrt{a_2}}{(1-x)v_1+xv_2}.$$

Consequently we have:

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will be better justified to subsitute $\frac{a}{v}$ by fRT_c, than $\frac{a}{b}$ (and afterwards $\frac{a_1}{v_1}$ by fRT_1 and $\frac{a_2}{v_2}$ by fRT_2), where f will vary in the same manner as v with temperature. For it is easy to show, that the expression for the vapour-tension for a single substance at low temperatures is $log\frac{a/v^2}{p}=\frac{a/v}{RT}-\int_l^v\frac{db}{v-b}$ (v is in the first two terms the liquid volume), whence we can deduce, in connexion with the empirical relation $log\frac{p_c}{p}=f\left(\frac{T_c}{T}-1\right)$, where f is circa 7, that $\frac{a}{v}=fRT_c$.

The error made by supposing v linearly variable with x, will certainly be much smaller than by putting $v=b$. In that way errors of at least 16% would be made, since $\frac{b}{v}$ will be nearly $5/6$ for liquids in the neighbourhood of the melting-point.

The quantities v_1 and v_2 can now also immediately be substituted by the experimentally determined values in the liquid state.

[1]) See VAN DER WAALS, These Proceedings of Oct. 8, 1902, p. 294.

[2]) Although there is no sufficient reason for this relation, I have supposed it *approximately* exact, also because only in this case a simple expression could be obtained for $\frac{\partial^2}{\partial x^2} log \frac{a}{v^2}$.

$$\frac{\partial}{\partial x} \log \frac{a}{v^2} = 2\left[\frac{\sqrt{a_2}-\sqrt{a_1}}{\sqrt{a}} - \frac{v_2-v_1}{v}\right],$$

and therefore

$$\frac{\partial^2}{\partial x^2} \log \frac{a}{v^2} = 2\left[\frac{(v_2-v_1)^2}{v^2} - \frac{(\sqrt{a_2}-\sqrt{a_1})^2}{a}\right] \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This expression can be reduced to a different form, and then we find:

$$\frac{\partial^2}{\partial x^2} \log \frac{a}{v^2} = \frac{2}{av^2}\,(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})\,\left[(v_2 \sqrt{a_1} - v_1 \sqrt{a_2}) + 2\,v\,(\sqrt{a_2}-\sqrt{a_1})\right],$$

whence it appears, that the factor $v_2 \sqrt{a_1} - v_1 \sqrt{a_2}$ occurs in the expression for $\frac{\partial^2}{\partial x^2} \log \frac{a}{v^2}$ as well as in that for $\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right)$.

Now when $v_2 \sqrt{a_1} = v_1 \sqrt{a_2}$ or $\frac{a_1}{v_1^{\,2}} = \frac{a_2}{v_2^{\,2}}$, when in other words the *critical pressures* of the two components are *equal*, then $\frac{\partial^2}{\partial x^2} \log \frac{a}{v^2}$ becomes $= 0$. But then *simultaneously* $\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right)$ will be $= 0$, and the whole longitudinal plait will disappear, (at the same time the curve $T_c = f(x)$ will then pass into a straight line).

We see therefore, that for occurrence of the phenomenon of partial miscibility at attainable, that is too say at not to low temperatures, the *critical pressures* of the two components *must differ as much as possible*.

Now this is *not* the case for the greater part of *normal* substances, and that is the explanation of the well known fact, that for mixtures of normal substances the phenomenon of limitated miscibility has been so very rarely found at the common temperatures.

When we substitute (5) and (6) in the equation (4), then we find finally:

$$\left.\begin{aligned} RT &= 2\,x\,(1-x)\,\frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v^3} : (1+\Delta), \\ \text{where} \quad & \\ \Delta &= 2\,x\,(1-x)\left[\frac{(v_2-v_1)^2}{v^2} - \frac{(\sqrt{a_2}-\sqrt{a_1})^2}{a}\right] \end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

This would be a pure parabola, if v and $1+\Delta$ were independent of x.

3. We will now determine the values of x and T for the "*critical point of miscibility*." For this the conditions $\frac{\partial \mu_1}{\partial x} = 0$ and $\frac{\partial^2 \mu_1}{\partial x^2} = 0$

combined must be satisfied, or — what is the same — the conditions

$$\frac{\partial \mu_1}{\partial x} = 0 \quad ; \quad \frac{dT}{dx} = 0,$$

as is obvious. Now from (7) follows, when $1 + \angle$ is supposed independent of x, which will be certainly permitted, in consequence of the small values of $\angle$ in the case of normal substances:

$$R\frac{dT}{dx} = \frac{2\left(v_2\sqrt{a_1} - v_1\sqrt{a_2}\right)^2}{1+\angle}\left\{\frac{1-2x}{v^3} - \frac{3x(1-x)}{v^4}(v_2-v_1)\right\},$$

as $v = v_1 + x(v_2-v_1)$. This expression becomes $= 0$, when

$$(1-2x)(1+rx) - 3rx(1-x) = 0,$$

where $r = \frac{v_2-v_1}{v_1}$. This yields:

$$rx^2 - 2(r+1)x + 1 = 0,$$

whence

$$x_c = \frac{1}{r}\left\{(r+1) - \sqrt{r^2+r+1}\right\}.$$

When $r = 0$, that is to say when $v_1 = v_2$, then $x_c = 0{,}5$. At all events this will be *approximately* the case, if $\angle$ should still be in any way dependent on x.

We will reduce now the equation (7) somewhat. With $a_1 = fRT_1v_1$ and $a_2 = fRT_2v_2$, where T_1 and T_2 are the critical temperatures of the components, these equations pass, after substituting x_c for x, into

$$\left.\begin{aligned} RT_c &= 2x_c(1-x_c)\frac{\left[v_2\sqrt{fRT_1v_1} - v_1\sqrt{fRT_2v_2}\right]^2}{v_1^3\left(1+x\frac{v_2-v_1}{v_1}\right)^3} : (1+\angle_c) \\ \angle_c &= 2x_c(1-x_c)\left\{\frac{(v_2-v_1)^2}{v_1^2\left(1+x\frac{v_2-v_1}{v_1}\right)^2} - \frac{\left(\sqrt{T_2v_2} - \sqrt{T_1v_1}\right)^2}{\left[\sqrt{T_1v_1} + x\{\sqrt{T_2v_2} - \sqrt{T_1v_1}\}\right]^2}\right\} \end{aligned}\right\},$$

or with $T_2 = \theta T_1$ and $v_2 = \varphi v_1$ into

$$\left.\begin{aligned} T_c &= 2fx_c(1-x_c)\frac{\varphi\left(\sqrt{\varphi} - \sqrt{\theta}\right)^2}{\left(1+(\varphi-1)x_c\right)^3}\,T_1 : (1+\angle_c) \\ \Delta_c &= 2x_c(1-x_c)\left\{\frac{(\varphi-1)^2}{\left(1+(\varphi-1)x_c\right)^2} - \frac{\left(\sqrt{\theta\varphi}-1\right)^2}{\left(1+\left(\sqrt{\theta\varphi}-1\right)x_c\right)^2}\right\} \end{aligned}\right\} \quad . \quad . \quad (8)$$

since $(\varphi - \sqrt{\theta\varphi})^2 = \varphi\left(\sqrt{\varphi} - \sqrt{\theta}\right)^2$.

We shall illustrate these equations by an example. In order to find the critical point as high as possible, we will choose two normal substances, of which the critical pressures differ as much as possible. We take therefore *ether* and *carbon disulphide.* The critical data are the following:

$$\begin{array}{l|l}
CS_2 & T_1 = 548^\circ \quad ; \quad p_1 = 76 \ atm. \\
ether & T_2 = 467^\circ \quad ; \quad p_2 = 35 \ atm.
\end{array}$$

In order to determine $\varphi = \frac{v_2}{v_1}$, we remark, that $v_1 = \frac{fR}{\gamma} . \frac{T_1}{p_1}$, $v_2 = \frac{fR}{\gamma} . \frac{T_2}{p_2}$, as for instance $\frac{a_1}{v_1} = fRT_1$ and $\frac{a_1}{{v_1}^2} = \gamma p_1$. We have therefore:

$$\frac{v_2}{v_1} = \frac{T_2}{p_2} : \frac{T_1}{p_1} = \frac{T_2}{T_1} \times \frac{p_1}{p_2},$$

that is to say $\underline{\varphi = \theta\, \pi,}$ where the proportion $\frac{p_1}{p_2}$ is represented by π.

Now for the designed substances $\theta = 0{,}852$, $\pi = 2{,}17$, so that we find $\varphi = 1{,}85$. Since $r = \varphi - 1$, the equation for x_c passes into

$$x_c = \frac{1}{\varphi - 1} (\varphi - \sqrt{\varphi^2 - \varphi + 1}), \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and hence we find for x_c the value 0,29. Further $\sqrt{\theta} = 0{,}923$, $\sqrt{\varphi} = 1{,}36$, $f = 7$, and so (8) becomes:

$$T_c = \frac{14 \times 0{,}206 \times 1{,}85 \times 0{,}191}{(1{,}247)^3} 548 : (1 + \Delta_c),$$

or

$$T_c = \frac{1{,}019}{1{,}94} 548 : (1 + \Delta_c) = 288 : (1 + \Delta_c).$$

We have further:

$$\Delta_c = 0{,}412 \left\{ \frac{0{,}723}{1{,}555} - \frac{0{,}0650}{1{,}153} \right\} = 0{,}412 \times 0{,}409 = 0{,}169,$$

so that we find for $1 + \Delta_c$ the value 1,17.

Hence T_c becomes $288 : 1{,}17 = 246 = -\underline{27^\circ\ C.}$

The critical point of the chosen substances lies therefore still a *thirty* degrees *beneath* the common zero of Celsius. And for the greater majority of other normal substances we will find for T_c still much smaller values — because the critical pressures will differ there in most of the cases less than in the case of ether and CS_2.

4. All that precedes now undergoes important modifications, when one of the two components is *anomalous*, specially *water*. For in the first place the *critical pressure* of the water is *very high*, not

less than 198 atm., so that it will differ much from the critical pressures of most of the other substances. And in the second place the value of v_1 is here so *extraordinarily variable* with the temperature. Water is in this respect exceptional in Nature, and gives therefore rise to very peculiar phenomena, which are not found with other substances, or not in that degree. Alcohol e.g. is also an anomalous substance, but neither is the variability of the molecular volume there particularly great, nor the critical pressure particularly high.

We know, that the variation of the molecular volume finds its cause in the decomposition of the *double molecules* with the temperature. Because v_1 gradually grows smaller and smaller, the quantity

$$(v_2\sqrt{a_1}-v_1\sqrt{a_2})^2.$$

which principally determines the value of T_c, will become greater and greater. And the initial value of that quantity is in the case of water as one of the components already higher than for mixtures of normal substances. This is connected with the high critical pressure of water, being 198 atm., whence can be calculated, that the critical pressure — if water continued to consist of only double molecules — would yet still amount to circa 66 atm., i.e. higher than that of most of the normal substances. [Of course the designed expression will increase with decreasing values of v, only when $\frac{\sqrt{a_1}}{v_1} > \frac{\sqrt{a_2}}{v_2}$, that is to say, when the critical pressure of the first component is greater than that of the second. This condition will nearly always be satisfied, when we assume water as the *first* component].

As said, the decrease of v_1 is very considerable in the case of water. I remember, that I found some years ago [1]), that for 18 Gr. water $v_1 = 19,78$ ccm., when all the molecules are *double*; and only $= 11,34$ ccm. for 18 Gr., when all the molecules are *single*. When therefore the temperature increases from nearly —90° C., where all the molecules are double (supposing, that the water had not congealed long before), to circa 230° C., where all the molecules have become single, then v_1 will diminish down to nearly $^4/_7$ of its original value.

[In the same Memoir I showed, that in this fact lies also the explication — qualitative as well as quantitative — of the well-known phenomenon of maximum density at 4° C.]

Now the consequence of this variability of v_1 will be, that the second member of (7) — we will represent it (divided by R) in

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[1]) Z. f. Ph. Chemie **31** (Jubelband VAN 'T HOFF), p. 1—16, specially p. 13.

the following by K — will be no longer a constant for a definite value of x, but a function of temperature.

If we draw therefore (see fig. 1) the straight line OM, which divides into halves the angle of coordinates (OT is the axis of temperature, OA' that of the values of K) — then for mixtures of *normal* substances the point of intersection of the *straight* line $K=$ const., which runs consequently parallel with the T-axis, with the line OM will represent the temperature, corresponding in the T,x-projection of the spinodal curve with the chosen value of x. If this were x_c, then we should find in this manner T_c. That temperature will be — as we have shown on the preceding pages — extremely low.

On the other hand, in the case of *anomalous* mixtures, that is here: where one of the components is an associative substance, the straight line AA' will transform itself into *two straight* lines, joined by a *curve* (see fig. 2). The first straight line corresponds then with the temperatures, where all the molecules are double, that is therefore in the case of water below — 90° C.; the second straight line will correspond with the temperatures, where all the molecules have become single — so for water above 230° C. The joining curve will correspond with the temperatures between — 90° C. and 230° C., where the process of dissociation of the double molecules is going on.

Several cases can occur here, which presently we will briefly discuss.

5. We should now have to deduce an expression for RT and Δ, analogous to (7), but this time for the case that one of the substances is anomalous. The required considerations and calculations will not be reproduced here, however, because I shall do so in the more ample Memoir, which will soon be published in the *Archives Teyler.* We therefore will limit ourself to the communication of the final result, viz.

$$\left.\begin{aligned} RT &= 2x(1-x)\left(1+\frac{1-\beta}{1+\beta}x\right)\frac{(v_2\sqrt{a_1}-v_{01}\sqrt{a_2})^2}{v^3}:(1+\Delta) \\ \Delta &= 2x(1-x)\left(1+\frac{1-\beta}{1+\beta}x\right)\left[\Sigma n_1\left\{\frac{(v_2-v_{01})^2}{v^2}-\frac{(\sqrt{a_2}-\sqrt{a_1})^2}{a}\right\}-\right. \\ &\left.-(1-\beta)\left\{\frac{v_2-v_{01}}{v}-\frac{\sqrt{a_2}-\sqrt{a_1}}{a}\right\}\right]. \end{aligned}\right\} \quad (10)$$

These expressions come in the place of the former expressions (7). Of course they are somewhat more complicated, but they have essentially the same form, as will be discussed amply in the designed Memoir. It will only be remarked, that $\Sigma n_1 = \frac{1+\beta}{2} + \frac{1-\beta}{2}x$, where β is the degree of dissociation of the double molecules; that $v_{01} = {}^1/_2 (1-\beta) v_0 + \beta v_1$, where v_0 is the molecular volume of the double molecules, and v_1 represents that of the single molecules; and then once more the relation $a_{12} = \sqrt{a_1 a_2}$ has been used, by which again the calculation of $\angle$ was practically possible.

The expression for a reduced, in consequence of $a_0 = 4a_1$, $a_{01} = 2a_1$, $a_{02} = 2a_{12}$, to

$$a = (1-x)^2 a_1 + x^2 a_2 + 2x(1-x) a_{12}.$$

That for b or v to $v = (1-x) v_{01} + x v_2$, where v_{01} has the meaning as is indicated above. (The index 0 relates to the double molecules, the index 1 to the single molecules of the associative substance: the index 2 relates to the second, normal substance).

As is already briefly indicated above, it will be principally the factor $(v_2 \sqrt{a_1} - v_{01} \sqrt{a_2})^2$, on which the phenomenon, studied by us, depends. *The great variability of the quantity v_{01} with the temperature is the only cause* of all these peculiar phenomena of partial miscibility, occurring in the case of mixtures, when one of the components is anomalous, specially water.

That factor will increase more and more with the temperature, because v_{01} decreases in consequence of the continual formation of new single molecules from the dissociating double molecules — a single molecule being much smaller than half a double molecule. (compare § 4).

It is evident, that the denominator v^3 (by v_{01}) will equally diminish with the temperature, so that the value of the second member of (10) will increase still more. The variations of the other terms have comparatively but little influence.

6. What will now be the different forms of the plait — i. e. in the T,x representation — when the course of the curve $K = f(T)$ (see § 4) is continually modified with the different components added to the water? (We call attention to the fact, that K represents the second member of (10), divided by R, and that the following figures indicate therefore the *graphical* solution of the equation $T = K$ with respect to T).

a. The case of normal substances has already been considered by us. It is represented by fig. 1. The spinodal curve will have the same form as in fig. 2.

b. In fig. 2 the straight part of the curve $K = f(T)$, where K has the initial value K_1 (all molecules are still double), intersects the line OM in the point A; whereas the curved part, and the second straight part, where K assumes the final value K_2 (all molecules have become single), lie wholly on the *right* of OM. The plait will consequently be identical with that of the preceding case — only with this difference, that the point A lies below — 90° C., where the dissociation of the double molecules begins, so that this point lies wholly *beyond* the region of attainable temperatures.

c. As soon as the value of K increases a little, we get the case of transition of fig. 3. The curve $K = f(T)$ *touches* now the line OM in B,C, and from this moment the *isolated* plait will begin to appear, extending itself above the just regarded normal plait, which lies in unattainable depth. Here it is only two coinciding critical points in the one point B,C.

d. When the value of K_1 is still a little greater, the case of fig. 4 will present itself, where the line OM is intersected, besides in A, in still two other points B and C. The isolated plait above the normal one is formed now, with two critical points, a *lower* one in B and an *upper* one in C. Everywhere between B and C K is $> T$, just as below A, so that we are, in consequence of $\frac{\partial^2 Z}{\partial x^2} < 0$, in the unstable region, i. e. within the spinodal line of the plait.

This case — or the case of fig. 6 — is realised by a great number of substances, also in the case of *two* anomalous substances [1]).

α. In some cases the *upper* critical point is found, as in the case of water and $CO^{CH_3}_{C_2H_5}$ (ROTHMUND), and of H_2O and *isobutyl-alcohol* (ALEXEJEW); propably also in the case of water and *ether* (KLOBBIE and ALEXEJEW), of H_2O and $CO\ (C_2H_5)_2$ (ROTHMUND), of H_2O and *ethyl-acetate* (ALEXEJEW), and of H_2O and *amyl-alcohol* (ALEXEJEW), in which latter cases, however, the point C was not reached. As to water and ether e.g., KLOBBIE has already found, that the values of x of the two coexisting liquid phases reapproach each other, when the temperature is lowered. That is an indication for the existence either of a lower critical point, lying still more down or of a contraction as in fig. 6.

β. In other cases it is only the *lower* critical point, that is observed, as in the case of water and *triethylamine* (ROTHMUND), water and *diethylamine* (GUTHRIE), and of water and *β-collidine* (ROTHMUND).

---

[1]) Many anomalous substances namely can be regarded as normal ones, because the variation of c is so small; only in the case of water this variation is exceptionally great.

According to these observations the first mixture has its critical point (*B*) at nearly 18° C., the third at 6° C.[1]).

In the case of water and *nicotine*[2]) Hudson (Z. f. Ph. Ch. **47**, p. 113) has observed the complete isolated plait. But here a hydrate is formed, being decomposed continually, when the temperature rises. The theory of the phenomenon remains however formally the same: everywhere, where a pretty considerable variaton in the value of *v* presents itself — whatever should be the cause of it — the existence of such a plait may be expected — as soon as the required conditions are satisfied.

Still another example is found in mixtures of *carbonic-acid* and *nitrobenzol* (Büchner), which makes it probable, that CO_2 in *liquid* state is an associative liquid. Indeed, there exist important reasons in the thermal behaviour of that substance which would confirm that supposition.

Aten has observed, that CH_3Cl and *pyridine* mix in every proportion, but that the *combination*, which is soon formed, is nearly unmixable with both components. In this case again there is found a *lower* critical point, for *both* plaits — i. e. for that, formed by CH_3Cl and the combination, and for that, formed by pyridine and the combination.

It is a matter of course that the existence of a *lower* critical point necessarily determines that of an *upper* one. With rise of temperature the *liquid* mixture approaches more and more to a *gaseous* one, where of course miscibility in every proportion takes place. (How the plait can transform itself there, and pass into the transversal plait, lies entirely without the plan of this inquiry).

Inversely we can *not* always conclude from the existence of an upper critical point to that of a lower one, because — even, when the connodal curve begins to contract downward — the case of fig. 6 can occur.

But this is certain, that when an *upper* critical point is found at ordinary temperatures, we have *always* to deal with the point *C*, and not with *A*, the latter always lying (see fig. 2) in the case of mixtures of water and a normal (or anomalous) substance below — 90° C., and in the case of mixtures of two normal substances (compare § 3) at most some thirty degrees below 0° C.

Nearly always there may therefore be expected the case of fig. 4,

---

[1]) Kuenen (Phil. Mag. [6] **6**, p. 637—653 (1903)) could however not confirm the existence of a lower critical point for diethylamine. In an earlier Memoir Kuenen has found also a *lower* critical point for mixtures of C_2H_6 and *ethyl-isopropyl-* and *butyl-alcohol*.

or that of fig. 6, when partial miscibility presents itself. The *normal* plait with the critical point in A will appear only in a great minority of cases, and can be regarded as highly exceptional. So the mixtures of water with *phenol* (**Alexejew**), with *succinitrile* (**Schreinemakers**), with *aniline* (**Alexejew**), with *isobutylic-acid* (id.), etc., etc. — which all present an upper critical point — will offer with great certainty examples of the very general case of fig. 6 or of that of fig. 4.

e. Fig. 5 again represents a transitory case, where the value of K_1 is still a little greater than in fig. 4. The two plaits — the normal one and the isolated one — will coincide from this moment into one *continual* plait.

f. This will be the case in fig. 6. It is observed for mixtures of water and *secondary butyl-alcohol* (**Alexejew**). But, as we already remarked above, many observations with an upper critical point may belong just as well — whether the compositions of the two coexisting phases approach each other at lower temperatures or not — to this case as to that of fig. 4. The example mentioned belongs with certainty to the class of fig. 6, because it is observed, that the values of x after beginning to approach each other diverge again at still lower temperatures.

Fig. 7 shows, that the contraction at D, where the curve $K = f(T)$ comes into the neighbourhood of the line OM, gradually vanishes, so that the plait at last again will assume the *normal* form — only with this difference, however, that the critical point C' of our quasi-normal plait will appear at higher temperatures than the critical point A of the real normal plait.

Remark. It will be superfluous to remark, that the *numerical* calculations by means of the formula (10) can be executed only then, when the conditions are satisfied, on which that expression is deduced. That will accordingly only be the case, when really p is to be omitted against $\frac{a}{v^2}$ (see § 2), that is to say at temperatures, which are not higher than circa half the critical temperature (in the ordinary meaning) of the mixture.

7. The question rises now, what will be the conditions to be satisfied, that the transitory cases of the figs. 3 and 5 may present themselves. Here too we only communicate the results of the calculations, that we have made on this subject. We found namely, that the *isolated* plait (fig. 4) is only possible, when the second (normal) substance has a *critical pressure between* circa 35 *and* 70 *atm.*, and

this nearly independent of the critical temperature of these substances (provided that the latter is between $^1/_2$- and 1-time of that of the water).

All normal [1]) substances, which possess a *critical pressure above* ± 70 *atm.*, mix in every proportion with water; all such substances, having a *critical pressure below* ± 35 *atm.*, will form a *continual plait* (fig. 6).

To the first group of substances belong those with relatively *small molecular volume* (many anorganic substances and salts); to the second group those with relatively *great molecular volume* (many organic substances).

As to the factor $1 + \Delta = 1 + x(1-x)\dfrac{\partial^2 \log p_c}{\partial x}$, the calculations have taught, that this factor at *higher* temperatures, where β comes into the neighbourhood of 1, can become very great, and also will be pretty strongly variable with x. So I found for that factor for $\beta = 1$ ($T = 230^\circ$) the values 2,57, 2,54, 2,25, 1,94 and 1,70, resp. for $x = 0{,}1$, 0,2, 0,3, 0,4 and 0,5. But at such high temperatures the deduced formulae are not longer exact, p being in that case no longer to be neglected against $^a/_{v^2}$.

However, for *lower* temperatures, where β approaches 0, $1 + \Delta$ will not differ much from 1, and will be little dependent on x. At these temperatures — and for *these* temperatures the formulae are deduced — $1 + \Delta$ can, when not neglectable, yet be regarded as a constant factor. So I found for $1 + \Delta$ the values 1,08, 1,10, 1,10, 1,09 and 1,08, resp. for $x = 0{,}1$ unto 0,5.

Finally, I have applied the formula (10) for the case of *triethylamine* and water, and found that, whenever the critical pressure, viz. 30 atm., lies below the above designed limiting pressure of 35 atm., the appearance of a lower critical point at circa 18° C. is not in contradiction with the given theory. It must not be forgotten here, that when the temperature, where β is practically $= 0$, lies above -90° C., the limit in question also will lie below 35 atm.

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[1]) And as we have already seen above, also many *anomalous* substances, where the variability of v is small.

Mathematics. — "*The equations by which the locus of the principal axes of a pencil of quadratic surfaces is determined*" by Mr. CARDINAAL.

1. The communication following here can be regarded as a continuation of the preceding one included in the Proceedings of Nov. 26 1904. It contains the analytical treatment of the problem, of which a geometrical treatment is given there. It ought to have been conducive to the finding of a surface of order nine; this has not been effected on account of the calculations becoming too extensive; however, the form of the final equation has been found.

2. In the first place the equation must be found of the cone of axes of the concentric pencil of quadratic cones, at the same time director cone of the locus of the axes of the pencil of surfaces. To this end we regard the intersection of the two cones, determining the pencil of cones, with the plane at infinity P_∞, and besides the isotropic circle situated in this plane; then we have the three equations in rectangular cartesian coordinates:

$$\begin{aligned}
A &\equiv a_{11}x^2 + a_{22}y^2 + a_{33}z^2 + 2a_{12}xy + 2a_{13}xz + 2a_{23}yz = 0,\\
B &\equiv b_{11}x^2 + b_{22}y^2 + b_{33}z^2 + 2b_{12}xy + 2b_{13}xz + 2b_{23}yz = 0,\\
C &\equiv x^2 + y^2 + z^2 = 0.
\end{aligned}$$

Out of these equations we find that of the cone of axes in the same way as we determine the Jacobian curve of a net of conics:

$$\begin{vmatrix} A_1 & B_1 & C_1 \\ A_2 & B_2 & C_2 \\ A_3 & B_3 & C_3 \end{vmatrix} = 0,$$

where A_1, A_2, A_3, etc. are the derivatives of A with respect to x, y, z.

So the equation of the cone becomes

$$\begin{vmatrix} x & a_{11}x + a_{12}y + a_{13}z & b_{11}x + b_{12}y + b_{13}z \\ y & a_{12}x + a_{22}y + a_{23}z & b_{12}x + b_{22}y + b_{23}z \\ z & a_{13}x + a_{23}y + a_{33}z & b_{13}x + b_{23}y + b_{33}z \end{vmatrix} = 0.$$

Without harming the generality we can always assume that the principal axes of one of the cones coincide with the axes of coordinates; from this ensues that we may put $b_{12} = b_{13} = b_{23} = 0$, by which the equation of the cone is simplified.

3. After having found the equation of this cone we can pass to the formation of the set of equations, by means of which is found the equation of the locus of the axes.

The equation of the pencil of quadratic surfaces now becomes

$$A + \lambda B = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where however A and B have a wider meaning than before, A being

$$a_{11}x^2 + a_{22}y^2 + a_{33}z^2 + 2a_{12}xy + 2a_{13}xz + 2a_{23}yz +$$
$$+ 2a_{14}x + 2a_{24}y + 2a_{34}z + a_{44},$$

and B being the same expression with the coefficients b.

Let us now put the coordinates of the centre of the surface (1) p, q, r and let us regard this centre as origin O' of a new system of coordinates with axes parallel to the original ones. We then arrive for surface (1) at an equation in x', y', z', in which the terms of order one are missing and those of order two possess the same coefficients. The principal axes of this surface are given by the three equations:

$$(a_{11}x' + a_{12}y' + a_{13}z') + \lambda(b_{11}x' + b_{12}y' + b_{13}z') + kx' = 0,$$
$$(a_{12}x' + a_{22}y' + a_{23}z') + \lambda(b_{12}x' + b_{22}y' + b_{23}z') + ky' = 0,$$
$$(a_{13}x' + a_{23}y' + a_{33}z') + \lambda(b_{13}x' + b_{23}y' + b_{33}z') + kz' = 0.$$

As could be foreseen the elimination of λ and k furnishes the same equation as was already found for the cone of axes.

If we wish to form the equation with respect to the original system of axes, we must put $x' = x - p$, $y' = y - q$, $z' = z - r$ and make use of the equations of condition for p, q, r:

$$\left.\begin{array}{l}(a_{11} + \lambda b_{11})p + (a_{12} + \lambda b_{12})q + (a_{13} + \lambda b_{13})r + a_{14} + \lambda b_{14} = 0,\\ (a_{12} + \lambda b_{12})p + (a_{22} + \lambda b_{22})q + (a_{23} + \lambda b_{23})r + a_{24} + \lambda b_{24} = 0,\\ (a_{13} + \lambda b_{13})p + (a_{23} + \lambda b_{23})q + (a_{33} + \lambda b_{33})r + a_{34} + \lambda b_{34} = 0.\end{array}\right\} \quad . \quad (2)$$

By this substitution the equations assume the following form:

$$\left.\begin{array}{l}(a_{11}x + a_{12}y + a_{13}z + a_{14}) + \lambda(b_{11}x + b_{12}y + b_{13}z + b_{14}) + k(x-p) = 0,\\ (a_{12}x + a_{22}y + a_{23}z + a_{24}) + \lambda(b_{12}x + b_{22}y + b_{23}z + b_{24}) + k(y-q) = 0,\\ (a_{13}x + a_{23}y + a_{33}z + a_{34}) + \lambda(b_{13}x + b_{23}y + b_{33}z + b_{34}) + k(z-r) = 0,\end{array}\right\} (3)$$

or written shorter

$$\left.\begin{array}{l}A_1 + B_1\lambda + k(x - p) = 0,\\ A_2 + B_2\lambda + k(y - q) = 0,\\ A_3 + B_3\lambda + k(z - r) = 0.\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The surface S_3 is obtained by eliminating p, q, r, k, λ out of the equations (2) and (4).

4. This elimination leads to extensive calculations as the variables appear also as products two by two. We shall here point out the

general course by which at the same time the application in special cases is rendered possible.

The equations (4) can be written as follows:

$$
\begin{aligned}
kp &= A_1 + B_1 \lambda + kx,\\
kq &= A_2 + B_2 \lambda + ky,\\
kr &= A_3 + B_3 \lambda + kz.
\end{aligned}
$$

Let us multiply each of the equations (2) by k and replace the values kp, kq, kr; we then obtain:

$$
\left.
\begin{aligned}
&(a_{11} + \lambda b_{11})(A_1 + B_1 \lambda + kx) + (a_{12} + \lambda b_{12})(A_2 + B_2 \lambda + ky) +\\
&(a_{13} + \lambda b_{13})(A_3 + B_3 \lambda + kz) + ka_{14} + kb_{14} \lambda = 0,\\
&\text{or:}\\
&(A_1 + B_1 \lambda) k + (a_{11} + b_{11} \lambda)(A_1 + B_1 \lambda) + (a_{12} + b_{12} \lambda)(A_2 + B_2 \lambda) +\\
&(a_{13} + b_{13} \lambda)(A_3 + B_3 \lambda) = 0.\\
&\text{We likewise find:}\\
&(A_2 + B_2 \lambda) k + (a_{12} + b_{12} \lambda)(A_1 + B_1 \lambda) + (a_{22} + b_{22} \lambda)(A_2 + B_2 \lambda) +\\
&(a_{23} + b_{23} \lambda)(A_3 + B_3 \lambda) = 0,\\
&\text{and finally:}\\
&(A_3 + B_3 \lambda) k + (a_{13} + b_{13} \lambda)(A_1 + \lambda B_1) + (a_{23} + b_{23} \lambda)(A_2 + B_2 \lambda) +\\
&(a_{33} + b_{33} \lambda)(A_3 + B_3 \lambda) = 0.
\end{aligned}
\right\} (5)
$$

If we reduce these equations and if we regard k and λ as variables, we shall get as result three quadratic equations, out of which k and λ can be eliminated. As however these equations are linear in k, the elimination of k can take place without any difficulty. By putting the values of k in the first and second equations equal to those in the third and the fourth we deduce from (5):

$$
\left.
\begin{aligned}
&(a_{11} + b_{11} \lambda)(A_1 + B_1 \lambda)(A_2 + B_2 \lambda) + (a_{12} + b_{12} \lambda\ (A_2 + B_2 \lambda)^2 +\\
&(a_{13} + b_{13} \lambda)(A_3 + B_3 \lambda)(A_2 + B_2 \lambda) = (a_{12} + b_{12} \lambda)(A_1 + B_1 \lambda)^2 +\\
&(a_{22} + b_{22} \lambda)(A_2 + B_2 \lambda)(A_1 + B_1 \lambda) + (a_{23} + b_{23} \lambda)(A_3 + B_3 \lambda)(A_1 + B_1 \lambda)\\
&\text{and}\\
&(a_{13} + b_{12} \lambda)(A_1 + B_1 \lambda)(A_3 + B_3 \lambda) + (a_{22} + b_{22} \lambda)(A_2 + B_2 \lambda)(A_3 + B_3 \lambda) +\\
&(a_{23} + b_{23} \lambda)(A_3 + B_3 \lambda)^2 = (a_{13} + b_{13} \lambda)(A_1 + B_1 \lambda)(A_2 + B_2 \lambda) +\\
&(a_{23} + b_{23} \lambda)(A_2 + B_2 \lambda)^2 + (a_{33} + b_{33} \lambda)(A_3 + B_3 \lambda)(A_2 + B_2 \lambda).
\end{aligned}
\right\} (6)
$$

When reduced these equations prove to be of order three in λ; we can write them in an abridged form:

$$\left.\begin{array}{l} M\lambda^3 + N\lambda^2 + P\lambda + Q = 0, \\ M'\lambda^3 + N'\lambda^2 + P'\lambda + Q' = 0, \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which give, according to the method of BEZOUT, the following resultant:

$$\begin{vmatrix} (MN') & (MP') & (MQ') \\ (MP') & (MQ') + (NP') & (NQ') \\ (MQ') & (NQ') & (PQ') \end{vmatrix} = 0. \quad . \quad . \quad (8)$$

5. From this is evident that the form of the final equation is found, but it is a very intricate one, as is proved from the values of the coefficients, given here:

$M = b_{11}\, B_1\, B_2 + b_{12}\, B_2^{\,2} + b_{13}\, B_2\, B_3 - b_{12}\, B_1^{\,2} - b_{22}\, B_1\, B_2 - b_{23}\, B_1\, B_3;$

$N = a_{11}\, B_1\, B_2 + b_{11}\, A_1\, B_2 + b_{11}\, A_2\, B_1 + 2b_{12}\, A_2\, B_2 + a_{12}\, B_2^{\,2} +$
$a_{13}\, B_2\, B_3 + b_{13}\, A_3\, B_2 + b_{13}\, A_2\, B_3 - a_{12}\, B_1^{\,2} - 2b_{12}\, A_1\, B_1 -$
$a_{22}\, B_1\, B_2 - b_{22}\, A_2\, B_1 - b_{22}\, A_1\, B_2 - a_{23}\, B_1\, B_3 - b_{23}\, A_3\, B_1 -$
$b_{23}\, A_1\, B_3\,;$

$P = b_{11}\, A_1\, A_2 + a_{11}\, B_1\, A_2 + a_{11}\, A_1\, B_2 + 2a_{12}\, A_2\, B_2 + b_{12}\, A_2^{\,2} +$
$b_{13}\, A_2\, A_3 + a_{13}\, A_2\, B_3 + a_{13}\, A_3\, B_2 - b_{12}\, A_1^{\,2} - 2a_{12}\, A_1\, B_1 -$
$b_{22}\, A_1\, A_2 - a_{22}\, A_1\, B_2 - a_{22}\, A_2\, B_1 - b_{23}\, A_1\, A_3 - a_{23}\, A_1\, B_3 -$
$a_{23}\, A_3\, B_1\,;$

$Q = a_{11}\, A_1\, A_2 + a_{12}\, A_2^{\,2} + a_{13}\, A_2\, A_3 - a_{12}\, A_1^{\,2} - a_{22}\, A_1\, A_2 - a_{23}\, A_1\, A_3.$

$M' = b_{12}\, B_1\, B_3 + b_{22}\, B_2\, B_3 + b_{23}\, B_3^{\,2} - b_{13}\, B_1\, B_2 - b_{23}\, B_2^{\,2} - b_{33}\, B_2\, B_3\,;$

$N' = a_{12}\, B_1\, B_3 + b_{12}\, A_1\, B_3 + b_{12}\, A_3\, B_1 + a_{22}\, B_2\, B_3 + b_{22}\, A_2\, B_3 +$
$b_{22}\, A_3\, B_2 + a_{23}\, B_3^{\,2} + 2b_{23}\, A_3\, B_3 - a_{13}\, B_1\, B_2 - b_{13}\, A_1\, B_2 -$
$b_{13}\, A_2\, B_1 - a_{23}\, B_2^{\,2} - 2b_{23}\, A_2\, B_2 - a_{33}\, B_2\, B_3 - b_{33}\, A_3\, B_2 -$
$b_{33}\, A_2\, B_3\,;$

$P' = b_{12}\, A_1\, A_3 + a_{12}\, A_3\, B_1 + a_{12}\, A_1\, B_3 + b_{22}\, A_2\, A_3 + a_{22}\, A_3\, B_2 +$
$a_{22}\, A_2\, B_3 + 2a_{23}\, A_3\, B_3 + b_{23}\, A_3^{\,2} - b_{13}\, A_1\, A_2 - a_{13}\, A_1\, B_2 -$
$a_{13}\, B_1\, A_2 - 2a_{23}\, A_2\, B_2 - b_{23}\, A_2^{\,2} - b_{33}\, A_2\, A_3 - a_{33}\, A_2\, B_3 -$
$a_{33}\, A_3\, B_2\,;$

$Q' = a_{12}\, A_1\, A_3 + a_{22}\, A_2\, A_3 + a_{23}\, A_3^{\,2} - a_{13}\, A_1\, A_2 - a_{23}\, A_2^{\,2} - a_{33}\, A_2\, A_3.$

6. With the aid of these expressions the equation of the locus of the axes can be determined for each separate case, which was the purpose of this paper; we shall conclude by giving a few observations.

a. Even in the general case abridgement is possible in the operation. If we assume that the axes of coordinates coincide with the principal axes of one of the surfaces, e. g. of $B = 0$, then $b_{12} = 0$, $b_{13} = 0$,

$b_{12} = 0$, $b_{14} = 0$, $b_{24} = 0$, $b_{34} = 0$, whilst also B_1, B_2, B_3 assume simple forms and all coefficients except Q and Q', are simplified.

At the same time this substitution shows that in equation (8) a factor may be omitted: if namely we make use of the above named values for b_{ik}, we shall find:

$$M = (b_{11} - b_{22})\, B_1\, B_2 \qquad M' = (b_{22} - b_{33})\, B_2\, B_3\,;$$

from this ensues that the first column of the determinant (8) is divisible by B_2. This divisibility is connected with the fact that the equation of the locus of the axes must become of order nine, whilst when developed the determinant (8) becomes of order twelve. So when a complete operation is executed factors must disappear out of (8).

b. Out of the former geometric treatment it is evident, that in some cases the locus of the axes S_9 breaks up. As one of the special cases appearing there the case of a circular base curve of the pencil was treated where S_9 broke up into a cubic surface and into a surface of order six. The equations of the algebraic treatment of this case become, when one chooses the plane XOY as the plane that is intersected according to a pencil of circles:

$$A \equiv a_{11}\, x^2 + a_{11}\, y^2 + 2a_{13}\, xz + 2a_{23}\, yz + 2a_{34}\, z + a_{44} = 0\,,$$
$$B \equiv b_{33}\, z^2 + 2b_{13}\, xz + 2b_{23}\, yz + 2b_{14}\, x + 2b_{34}\, z = 0.$$

From these equations the simplified values for M, N .... can be deduced.

(February 23, 1905).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday February 25, 1905.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 25 Februari 1905, Dl. XIII).

CONTENTS.

The following papers were read:

Physiology. — *"On the osmotic pressure of the blood and urine of fishes."* By Dr. M. C. Dekhuyzen at Utrecht. (Communicated by Prof. C. A. Pekelharing.)

(Communicated in the meeting of November 26, 1904).

Migratory fishes (eel, salmon, shad) move in a relatively short time from sea-water, having an osmotic pressure of about 24 atmospheres, into fresh water, in which this pressure is $^1/_4$ of an atmosphere or less, without experiencing any harm. And this same transition also takes place in the opposite direction. It is very mysterious how such an emancipation from the laws of osmotic pressure is possible. It is known in general outlines that bony fishes, as well in salt as in fresh water, keep up an osmotic pressure in their blood which is relatively independent of that of the surrounding medium. But it is unknown between what limits the organism regulates the percentage of salt (for this is the principal factor) in the different fluids of the body, or by what means it keeps up this percentage. It is certain that bony fishes are in general *stenohaline*, i.e. that each species is bound to an osmotic pressure of the water in which it lives, and which must not vary too much and especially not too quickly. A behaviour like that of the migratory fishes is exceptional. The Baltic Sea which contains about all gradations between salt and fresh water and the fauna of which has often been studied, furnishes a proof of the statements made. Of every species of fish, found in the Baltic Sea, I have traced the range of distribution, and the lists, for the publication of which we have no room here, show that most fresh water fish go some length into the brackish water and most sea-fish sustain a certain diminution of the percentage of salt, but that certain limits are not exceeded.

If we want to penetrate into the mechanism of these physiological phenomena it is of primary necessity, to know the osmotic pressure of the blood of the various species of fish. Some determinations were made by BOTTAZZI and RODIER. About five years ago I began to take part in these measurements under very unfavourable circumstances with sea-fish that had been transported alive from Katwyk to Leyden. These animals were mostly alive, in any case entirely fresh. The results were not published until in the summer of 1904 they appeared to be quite concordant (and sometimes fully to agree) with results that had been obtained under more favourable conditions.

The excellent opportunity of obtaining live sea-fish in great variety, afforded by the fishmarket at Bergen in Norway, induced me last summer to take up the investigation again and to extend it. After that determinations were made on fresh-water fish from the environs of Utrecht and finally I was enabled through the kindness of Dr. KERBERT, director of the zoological garden and aquarium at Amsterdam, to study sea and freshwater fish, among these species that are difficult to procure. I wish to express here my indebtedness to Dr. KERBERT.

At Bergen the fish are offered for sale alive in a large number of open wooden troughs through which a vigorous current of sea-water is passed, which, as I was assured, is pumped up from the fjord at a great distance from the town. The fish are *not* entirely normal, however; the catching, the lack of food, the transport, their being handled by sellers and buyers, all harm the animals. Before they come into the market tanks, namely, they swim in caufs, closely packed together in the surface water of the harbour, which sometimes is considerably diluted by the rains. There are reasons for assuming that these influences make themselves felt in the osmotic pressure of the blood. An investigator who should stay for a long time at Bergen, choose his material carefully, keep it for some time in aquaria and note for each specimen everything that could have any influence, would without doubt obtain more constant results than can be published here. Still it would be more recommendable to accompany the fishermen and to collect blood and urine immediately after the catching. The figures here given must be judged as one of the first attempts in this almost unexplored region. Only during and by my investigation I have become aware of the necessity of taking the condition of health of the animals very much into account.

The specimens bought were conveyed to the biological station either in pails of seawater or without this precaution, a distance of twenty minutes. and placed there again in aquaria in which seawater circulated containing about 32 °/₀₀ salt, corresponding to a freezing point of — 1.731° to — 1.742°. The fishes that showed signs of debility were examined first, the others remained for some hours and even for two or three days in a spacious aquarium without special food. Many specimens proved to have still filled stomachs and to lodge few parasites, others were in a less satisfactory condition, but all these details were not recorded. The quantity of blood furnished by each fish is relatively small and varies as well with different species as with different individuals. As a rule, for a determination of the freezing point the blood of several specimens is required, since ten to fourteen cubic centimetres must be put into the freezing tube. The fishes were washed in tapwater, well wiped and their tails cut off with a pair of bone-scissors. Sometimes it appeared to be necessary to make an incision in the heart; in this case the gills were once more cleaned from seawater with a dry towel.

Would it not be better to use serum? This does not appear to be necessary to me, since the same sample of blood generally gives the same freezing point in repeated measurements and later a serum separates which as a rule is not coloured red, even with Raja clavata and Trygon pastinaca which are supercooled to — 2.7°. Also Hedin and Hamburger [1]) have found that it is not necessary to separate the serum.

In order to diminish the quantity of blood necessary for a determination, which is desirable especially with small or rare species, I

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[1]) Hamburger, Osmotischer Druck und Ionenlehre in den medicinischen Wissenschaften. Wiesbaden 1902. I. p. 453.

have tried whether it is admissible to add some soft organs, spleen or liver to the blood. With the blood of three specimens of a freshwater fish from Surinam, *Erythrinus unitaeniatus*, Spix, the same freezing point was found twice with the bulb of the thermometer not quite immersed, — 0.577°; then the livers of two specimens were added and — 0.60° was found. So improvement must not be sought in this direction [1]. With the rabbit still more considerable differences were obtained, probably on account of the conversion of glycogen into glycose.

The determinations were made with an in many respects modified Beckmann apparatus, of which the description will be given later. Here it may suffice to remark that if a supercooling of 0.5° is used as well for the determination of the zero point as of the freezing point, the figures obtained for pure salt solutions are very accurate. For 1 $^0/_0$ NaCl (1 gram NaCl dissolved in 100 grams of water, the weights reduced to a vacuum) the apparatus gives — 0°.589, the result of the "Präzisionskryoskopie" (Hamburger l. c. pag. 96). Beckmann's correction for increase of concentration with supercooling was always applied, amounting for 0°.5 to $\frac{1}{160}$ or $\frac{1}{80 \div 0.5}$ (80 calories being the latent heat of melting ice). The temperature of the cooling bath was — 2°.5, when necessary it was lowered to — 2°.9 by strong stirring.

We will first deal with the results obtained with freshwater animals. Let Δ be the freezing point in degrees centigrade, omitting the — sign.

Freshwater bony fishes.

	Δ	
Perch, Perca fluviatilis L.	0.507 0.509	2 and 5 specimens from Utrecht.

Remark. The perch occurs in the whole Baltic sea as far as the Sound, i.e. in water containing to 12 $^0/_{00}$ salt and with Δ = 0.64.

Carp, Cyprinus carpio L.	0.527 0.540	1 spec. from Bergen. 1 „ „ the Amsterdam Aquarium, lived in water of Δ = 0,039.

Remark. The carp seldom penetrates into the Baltic sea, oftener into the Asow and Caspian seas.

Tench, Tinca vulgaris Cuv.	0.466 0.514	1 resp. 3 spec. from Utrecht, caught healthy in October and kept some time in the caufs.

Remark. The tench goes from the Haffs and bays as far as Gothland, where Δ is about 0.42.

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[1] By reducing the size of the freezing tube and by using a smaller Beckmann's thermometer of an old pattern, the quantity required can be reduced to 5 or 6 cc. By means of salt-solutions it will be controlled how far the results need correction.

Pike, Esox lucius L.	0.519 0.526 0.530	Resp. 4, 5 and 3 freshly caught spec. from Utrecht, Sept. and Oct., some of them examined in a half dead condition.

REMARK. The pike in the S.E. part of the Baltic Sea leaves the coast to fairly great distances and is occasionally caught near Bohuslän, where Δ is at least 0.69. Goes even some distance into the Arctic sea [1].

Rudd, Leuciscus erythrophthalmus L.	0.495	18 fine spec. from the Amsterdam Aquarium, Nov. occurs in all brackish bays of the Baltic Sea.
Bleak, Abramis blicca, Bloch.	0.497	12 fine spec. Aq. Amst. Nov.

REMARK. In the Baltic sea the bleak occurs in the brackish bays.

Trout, Salmo fario L.	0.567	1 fine spec. Aq. A'dam. Nov.

REMARK. The trout is a freshwater fish which seldom occurs in the brackish haffs, but belongs to the Salmonidae, a family of migratory fishes, fishes of the sea-coast and freshwater. NÜSSLIN looks upon them as original seafish.

Waranga, Erythrinus unitaeniatus Spix.	0.577	3 fine spec. Aq. A'dam. Nov.

REMARK. Surinamian freshwater fish, living in water of 20° C. By evaporation during the collection of the blood the number is probably slightly too high. Also the quantity of blood available (8 cc.) was somewhat too small. They belong to the Characinidae, old genuine inhabitants of freshwater (Ostariophysi).

Average of 13 observations on freshwater bony fishes 0°.521. Excluding the trout and waranga, the first as being a Salmonida, the other because the observation is less reliable than the others and because we have here a fish of which the somatic temperature is higher than that of the others, we obtain an average value of 0°.512, round which the 11 observations are pretty regularly grouped.

To these I can add still six measurements on other cold-blooded freshwater vertebrates:

Lamprey, Petromyzon fluviatilis L.	0.473 0.500	Observations at Leyden, on six, resp. five specimens in tolerably good condition, made in 1899.
Frog, Rana esculenta L.	0.464 0.465	id. $\frac{8}{11}$ fine spec, caught in the autumn.
Salamandra maculosa. Laur.	0.479	37 spec., Sept. 1904, animals sent from Berlin, kept a day in a terrarium with a dish of water.
Fr.water turtle, Emys europaea. Gray.	0.474	Observation of BOTTAZZI 1897, quoted from R. QUINTON [2].

Average of these: 0°.476 and of the above mentioned eleven together with these six: 0°.499.

The freezing point of freshwater is about 0°.02. BOTTAZZI's Emys lived in water of this freezing point. In the tanks of the Amsterdam

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[1] PALACKY, Die Verbreitung d. Fische. Prag. 2e Aufl. 1895. p. 54.

[2] R. QUINTON. L'eau de la Mer, milieu organique. Paris 1904, p. 441.

aquarium a somewhat brackish water circulates of $\Delta = 0.039$ (originally water from the river Vecht). The percentage of salt of the lake of Geneva is given in Carl Vogt's *Lehrbuch der Geologie* I. p. 53 as $0.1574^0/_0$ which would point to a freezing point of only $0^\circ.01$. According to the figures collected by Dubois (see *Verslagen* 1900 p. 12 and 30) Δ in Lakes Wener and Wetter is still lower.

The osmotic pressure in atmospheres at 0° which we shall henceforth denote by P_0, is obtained by multiplying Δ by the factor 12.08 according to Stenius [1]) or 12.03 according to Jorissen [2]) and hence is in freshwater of the order of $^1/_4$ to $^1/_8$ atmosphere. In such a medium the cold-blooded vertebrate animals, breathing mostly through gills, *maintain in their blood an osmotic pressure of six atmospheres!* With birds and mammals (see the table of Hamburger, l. c. I. p. 456) also a pretty constant freezing point of the blood has been found. I have proposed to call the power of keeping P_0 at a certain level, albeit within certain limits "*ideotony*" [3]), a property comparable with the homoiothermic power. That also the freshwater bony fishes possess this ideotony can hardly be doubted from the results communicated. The limits between which the figures of the same species lie, are narrow, only in the tench the differences are fairly considerable. The ideotony is most conspicuous when the agreement between the cold-blooded freshwater vertebrates among each other and the great difference with P_0 of the surrounding medium are remembered. One is led to the supposition that for these animals which indeed are not closely related: Cyclostomes, Teleosteans, Amphibians and a reptile, the P_0 of about 6 atmospheres is an *optimum*. For warm-blooded animals there seems to be a tendency to maintain P_0 at $6^3/_4$ to $7^1/_4$ atmospheres; Δ's of 0.570 with man and of 0.6 to 0.625 with mammals and birds are namely kept up with great constancy.

The kidneys are the regulators. For the Δ of the urine of man varies between 0.12 and 3 (Hamburger l. c. II. p. 317) when the separately discharged portions are examined, whereas Δ for the whole quantity of 24 hours varies from about 1.3 to 2.4. For normal man Schoute [4]) found that Δ of the blood, provided digestion were eli-

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[1]) Stenius. Öfversigt af Finska Vetenskaps-Societetens Förhandlingar 46. No 6. 1903—4.

[2]) W. P. Jorissen. Physisch-chemisch onderzoek van zeewater. Chem. Weekbl. 1e jaarg. No 49, p. 731. Sept. 1904.

[3]) M. C. Dekhuyzen. Ergebnisse von osmotischen Studien, namentlich bei Knochenfischen, an der Biol. Stat. d. Berg. Museums. Bergens Museums Aarbog. 1904. No 8.

[4]) D. Schoute. Het physisch-chemisch onderzoek van menschelijk bloed in de kliniek. Diss. Groningen. 1903.

minated, by taking the blood in the morning before breakfast, only varies between 0.56 and 0.58.

We can only to a limited extent imagine why the percentage of salt (for this is the chief point) of blood and lymph may only vary between narrow limits. The globulines require a certain concentration of "medium salts" in order to remain in solution. If horse serum is diluted with $1^1/_2$ volume of distilled water, a precipitate is already formed, i. e. with a percentage of salt corresponding to $\angle = 0.24$. Why an increased percentage of salt should be injurious is less clear. Danger for precipitation of albumens would only occur with much higher concentrations, at any rate with horse serum. Yet the fact, found by RODIER[1]) that the blood and the somatic fluids (pericardial and peritoneal) of rays and sharks are isotonic with seawater but contain less salt, the deficiency being compensated by the retention of 2 to 2.7 $^0/_0$ of urea, points to a strong need of the organism of the Vertebrates to keep the percentage of salt below a certain value. GRIJNS[2]) has found that blood-cells are permeable for urea so that this substance helps to bear the osmotic pressure against the seawater but discharges the cells of a third of 23 to 24 atmospheres. I have proposed l. c. to call this power of being isotonic with respect to seawater but of taking away from the cells themselves part of the osmotic pressure "*metisotony*".

The blood of Teleosteans has a freezing point which differs considerably from that of the seawater, in which they live. They possess ideotony but the individual differences are greater than have been remarked with the remaining vertebrates, so that it appears that they only imperfectly possess the faculty of rendering their P_0 independent of the surrounding medium. Before the figures are given, a summary of Δ and P_0 of different seawaters may be inserted. The numbers have been taken from M. KNUDSEN's Hydrographische Tabellen, from PETTERSON's Review of Swedish hydrographical research in the Baltic and North seas and from MOEBIUS und HEINCKE, Die Fische der Ostsee[3]).

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[1]) RODIER. Sur la pression osmotique du sang et des liquides internes des poissons sélaciens. Comptes rendus. Dec. 1900. p. 1008.

[2]) G. GRIJNS. Ueb. d. Einfluss gelöster Stoffe auf die rothen Blutzellen. Pflüger's Archiv. 63. 1896. p. 86.

[3]) M. KNUDSEN. Hydrogr. Tab. Kopenhagen 1901, PETTERSSON in Scottish geographical Magazine 1894. X.; MOEBIUS u. HEINCKE. Fische d. Ostsee. Berlin 1883.

Salt $^0/_{00}$. (grams of seasalts in 1000 gr. seawater).	Absolute spec. gr. at 0° (compared with aq. dest. of 4°).	Δ	P_0 in atmospheres.	
6	1.00478	0.318	3.8	Gulf of Bothnia in summer.
7	1.00559	0.371	4.45	Surface water (till 60 M.) of the Baltic sea proper between Rügen and Gothland in summer. With 7.5$^0/_{00}$ salt, M. and H. assume the limit between brackish and salt water.
8	1.00640	0.424	5.09	
9	1.00721	0.478	5.74	
10	1.00802	0.531	6.37	Water of the shallow part of the Baltic sea south of the Danish isles in summer.
12	1.00963	0·639	7.67	
20	1.01607	1.074	12.89	The same in winter (Moebius and Heincke).
32	1.02571	1.739	20.9	Seawater in the fjord before Bergen, 8 M. below the surface in summer.
35	1.02813	1.908	22.9	Northern Atlantic.
38	1.03055	2.078	24.9	Δ Seawater, Gulf of Naples, in Nov. 1903, 2.105. Δ Seawater as it circulates in the tanks of the Amsterdam aquarium 2.085.

Bony fishes living in the sea.

		Δ	
Gadus morrhua L.	Cod,	0.644	2 apparently normal spec. Aq. Amsterdam, Nov. 1904.
„ „	„	0.673	1 spec. bought on Monday at Bergen, remnant of the fish supply of the end of the preceding week.
„ „	„	0.708	8 spec. from Katw. immediately conveyed to Leyden.
„ „	„	0.721	8 spec. id.
„ „	„	0.724	„ „ „
„ „	„	0.729	13 „ „ (April 4 1900, an ample quantity of blood had been taken from 13 fine spec.).
„ „	„	0.729	Bergen 1904, summer, 3 large spec.
„ „	„	0.742	Leyden, as above.
„ „	„	0.744	Bergen, „ „ 2 spec.
„ „	„	0.753	„ „ „ 3 „
„ „	„	0.808	Leyden „ „ 6 „
„ „	„	0.811	„ „ „ 8 „

Remark. The cod penetrates very far into the Baltic Sea. We do not mean to assert that individuals caught in the Bothnian gulf and not larger than 45—50 centimetres have swum in from the Atlantic. They may very well belong to local races, propagating in the brackish water and which do not reach a greater length. Near Stockholm the cod only reaches a length of 60 centimetres, in the Sound 80 to 90 cm. at the utmost, on the coast of Bohuslän 90 cm., but near the Lofoden Islands even 140 to 150 cm. Also the common mussel is much smaller in the brackish water of the eastern parts of the Baltic sea than in the more salt containing sea.

In the Gulf of Bothnia the percentage is in summer north of the Quarks $3-4^0/_{00}$, Δ 0.159 to 0.212, P_0 1.9 to 2.54 atm., north of Stockholm resp. $5^0/_{00}$, 0°.265, 3.18 atm., at Stockholm $6^0/_{00}$, 0°.318, 4 atm., on the north coast of Gothland $7^0/_{00}$, 0°.37, 4.45 atm., and till Rügen—Schonen 7 to $8^0/_{00}$, 0°.424, 5 atm. At Bohuslän the salinity of the surface is in summer $13^0/_{00}$, $\Delta = 0°.69$, but in the depth North sea water occurs of 32 to $33^0/_{00}$ and 1.8°.

Δ

Gadus aeglefinus L. Haddock. 0.767 Leyden, summer, spec. were dead but fresh.

Remark. The haddock does not penetrate further than the Mecklenburg coast.

		Δ		
Gadus virens L.,	Coalfish, Green Cod	0.760	Bergen.	
„	„	0.761	„	3 spec.
„	„	0.837	„	3 „
„	„	0.838	„	

Remark. Gadus virens does not penetrate further than the bay of Kiel and is rare there. In the fishmarket at Bergen it is always supplied in large quantities but generally in a bad condition, showing wounds and traces of having bled, many specimens lie on their backs at the surface and breathe little. When a purchase was made good specimens were selected, but I think it very probable that the animals whose blood froze at — 0°.837 and — 0°.838 were abnormal.

Δ

Gadus merlangus, L. Whiting 0.760 Bergen. 14 spec.

Remark. The whiting enters the Baltic Sea with difficulty, about as far as Bornholm. Only once it has been caught near Gothland.

Δ

Molva vulgaris, Flemm. Ling, 0.716 Bergen. 3 fine spec.

Remark. The ling no more than G. virens penetrates into the Baltic Sea.

Δ

Molva byrkelange (Walb.), Trade Ling, 0.730 Bergen, 4 fine spec. were dead but fresh.

Remark. Deep sea fish, not to be had alive. Had been caught at a depth of 400 metres. Does not come further than the Cattegat.

Δ

Motella tricirrata (Bloch), Whistler, 0,605 Bergen.

Remark. Motella tricirrata has only once been caught near Göteborg

Hippoglossus vulgaris, Flemm., Halibut, $\overset{\Delta}{0{,}671}$ Bergen. The specimen suffered from a disease of the skin, had lived long in the aquarium and threatened to die.

REMARK. The halibut does not wander into the Baltic sea further than Mecklenburg,

Pleuronectes platessa L., Plaice. $\overset{\Delta}{0.672}$ Bergen.
„ „ 0.675 Leyden.

REMARK. The plaice goes as far as Stockholm. The Pleuronectides everywhere show a tendency of penetrating into brackish or even fresh water. The flounder has been found in the Moselle near Metz. WICHMANN found species of flounder in small mountain lakes of New Guinea.

Pleuronectes microcephalus Donovan, Lemon Dab $\overset{\Delta}{0.681}$ Bergen.

REMARK. P. microcephalus very rarely comes as far as Eckernförde.

Labrus bergylta Ascan., Ballan Wrasse $\overset{\Delta}{0.694}$ Bergen. 3 spec.
„ „ 0.704 „ 6 „ of which one very ill, liver and intestine full of nematodes.
„ „ 0.708 „

REMARK. This Labrus is only seldom found in the western part of the Baltic sea, where the freezing point is in summer about —0°.6, —1° in winter.

Labrus mixtus L. Blue lipfish, Striped Wrasse $\overset{\Delta}{0.681}$ Bergen. 4 spec. } all ♀
„ „ 0.714 „ 5 „

REMARK. L. mixtus (♂ red, ♀ blue) seldom comes as far as the Sound.

Conger vulgaris Cuv. Conger-eel. $\overset{\Delta}{0.696}$ 3 spec. Aquar. Amsterdam.
„ „ 0.786 1 „ Bergen.

REMARK. Only seldom caught in the Baltic sea, repeatedly in the lower course of the Weser.

Salmo trutta L. Sea or Bull trout. $\overset{\Delta}{0.785}$ 6 spec. Bergen, caught with the rod in the fjord, in bad condition and partly dead.

REMARK. The Sea trout is an anadromous migratory fish.

Labrax lupus Cuv. Bass, $\overset{\Delta}{0.720}$ 1 spec. Aquar. Amsterdam.

REMARK. Rare in the western part of the Baltic sea.

Trigla hirundo Bloch. The gurnard, $\overset{\Delta}{0.669}$ 2 spec. Aquar. Amsterdam

REMARK. Not often occurring in the western part of the Baltic sea.

	Δ			
Anarrhichas lupus L., Sea-wolf,	0.665	2 spec.	Bergen.	The fishermen use to beat out the teeth of these somewhat dangerous animals; in any case the sea-wolves arrive at the market alive but not in a normal condition. They react slowly and die when they are too much handled.
„ „	0.681	1 „	„	
„ „	0.769	3 „	„	

Remark. The sea-wolf penetrates at the utmost as far as the coast of Pomerania.

The average of these 38 observations is $\Delta = 0^\circ.7245$ or $P_0 = 8.7$ atmospheres. The figures are grouped pretty regularly round this: 13 between 0.600 and 0.700, 13 between 0.700 and 0.750, 12 between 0.750 and 0.850. The average lies fairly well at the same distance from the two extreme values. By omitting the extreme values 0.605 for Motella, 0.808, 0.811, 837 and 0.838 for codfish and G. virens, which latter pretty certainly are based on pathological deviations, the average is only little shifted and becomes 0°.716.

The differences between the extreme values and the average are relatively large, 0.120 and 0.113, about $^1/_6$ of the probable normal value. If the 5 extreme figures are rejected, the deviations from the new average, 0.716, are only 0.072 and 0.070. We found a similar result with the freshwater fishes; only after rejecting the values for waranga and trout we obtained an average of 0.499, differing only 0.041 and 0.035 from the extremes.

If we bear in mind that these fishes live in a medium of which the osmotic pressure is 21 to 23 atmospheres or even more, no one will object to ascribing *ideotony* to these animals. But the considerable oscillations in P_0, which we noticed e. g. in the cod, give the impression that the power of maintaining P_0 at a certain level, is limited. And one is involuntarily reminded of the oscillations in somatic temperature which homoiothermic organisms show with many disturbances in the general well-being.

There exist in literature still a few data concerning the freezing point of the blood of bony fishes living in the sea. Bottazzi [1]) found with *Charax Puntazzo* Gm. — 1°.04 and — 1°.035, with *Serranus gigas* L. — 1°.035 and — 1°.034, but these figures do not deserve

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[1]) F. Bottazzi. La pression osmotique du sang des animaux marins. Arch. ital. de biologie 28, p. 67, 1897.

too much confidence as he was wont to use a cooling bath of —12° [1]). Neither could he apply the later published correction of BECKMANN. With *Chelone imbricata* L. (sea-turtle) he found —0°.61 and —0°.62.

RODIER [2]) found in a Ganoid *(sturgeon?)* Δ = 0°.76, in *Lophius piscatorius* L. 0°.68 and 0°.80, in *Orthagoriscus mola* L. 0°.80, in the sea-turtle *Thalassochelys corticata* Rondelet 0°.602 and in a mammal, living in the sea, the grampus *Phocaena communis* Less 0°.74.

The numbers obtained for the blood of the eel *Anguilla vulgaris* Flemm. are very remarkable. With vigorous specimens I found formerly at Leyden — 0.773°, at Bergen — 0.653°, at Utrecht — 0.587°. Now the eel belongs to a family of tropical sea-fish; most species occur in the Dutch Indian Archipelago, they often go into brackish water, others are deep-sea animals. Our common eel excellently bears quick variations of the percentage of salt. Born in the sea, it enters the river mouths as a young animal and remains in fresh water until the time of propagation approaches. The eel which is caught in the fresh or somewhat brackish waters of Frisia, is put at Workum into caufs into which the seawater has free entrance, goes to London and is sold on the Thames from these caufs. The layer of slime, with which their skin is covered facilitates this transition. PAUL BERT [3]) noticed that all the eels which he put from the fresh water into the seawater himself, supported the sudden change, whereas those which his assistant handled, all died. He used a little net, whereas the assistant took them with his hand, held them in a rough towel and in this way removed the layer of slime.

The eel shows in its osmotic pressure sometimes the type of a seafish, sometimes it approaches that of a freshwater fish. The high P_0 with the trout, as an original migratory fish, now also becomes to some extent explainable.

Here a field of study lies open which may be urgently commended to the *Committee for the international investigation of the sea.*

How do the marine bony fishes maintain in their blood a so much lower osmotic pressure than exists in the seawater? Some observations on the urine of the cod, sea-wolf and G. virens can perhaps throw some light on this question. The Δ of the urine was always lower, the osmotic pressure less than that of the blood.

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[1]) G. FANO et F. BOTTAZZI, Sur la pression osmotique du serum en différentes conditions de l'organisme. Arch. ital. de biol. 26, p. 46, 1896. See especially p. 47.

[2]) HAMBURGER l. c. I. p. 466. The original article of RODIER in Travaux des laboratoires d. l. soc. sc. et station zoolog. d'Arcachon. 1899. p. 103, I have not at my disposal.

[3]) P. REGNARD, La vie dans les eaux. p. 438. Paris. 1891.

With a large specimen of the sea-wolf, whose blood had given Δ 0.681°, the urine gave 0.631°. With other individuals I found 0.555°. The urine taken from some twenty specimens of G. virens gave Δ 0.630°. With the cod 0.652 and 0.619 have been stated.

It is very simple to take the urine. A sea-wolf, e.g. is taken behind the gills and suddenly lifted from the seawater, the skin of the belly is dried, while the assistant stands ready for collecting the urine which often is ejected in a vigorous jet. By some pressure on the belly a little more is obtained, but often the "bladder" (the extended part of the ureters) is empty. Most animals gave little or nothing and were given back to the seller so that a comparison of Δ of the blood and urine was only possible in exceptional cases. At Bergen I had for the three species that were studied, found not a single figure for Δ that was lower for the blood than for the urine. At Amsterdam, however, it has appeared that there also occur specimens, the blood of which shows a still somewhat smaller osmotic pressure than any of the urines (cod).

The remarkably low P_0 of the secreted product of the kidneys with marine Teleosteans certainly points to this: that these animals do not keep the osmotic pressure in their blood 23—8.6=14.4 atmospheres lower because the kidneys so quickly eliminate the surplus of salts taken in. The relative richness in water of the urine rather points to these fishes *resorbing* from the sea-water in opposition to the osmotic pressure, hence by using chemical energy, water or if one prefers, a diluted solution of salt. But REGNARD has stated (l.c. p. 391) that certain freshwater fishes secrete from their gills soluble carbonates! About the mechanism of ideotony we are still in the dark.

Physiology. — "*On the relative sensitiveness of the human ear for tones of different pitch, measured by means of organ pipes.*"

By Prof. H. ZWAARDEMAKER Cz.

(Communicated in the meeting of January 28, 1905.)

Almost simultaneously, but by different methods, the relative sensitiveness of the human ear as depending on pitch, was investigated by MAX WIEN [1]) and by F. H. QUIX and myself [2]). The result of

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[1]) MAX WIEN. Physik. Ztschr. IV p. 69. Pflüger's Archiv Bd. 97. p. 1. 1903.

[2]) ZWAARDEMAKER and QUIX. Ned. Tijdschr. v. Geneesk. 1901 II p. 1374: 1902 II p. 417. and Engelmann's Archiv. 1902 suppl. p. 367.

these parallel investigations were concordant in some respects, different in others. They agree in this that:

1st. there is only one maximum of sensitiveness;

2nd. that this maximum lies at g^4;

3rd. that the zone of fair sensitiveness extends from c^1 to g^5.

4th. that outside this region toward the limits of the scale the sensitiveness diminishes very strongly.

They differ in this that:

1st. with MAX WIEN the sensitiveness still diverges very much within the zone of fair sensitiveness, whereas with us it is of the same order.

2nd. that the perceptible minimum for the most sensitive point is with him 100.000.000 times smaller than with us.

In this state of affairs it seemed desirable once more to determine the perceptible minima throughout the whole scale by an entirely different method. Telephone as well as tuning-forks ought thereby to be avoided. So we had recourse to wide roofed organ pipes of which a wooden set of uniform pattern, extending from C to g^4 was at our disposal which partly coincided with the well-known EDELMANN whistles and could be continued by the Galton whistle.

Some series of such experiments were made, partly on the heath at Milligen, partly in the gallery of the university library at Utrecht, partly in the sound-tight room of the physiological-laboratory. Since the results, generally speaking, agree fairly well and a full account of them will be published later, for the present only two series taken under the simplest conditions, will be dealt with. These are: *a*, the concluding series on the heath, *b*, in the gallery. The arrangement, which was the same for both, will first be described.

The organ pipe which serves as the source of sound, is mounted vertically on a stand, near the floor, with as little contact as possible. It is connected with a HUTCHINSON spirometer. Close under the air-room of the organ pipe and connected with this latter by a wide opening, is a ligroine manometer. The manometer being bent into an obtuse angle as little as $^1/_4$ mm. of waterpressure can be read. The spirometer is now loaded with a little box containing sand, so that it forces out the air very regularly and causes the organ pipe to emit a soft sound without an audible frictional noise and without partial tones. The air used is read off on the scale of the spirometer and calculated per second by at the same time starting a timing watch. The product of the volume of air, pressure and acceleration of gravity (all in cm.) then give the energy supplied per second in ergs.

What part of this energy is converted into sound is unknown. WEBSTER [1]) values the "efficiency" at 0,0013 to 0,0038; RAYLEIGH [2]) on the other hand supposed in 1877 as a preliminary estimate, that all was converted into sound ("supposing the whole energy of the escaping air converted into sound and no dissipation on the way"). The truth will probably lie between these two, since we have always paid attention to clear and easy sounding. For such a case MAX WIEN remarked in 1888: A loss of energy certainly takes place, first on account of the fact that part of the air-current is not converted into sound-waves at all, but is lost by the formation of vortices, partly inside, partly outside the pipe. We shall see later that this part is small only for a definite position of the lip of the pipe and for a definite pressure. A second loss of energy takes place by friction on the walls of the pipe and by tremors imparted to them; a third on the way between source and observer by friction on the floor, motion of the air (wind) and viscosity of the air. This latter part especially is relatively large with RAYLEIGH, since by viscosity a loss of energy of ± 22°/₀ took place [3]).

If 22°/₀ is considered relatively much, we may assume that MAX WIEN at that time supposed for the losses by other causes a similar or smaller amount. But whatever the "efficiency" of the supplied energy may have been, there is no reason for assuming that it has been appreciably different for the different pipes. The wooden pipes at any rate belonged to the same set of uniform pattern. So the method suffices for comparative measurements.

While one observer read the scales of spirometer and manometer, the other moved to the greatest distance at which the tone was just heard and recognised ("Erkennungsschwelle"). This distance was then later taken as the radius of a hemisphere through which the energy of the sound spread.

A. *Experiments on the heath at Milligen.*

Perfectly level ground, trees only at 600 metres. Quiet, fine evening, October 19, 1904. Acoustical observer F. H. QUIX, optical observer H. F. MINKEMA (See Table I).

B. *Experiments in the gallery of the university library.*

Afternoon of January 3, 1905. Acoustical observer H. ZWAARDEMAKER, optical observer H. F. MINKEMA. (See Table II).

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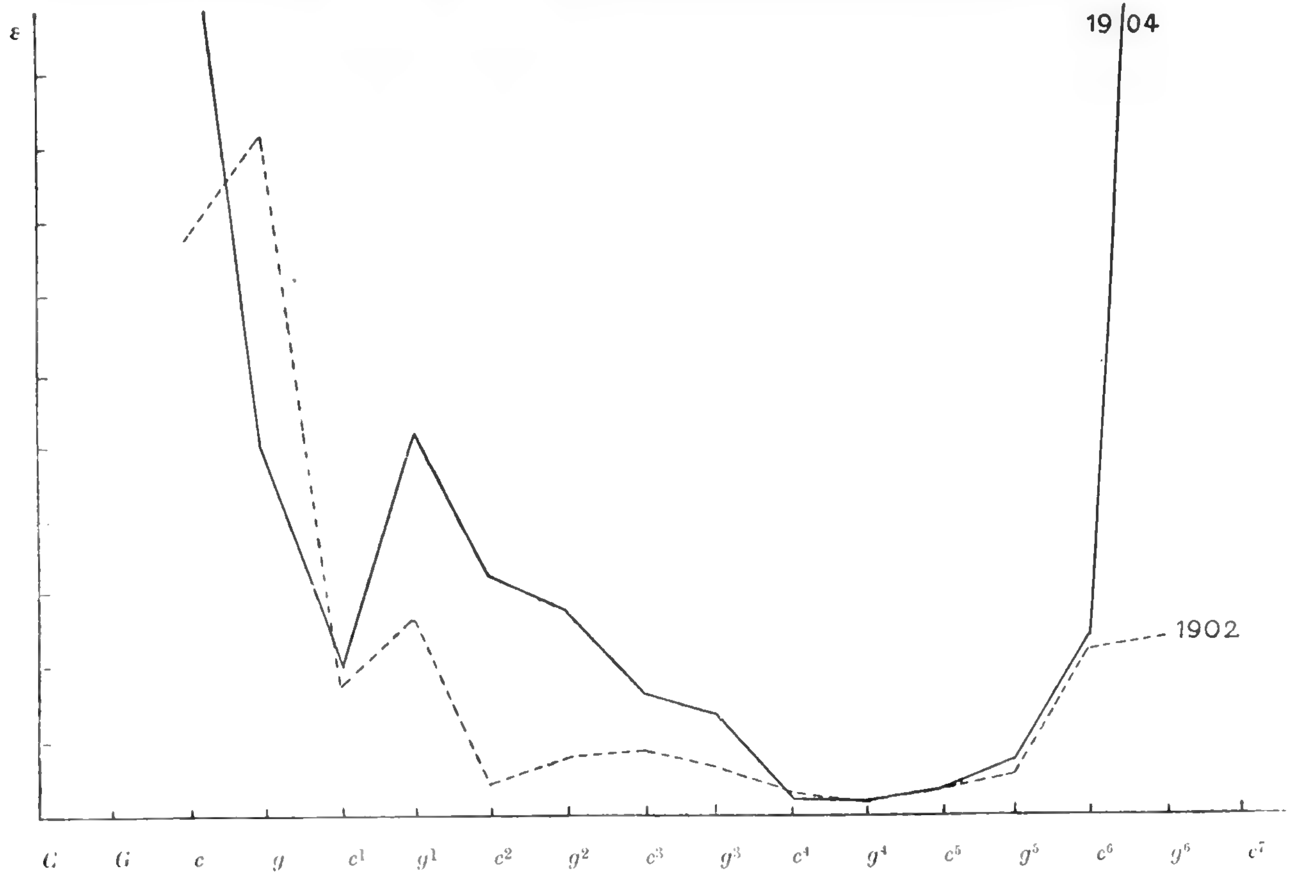
[1]) A. G. WEBSTER Boltzmann's Festschrift 1904 p. 870

[2]) RAYLEIGH Proc. Roy. Soc. vol 26 p. 248 1877.

[3]) M. WIEN, Die Messung der Tonstärke, Inauguraldissertation. Berlin 1888 p. 45.



Minima perceptibilia in the course of the scale; the minimum for $g^4 = 1$
(absolute value of the chosen minimum: in 1902 $0.79.10^{-8}$ Erg, in 1904 $0.32.10^{-8}$ Erg).

I. *Experiments on the heath at Milligen*, Oct. 19, 1904. 3rd series; acoustical observer F. H. Quix, optical observer H. F. Minkema.

Source of sound.	Pitch.	Frequency.	Air-supply per sec. in cc.	Water-pressure under the pipe in cm.	Energy supplied p. second vol. × press. × 981 (in ergs.)	Distance of the observer in M.	Surface of a hemi-sphere in cm², the distance being the radius.	Energy of the sound at the limit of audibility per sec. and per cm² in ergs.	Energy of the sound on the tympanum per number of necessary periods in ergs.	Number of necessary periods.	Remarks.
Roofed wooden organ-pipes	*C*	64	238	0.68	15.9 10^4	80	4.0 10^8	39 10^{-5}	411.5 10^{-8}	2	
»	*G*	96	208	1.60	32.7 »	100	6.3 »	52.0 »	361.0 »	2	
»	*c*	128	69 4	0.40	2.7 »	60	2.3 »	12 0 »	62.7 »	2	
»	*g*	192	75	0.46	3.4 »	150	14.1 »	2.4 »	8.3 »	2	
»	c^1	256	44 6	0.40	1.8 »	150	14.1 »	1.2 »	3.2 »	2	
»	g^1	384	43.4	0.74	3.1 »	100	6.3 »	5 0 »	8.7 »	2	
»	c^2	512	28.9	0.91	2.6 »	100	6.3 »	4.1 »	5 4 »	2	
Large Edelmann whistle	g^2	768	58.4	1 25	7.4 »	145	13.2 »	5.4 »	4.7 »	2	
	c^3	1024	69.4	1.65	11.2 »	205	26.4 »	4.3 »	2 8 »	2	
»	g^3	1536	113.6	2.51	28.0 »	280	49.2 »	5.7 »	2.5 »	2	
Small Edelmann whistle.	c^4	2048	64.1	2.74	17.2 »	505	160.2 »	1.1 »	0.4 »	2	
	g^4	3072	63.3	2.79	17 3 »	430	116.4 »	1.5 »	0.3 »	2	
Galton	c^5	4096	46.4	3.02	13.7 »	275	47.5 »	2.9 »	0.6 »	2.5	
whistle.	g^5	6144	43	3 02	12.7 »	250	39.3 »	3.2 »	1.0 »	5.5	
»	c^6	8192	46.7	3.14	14 4 »	220	28.1 »	5.1 »	4.2 »	20	
»	g^6	12288	43.8	3.25	14.0 »	70	3.1 »	45.5 »	24.8 »	20	
»	c^7	16384	45.8	3.25	14.6 »	20	0.3 »	581.3 »			

Now, if for the present we only take into account the energy supplied and neglect the necessary loss of energy in the organ pipe and in the air; if we further assume the validity of the theoretical law of distances (extension over a hemisphere), we obtain the following results:

1. that the sensitiveness of our ear has only one maximum, lying in the four times marked octave.

2. that there is a zone of fair sensitiveness, extending from g^1 to g^5.

3. that outside this zone the sensitiveness diminishes very rapidly.

4. that in the zone of fair sensitiveness the perceptible minima are of the same order.

5. that, for the most sensitive part of the scale the perceptible minimum is $0{,}32 \times 13^{-8}$ ergs for Mr. QUIX, $1{,}9 \times 10^{-8}$ ergs for myself.

The true perceptible minimum for the most sensitive point of the scale will of course lie lower. How much lower cannot be determined for the present, but at any rate the perceptible minimum found with organ pipes certainly remains a million times greater than that which was calculated by MAX WIEN from his telephone experiments. The minima, found on the heath and in the library, are in satisfactory agreement, however, with the minimum which we formerly calculated for tuning-forks, using the data of TÖPLER and BOLTZMANN [1].

Taking into account the "efficiency" of an organ pipe, found by WEBSTER (0,0013 and 0,0038), the perceptible minimum for the most sensitive point of the scale becomes lower, namely 0,45 to $1{,}3.\ 10^{-11}$ ergs, but it does not reach the amazingly small value of MAX WIEN's telephone experiments by a long way. Even if we assume that one hears better at night in the profound silence of a laboratory, than on the heath, not to mention an afternoon hour in the library, yet this difference is by no means accounted for. But I see no reason why the results of experiments made on perfectly level ground, far from woods or buildings, which, according to MAX WIEN's former valuable investigations, fall perfectly under the theoretical law of the distribution of sound, should deserve less confidence than experiments with a telephone, which require very complicated calculations.

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[1] TÖPLER u. BOLTZMANN. Ann. d. Physik u. Chemie Bd. 141 p. 321.

II. *Experiments in the university library* January 3, 1905; acoustical observer H. ZWAARDEMAKER, optical observer H. F. MINKEMA.

Source of sound.	Pitch.	Frequency.	Air-supply per sec. in cc.	Water-pressure under the pipe in cm.	Energy supplied p. second, vol. × press. × 981 (in ergs.)	Distance of the observer in M.	Surface of a hemi-sphere in cm²., the distance being the radius.	Energy of the sound at the limit of audibility per sec. and per cm². in ergs.	Energy of the sound on the tympanum per number of necessary periods in ergs.	Number of necessary periods.	Remarks.
Roofed wooden organ-pipes	C	64	166.6	0.57	9.3 10^{4}	48	0.2 10^{8}	457.8 10^{-5}	4768 10^{-8}	2	
	G	96	138.8	1.08	14.7 »	19	0.2 »	648.7 »	4515 »	2	
»	c	128	96.1	0.91	8.6 »	27	0.5 »	187.4 »	976 »	2	
»	g	192	83.3	0.57	4.7 »	42	1.1 »	42.0 »	146 »	2	
»	c^1	256	45.4	0.51	2.3 »	42	1.1 »	20.5 »	53.4 »	2	
»	g^1	384	31.3	0.4	1.2 »	45	1.3 »	96.6 »	16.8 »	2	
»	c^2	512	25	0.63	1.5 »	58	2.1 »	7.3 »	9.5 »	2	
»	g^2	768	27.2	0.91	2.4 »	62	2.4 »	10.1 »	8.7 »	2	
»	c^3	1024	22.7	0.97	2.2 »	65	2.7 »	8.1 »	5.3 »	2	
»	g^3	1536	20	1.08	2.1 »	65	2.7 »	8.0 »	3.5 1	2	
»	c^4	2048	18.5	1.37	2.5 »	66	2.7 »	9.1 »	3.0 »	2	
»	g^4	3072	14.5	1.94	2.8 »	70	3.1 »	9.0 »	1.9 »	2	end of the gallery
Galton whistle.	c^5	4096	28.6	1.25	3.5 »	71	3.2 »	11.1 »	2.3 »	2.5	
	g^5	6144	29.4	1.94	5.6 »	69	3.0 »	18.7 »	5.6 »	5.5	
»	c^6	8192	27.7	1.54	4.2 »	42	1.1 »	37.8 »	30.7 »	20	
»	g^6	12288	37	1.54	5.6 »	25	0.4 »	142.4 »	77.2 »	20	
»	c^7	16384	35.7	2.28	8.0 »	20	0.3 »	317.9 »			

Chemistry. — *"Critical terminating points in three-phase lines with solid phases in binary systems which present two liquid layers."*

By Prof. H. W. Bakhuis Roozeboom and Mr. E. H. Büchner.

(Communicated in the meeting of January 28, 1905).

Up to the present only one critical terminating point has been found in systems of one component, namely in the equilibrium liquid-vapour. If this is represented by a *p, t*-line this suddenly terminates in the point where liquid and vapour have become identical. There exist at the moment no well-founded reasons to assume critical terminating points also in the equilibria solid-liquid and solid-vapour. We will not further consider these here.

In systems of two components we get instead of a critical point liquid-vapour, a critical line K_1K_2 which connects the critical points of the components. In a *p, t, x*-diagram this line runs in space, here its *p, t*-projection is only indicated. (AK_1 and BK_2 are then the equilibria-lines liquid-vapour for the components *A* and *B*). If there is a homogeneous mixing for all concentrations in the liquid phase, this will then be the *only* critical line.

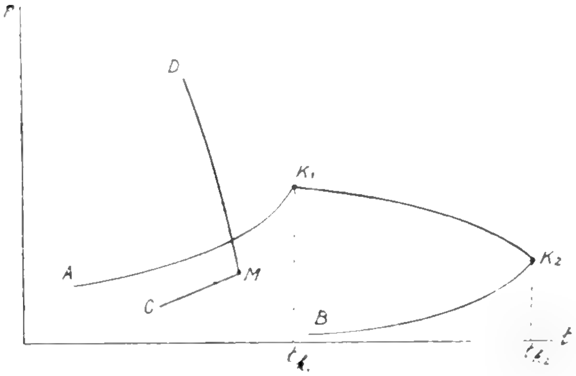

Fig. 1.

The recent researches of Smits[1]) have shown how in some binary mixtures the equilibrium line for solid *B* with liquid and vapour may meet this critical line (it is necessary that the melting point of *B* should be situated higher than K_1). There are then two such meeting-points *p* and *q* with the two parts *o p* and *qB* of the three-phase line. This line therefore acquires two critical terminating points owing to its meeting the critical line liquid-vapour. Between *p* and *q* both lines cease to exist.

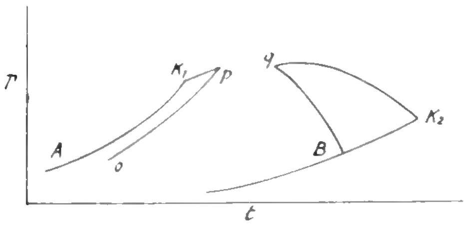

Fig. 2.

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[1]) These Proceedings 1904.

Other cases of similar critical terminating points through the meeting of three-phase lines in binary mixtures might be conceived when no homogeneous mixing in all concentrations is possible in the liquid phase and when, therefore, two liquid layers are possible. It was of great importance for the knowledge of the conditions of existence of solid phases at high temperatures and pressions to also trace the critical terminating points in similar cases. If we indicate the two liquid layers by L_1 and L_2, the vapour by G and the one or other component in the solid state by S, then besides the three-phase line SLG, two other three-phase lines SL_1L_2 and L_1L_2G will be possible. In order to trace the critical terminating points of these lines we first consider the line $L_1 L_2 G$. Here we first take exclusively the cases where the p,x-diagram has the form of Fig. 3, in which G, L_1 and L_2 indicate pressure and concentration of coexisting vapour with two liquid layers. The three-phase pressure for this system lies, therefore, between the vapour pressure of liquid A and B (P_1 and P_2)[1]. The p,t-line CM for the three-phase equilibrium $L_1 L_2 G$ is situated accordingly in Fig. 1 between AK_1 and BK_2.

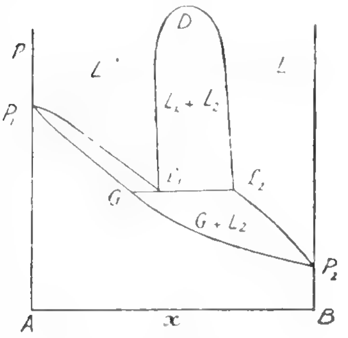

Fig. 3.

On elevation of temperature L_1 and L_2 may approach each other, or recede. If the first happens and if they still coincide below the line K_1K_2, for instance in M, then the two layers become identical, a case of which many instances have been found by **Alexejew** and **Rothmund**. This point has been quite properly called a critical point. This critical terminating point of the line for L_1L_2G must of course necessarily be a point of intersection with a critical line. The said critical line is the line DM in Fig. 1.

If the liquids L_1 and L_2 can be made to mix more completely by an increase of pressure a mixing point D will be found to exist in Fig. 3 at a sufficiently high pressure. If now L_1 L_2 approach each other at a higher t, D will then be situated at a lower pressure whilst the concentration in the mixing point may differ. In this way is obtained the critical line DM for the phases L_1L_2. Its one terminating point lies at the meeting point M where G occurs together with L_1L_2 and where consequently the lowest possible pressure is

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[1] The other case where the three-phase pressure is higher than those two does not lead to materially different results.

attained. In the upper direction a terminating point would only be conceivable in the case of the occurrence of a solid phase. If an increase of pressure promotes the separation of the two layers, DM would then run from the point M to the right instead of to the left.

In the case, therefore, in which the two liquid layers possess an upper mixing point M which lies below K_1K_2, the critical lines K_1K_2 for GL and DM for L_1L_2 are quite independent of each other.

If, however, the upper mixing point is not yet reached below K_1K_2, CM will continue up to a meeting point with K_1K_2. As the phases occur in the order GL_1L_2, G will then become identical with L_2 in O, Fig 4.

The critical line K_1O is here at the same time broken off. From a consideration of a series of p, x-diagrams for successive temperatures we may, according to Mr. BÜCHNER, easily demonstrate graphically that the other end of the critical line GL, which commences in K_2 now amalgamates with the upper part of the critical line L_1L_2 the lower continuation of which is not realisable owing to the absence of M. In this way is formed the critical line K_2PD whose upper part may eventually also run to the right.

A junction of the three-phase line GL_1L_2 with the critical line GL in O will, secondly, always take place when L_1 and L_2 diverge by an elevation of temperature. This may frequently occur with two liquid layers which have a lower mixing point M^1. The three-phase line GL_1L_2 then terminates in O by intersection with the critical line GL and in M^1 by intersection with the critical line M^1P for $L_1 = L_2$. From the p, x-diagrams we may now again deduce that the upper continuation of this line is not now realisable because the lower part coincides with the second part of the critical line GL which proceeds from K_2. In this way the critical line M^1PK_2 originates.

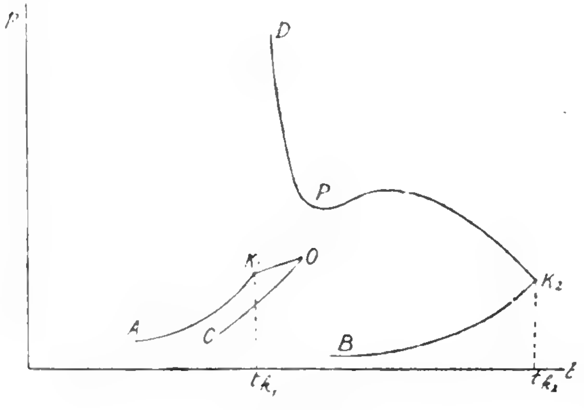

Fig. 4.

Lately, KUENEN has found instances of the cases represented by Figs. 4 and 5.

The figures 1, 4 and 5 exhibit the three main types of the manner in which the three-phase line meets either the critical line GL or the critical line L_1 L_2 and then finds 1 or 2 terminating

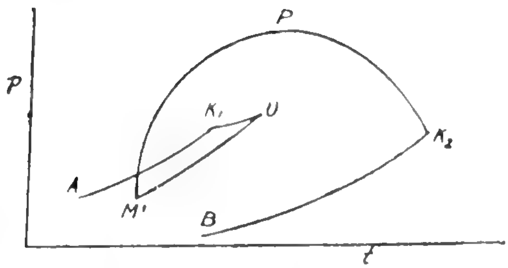

Fig. 5.

points, also of the fusion of parts of the one critical line with those of the other.

In the second place we will now consider the occurrence of critical terminating points on those three-phase lines where one of the phases is solid. We may then limit ourselves to the case where B occurs as a solid phase as no critical phenomena can occur in presence of solid A.

In many cases where the line GL_1L_2 proceeds to lower temperatures the solid phase will occur in a point Q. According to previous research by myself, 4 three-phase lines then meet in the quadruple point Q. If we take the case of Fig. 1 we obtain in Fig. 6 QM for GL_1L_2, QB for GL_2S, EQ for GL_1S, whilst QN indicates the equilibrium of the solid phase S with the liquid layers L_1L_2. Similar lines have been formerly studied by me in cases where hydrates of SO_2 HBr, HCl occurred as solid phases. For the component B as solid phase their courses will be analogous, and like all ordinary melting lines the direction will diverge only a little from the vertical either to the right or the left according to the volume differences of the phases.

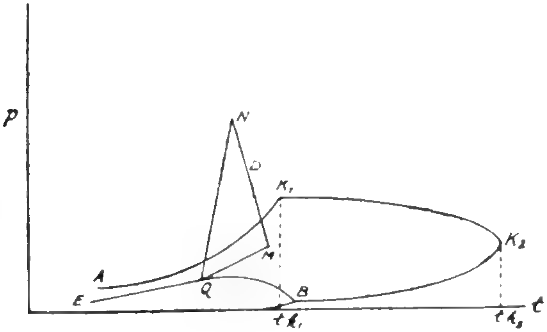

Fig. 6.

If the line runs to the right and the critical line MD to the left there might be a possibility of their meeting in a critical terminating point N as the two liquid layers might here become identical in presence of solid B. The chances that this will occur with an attainable pressure only exist when Q and M do not differ too much in temperature.

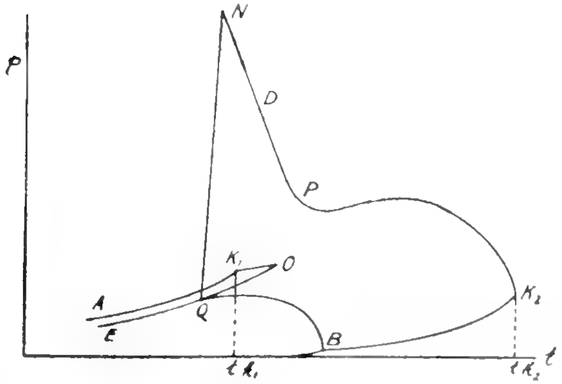

Fig. 7.

Fig. 7 represents a similar meeting point N for the case corresponding with Fig. 4. Far greater chance of attaining a critical terminating point of the line L_1L_2S is offered by the case of Fig 5 which would lead to Fig. 8. The line OQ is here supposed not to proceed as far as the lower mixing point M' because the solid phase occurs previously at Q. For this reason the downward continuation of the critical line $L_1 = L_2$ is wanting.

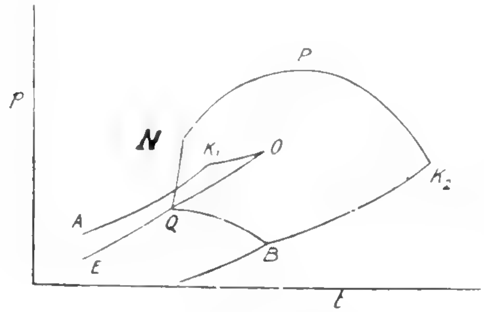

Fig. 8.

If, however, the mixing point M' should lie but very little below Q (metastable) the point of intersection N might be found at a comparatively low pressure. Mr. Büchner has frequently noticed a similar proximity of M' and Q in systems of all kinds of organic substances which on being dissolved in liquid CO_2 give rise to two layers.

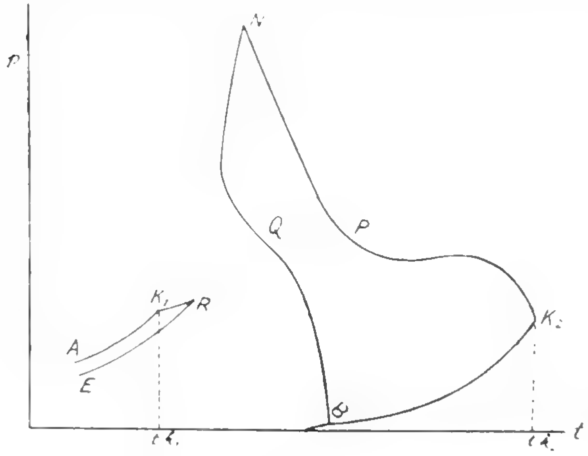

Fig. 9.

Besides the three cases fig. 6, 7, 8 in which there exists a critical terminating point of the line QN a fourth type is possible. This occurs when the liquid on the line EQ already becomes critical with the vapour before Q has been reached, that is before the second liquid occurs in presence of the solid phase. ER then intersects the critical line liquid-vapour in a critical point R which quite corresponds with the point p of Smits (fig. 2). The line QO is now wanting, namely, below R we notice nothing of a second liquid. Mr. Büchner has here again graphically deduced that in this case the line QB, for the second series of liquids in presence of solid B and vapour, fuses with QN to a single line BQN where the one fluid phase has the character of vapour on the lower part and of liquid on the upper part, whilst these however, gradually pass into each other.

In this case, like in fig. 4 the lower part of the critical line GL

fuses with the upper part of the critical line L_1L_2, K_2PN, and we have here again the possibility that the line BQN also possesses a critical terminating point N. This point bears some resemblance to the second critical terminating point found by Smits in q fig. 2. That we are dealing in fig. 9 with a region of two liquid layers could only be made plainly visible, if, owing to the non-appearance of the solid phase, two liquids, in presence of vapour (metastable), occurred below R. Otherwise it is only the peculiar course of BQN, which shows that we have this type.

Mr. Büchner has succeeded in finding a case where this course could be indicated (although N remained unattainable). Fig. 10 gives a correct representation of the p, t-lines ER and BQ for solid diphenylamine in presence of solution in liquid CO_2 and in vapour very rich in CO_2, on ER, and in presence of a much more diphenylamine-containing second liquid phase on BQ. The point R is situated only 0°.6 above the critical point of pure CO_2, consequently diphenylamine is but very sparingly soluble in CO_2 at that temperature.

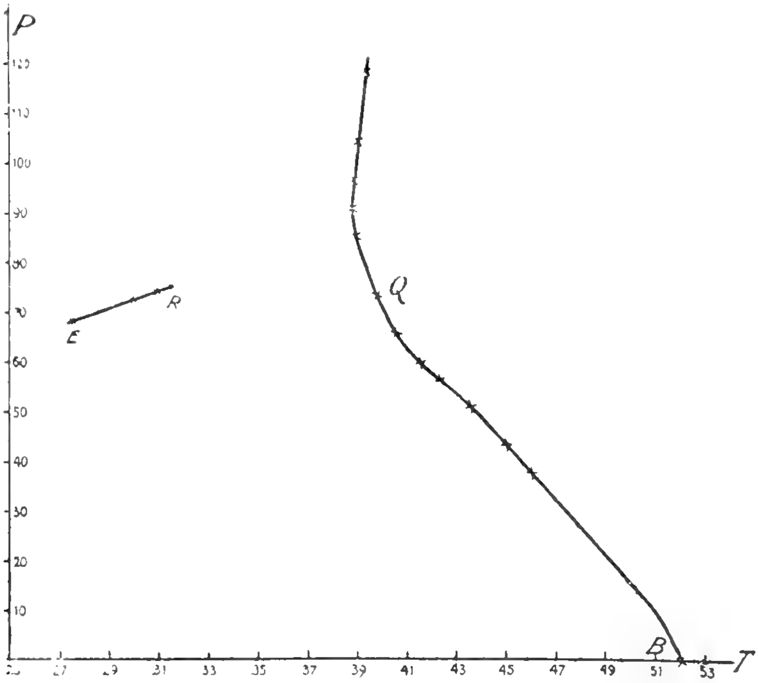

Fig. 10.

Between 31°6 and 38°8 two liquid phases are not capable of existing in presence of solid diphenylamine; above these we again find the second three-phase line with two fluid phases now much richer in diphenylamine. This line was determined up to 120 atm. pressure. The significance of all the regions in which three-phase lines are absent can only be expressed by a series of p, x-diagrams.

The above considerations foreshadow the possibility of enunciating in general terms the conditions for the existence of a solid phase in presence of one or two fluid ones, when traversing the region of the critical phenomena of those latter ones, also for those binary mixtures which in the liquid state are not miscible in all proportions.

Mathematics. — "*On non-linear systems of spherical spaces touching one another.*" By Prof. P. H. SCHOUTE.

1. Before passing to our real investigation it is necessary to find how many spherical spaces touch $n+1$ spherical spaces given arbitrarily in the n-dimensional space S_n. And in its turn the answer to this question demands a knowledge of the situation of the centres of similitude of those given spherical spaces. So we start with a study of these centres of similitude. To this end we represent the spherical space, which is in S_n again the locus of the points situated at a distance r from the centre M, by the symbol $Sp_n(M, r)$.

2. Just as is the case with two circles lying in the same plane, two spherical spaces $Sp(M_1, r_1)$ and $Sp(M_2, r_2)$ lying in S_n admit of two centres of similitude on the line $M_1 M_2$ connecting the centres, an external one U_{12} and an internal one I_{12}; through U_{12} pass the lines $P_1 P_2$ connecting the extremities P_1, P_2 of direct parallel rays, through I_{12} pass the lines $P_1 P'_2$ connecting the extremities P_1, P'_2 of opposite parallel rays.

Supposing that in S_n a number of $n+1$ spherical spaces $Sp(M_k, r_k)$, $(k = 1, 2, \ldots, n+1)$ is given arbitrarily, we shall now investigate the situation of the $(n+1)_2$ pairs of centres of similitude $(U_{p,q}, I_{p,q})$ with respect to each other. To this end we first notice that the three pairs of centres of similitude of the three spherical spaces $Sp_n(M_i, r_i)$, $(i = 1, 2, 3)$ form the three pairs of opposite vertices of a complete quadrilateral, each of the four triplets of points

$$(U_{12}\,U_{13}\,U_{23}),\quad (U_{12}\,I_{13}\,I_{23}),\quad (I_{12}\,U_{13}\,I_{23}),\quad (I_{12}\,I_{13}\,U_{23})$$

consisting of three points of a right line; we indicate these lines in the given order by

$$l_{123}\quad,\quad l_{12}^{(3)}\quad,\quad l_{13}^{(2)}\quad,\quad l_{23}^{(1)}$$

If we now further regard the $n-1$ pairs of lines $(l_{12p}, l_{12}^{(p)})$ through

U_{12} and the $n-1$ pairs of lines (l_{1p}^{2}, l_{2p}^{1}) through I_{12} — where successively p assumes the $n-1$ values $3, 4, \ldots, n+1$ —, we see immediately that each space S_{n-1} through $n-1$ lines l through U_{12} (or I_{12}) — with all indices p differing mutually — contains one of the two centres of similitude of each of the $(n+1)_2$ pairs $(U_{p,q}, I_{p,q})$. Thus a space S_{n-1} through $n-1$ lines l through U_{12} will contain the point $U_{p,q}$ or the point $I_{p,q}$, according to the two lines l with p and q as third index being of the same kind or not; just the reverse is found for a space S_{n-1} through $n-1$ lines l through I_{12}. As the choice of the lines l corresponds in both cases to $n-1$ bifurcations 2^{n-1} of those spaces S_{n-1} pass through each of the two points U_{12}, I_{12}. So the theorem holds good:

"We can indicate 2^n spaces S_{n-1}, each of which contains $(n+1)_2$ centres of similitude of a system of $n+1$ spherical spaces Sp_n given arbitrarily in S_n, and namely one of each of the $(n+1)_2$ pairs $(U_{p,q}, I_{p,q})$."

We need not enter into further details about the situation of the centres of similitude for the purpose we have here in view.

3. From the well known properties of the figure consisting of two circles and their centres of similitude we read (fig. 1):

$$\left.\begin{array}{l} UP_1^u : UP_2 = r_1 : +r_2 \\ IP_1^i : IP_2 = r_1 : -r_2 \end{array}\right\} , \quad \left.\begin{array}{l} UP_1^u \,.\, UP_2^u = UC_1^u \,.\, UC_2 \\ IP_1^i \,.\, IP_2^i = IC_1^i \,.\, IC_2 \end{array}\right\} .$$

With the aid of these relations we can easily find the following

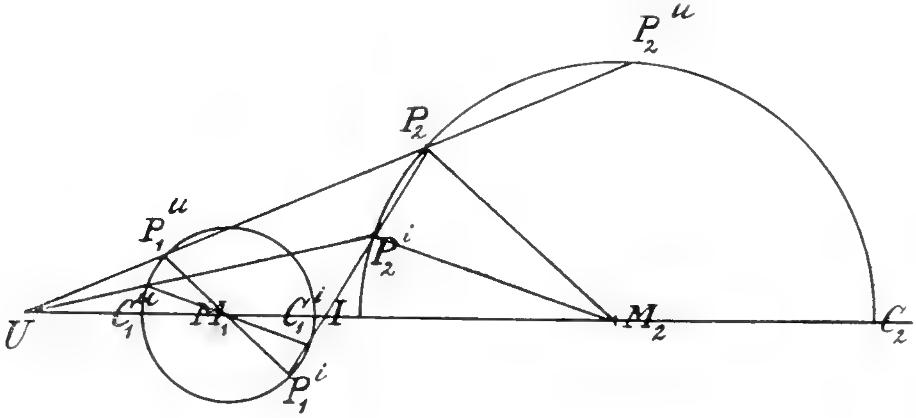

Fig. 1.

theorems, where for $Sp_n(M_1, r_1)$ and $Sp_n(M_2, r_2)$ we shall write the abridged form $Sp_n^{(1)}$ and $Sp_n^{(2)}$.

"The spherical spaces $Sp_n^{(1)}$ and $Sp_n^{(2)}$ are homothetic and directly similar with U, homothetic and inversely similar with I as centre of similitude and $\pm \frac{r_1}{r_2}$ as quotient of similitude. The points corresponding to each other, P_1^u and P_2 in the first case and P_1^i and P_2 in the second, are called *homologous*."

"The spherical spaces $Sp_n^{(1)}$ and $Sp_n^{(2)}$ correspond to each other in an inversion with U as centre and $UC_1^u \,.\, UC_2$ as positive power and in an inversion with I as centre and $IC_1^i \,.\, IC_2$ as negative power. The points P_1^u and P_2^u corresponding to each other in the first case and P_1^i and P_2^i in the second are called *antihomologous*. And the two inversions appearing in these theorems shall furtheron be indicated for shortness' sake by the symbols $U(1, 2)$ and $I(1, 2)$."

"Each spherical space Sp_n through a pair of antihomologous points P_1 and P_2 of $Sp_n^{(1)}$ and $Sp_n^{(2)}$ cuts these spherical spaces at equal angles. If the spherical space Sp_n through P_1 and P_2 touches the spherical space $Sp_n^{(1)}$ in P_1, it will touch the spherical space $Sp_n^{(2)}$ in P_2. And these contacts will be of the same kind or not, according to U or I being the centre of the antihomologous correspondence."

In connection with the general theorem concerning the situation of the centres of similitude the second and the third of these three simple theorems form the foundation of a method of solving the problem to construe a spherical space Sp_n touching $n+1$ spherical spaces $Sp_n^{(1)}$, $Sp_n^{(2)}$, . . . $Sp_n^{(n+1)}$ given arbitrarily in S_n. As will immediately be evident, to each of the 2^n spaces S^{n-1} through $(n+1)_2$ centres of similitude answers a pair of tangent spherical spaces Sp_n and the contact of one of these spherical spaces with $Sp_n^{(p)}$ and $Sp_n^{(q)}$ is of the same kind or not, according to the chosen space S_{n-1} containing of the centres of similitude $U_{p,q}$, $I_{p,q}$ of $Sp_n^{(p)}$ and $Sp_n^{(q)}$ either the first or the second. So 2^{n+1} is the number of the theoretic solutions. And if we indicate external contact by $+$ and internal contact by $-$, then the 2^n pairs of solutions are indicated by the pairs of completely opposite combinations of signs of the series consisting of $n+1$ terms

$$\pm \quad \pm \quad \pm \quad . \; . \; . \; . \; . \; . \; . \; . \quad \pm,$$

where the two solutions of a selfsame pair correspond in all signs or differ in all signs.

The construction of the tangent spherical spaces proves the above assumed concerning the number of the solutions and their connection with the 2^n spaces S_{n-1}. We give it here — to avoid prolixity — for the case $n = 4$ in a form, in which it is immediately transferable to the case of an arbitrary n. It is:

a. "If in S_4 the spherical spaces $Sp_4^{(1)}$, $Sp_4^{(2)}$, ... $Sp_4^{(5)}$ are given arbitrarily, if d_{123}^{45} is the space through the points

$$U_{12}, U_{13}, U_{23}, U_{45}, I_{14}, I_{24}, I_{34}, I_{15}, I_{25}, I_{35}$$

and if P_1 is an entirely arbitrary point of $Sp_4^{(1)}$, then the antihomologous points P_2, P_3, P_4, P_5 of P_1 in the inversions $U(1, 2)$, $U(1, 3)$, $I(1, 4)$, $I(1, 5)$ are to be determined and the spherical space $Sp_4(P)$ through the five points P_1, P_2, P_3, P_4, P_5."

b. If ε_1 is the plane of intersection of d_{123}^{45} with the radical space of $Sp_4^{(1)}$ and $Sp_4(P)$, let us bring through ε_1 two spaces touching $Sp_4^{(1)}$ and let Q_1 and Q_1' indicate the points of contact."

c. Finally must be determined the pairs of points (Q_2, Q_2'), (Q_3, Q_3'), (Q_4, Q_4'), (Q_5, Q_5') which are antihomologous to (Q_1, Q_1') in the inversions $U(1, 2)$, $U(1, 3)$, $I(1, 4)$, $I(1, 5)$ and the spherical spaces $Sp_4(Q)$ and $Sp_4(Q')$ passing through the quintuples of points Q_1, Q_2, ... Q_5 and Q_1', Q_2', ... Q_5'. These spherical spaces $Sp_4(Q)$ and $Sp_4(Q')$ form one of the 2^n pairs of solutions of the problem."

The proof of this construction is plain. When P_1 moves over $Sp_4^{(1)}$ the power of each of the ten centres of similitude lying in d_{123}^{45} with respect to the spherical space $Sp_4(P)$ remains unchanged; consequently the spherical spaces $Sp_4(P)$ which are possible form a pencil with d_{123}^{45} as common radical space and ε_1 is a common radical plane of $Sp_4^{(1)}$ with each of the spherical spaces $Sp_4(P)$ of that pencil. If now we choose for P one of the two points of contact Q or Q' of $Sp_4^{(1)}$ with a space through ε_1, then this tangent space must likewise touch the spherical space $Sp_4(Q)$ or $Sp_4(Q')$ passing through this point in the same point, etc.

We have now arrived at the first part of our investigation proper concerning the system of the spherical spaces Sp_n touching n spherical spaces $Sp_n(M_k, r_k)$, $(k = 1, 2, \dots n)$ given arbitrarily in S_n and we reduce the general case — following the way indicated by REYE for our space — to a simpler one, in which the centres M_k of the n spherical spaces which must be touched lie in a space S_{n-2}.

The centres M_k of the n given spherical spaces $Sp_n(M_k, r_k)$ determine a space S_{n-1}, intersecting these spherical spaces according to "central spherical spaces" $Sp_{n-1}(M_k, r_k)$, thus intersecting them at right angles. Let O be the radical centre of these n spherical spaces Sp_{n-1} and r^2 the power of this point with respect to the spherical spaces Sp_{n-1}, provisionally supposed to be positive. Then the spherical space $Sp_{n-1}(O, r)$ lying in S_{n-1} intersects at right angles the n spherical spaces $Sp_{n-1}(M_k, r_k)$, thus also the n spherical spaces $Sp_n(M_k, r_k)$. So an inversion with an arbitrary point O' of the surface of the spherical space $Sp_{n-1}(O, r)$ as centre makes the n given spherical spaces $Sp_n(M_k, r_k)$ and the spherical space $Sp_{n-1}(O, r)$ cutting them at right angles to pass into n new spherical spaces Sp'_n and a space S_{n-2} cutting them at right angles. This special case where the centres M'_k of the n spherical spaces which must be touched lie in a space S_{n-2} shall be treated first.

5. If Sp''_n is a spherical space touching the n new spherical spaces Sp'_n, then this spherical space Sp''_n rotating round the space S_{n-2} through the n centres M'_k will touch in any position the n spherical spaces Sp'_n and will thus form a singular infinite series of tangent spherical spaces. In an arbitrary space S_{n-1} through the axial space S_{n-2} we find according to the results obtained above 2^{n-1} pairs of spherical spaces Sp''_{n-1}, touching the central spherical spaces Sp'_{n-1} — lying in S_{n-1} — of the n spherical spaces Sp'_n, and as a matter of course each of these pairs consists of two spherical spaces Sp''_{n-1} lying symmetrically with respect to S_{n-2}. As each of those pairs by rotation leads up to a singular infinite series there are 2^{n-1} of such series. The spherical spaces of each of those series are enveloped — compare my preceding communication on page 492 — by an n-dimensional torus $T_{n,1}$; their centres lie on a circle. And if we confine ourselves to one of the 2^{n-1} series, we can extend the system of the n touched spherical spaces Sp'_n to a n—2-fold infinite series by representing to ourselves all the spherical spaces described

out of the points of S_{n-2}, in such a way that they touch one of the spherical spaces of the singular infinite series, thus all the spherical spaces of that series too.

6. If we now confine ourselves to a single series of the 2^{n-1} singular infinite series we have found two systems of spherical spaces possessing the remarkable property that each spherical space of one touches all the spherical spaces of the other. Of these two systems one is a singular infinite series of equally large spherical spaces with a circle $C(M_0, r_0)$ having M_0 and r_0 as centre and as radius and lying in the plane ε_0 as locus of centres, whilst the other is an $n-2$-fold series with the space S_{n-2} perpendicular in M_0 to ε_0 as locus of centres. How do these two systems transform themselves if we apply to both — in order to return to our n given spherical spaces Sp_n — the inversion with O' as centre and the formerly used power?

To answer this question is made easy by the observation that the n-dimensional figure consisting of the two systems Sy'_1, Sy'_{n-2} and their inverse systems Sy_1, Sy_{n-2} have a plane of symmetry, the plane σ through M_0, O' and the projection O'' of O' on S_{n-2}. This plane σ forming the plane of fig. 2 has with ε_0 in common the diameter m' parallel to $O'O''$ of the circle $C(M_0, r_0)$ and is according to that line m' perpendicular to ε_0; so it is a plane of symmetry for Sy'_1. It has moreover with S_{n-2} the line M_0O'' in common and is according to that line a perpendicular to Sy_{n-2}; so it is also a plane of symmetry for Sy'_{n-2}. And if it is a plane of symmetry for Sy'_1 and Sy'_{n-2}, then it is so too for Sy_1 and Sy_{n-2}, because it contains the centre O' of the inversion.

We prove to begin with that the centres of the spherical spaces of Sy_1 lie in a conic. To this end we regard in the plane of symmetry σ (fig. 2) the points of intersection M', M'' with the circle $C(M_0, r_0)$, the circle of section $C(M_1, r_1)$ with the spherical space $Sp''_n(M_1, r_1)$ of Sy'_1 and the point O of the line $M'O'$, for which $M'O'.M'\overline{O} = r_1^2$. Then point A of a, which is at an equal distance from O' and $\overline{O}$, is the centre of a sphere $Sp_3(A, AO')$ with AO' as radius, intersecting $Sp''_n(M', r')$ and so all spherical spaces Sp''_n of the singular infinite series at right angles. This sphere is transformed by the inversion with O' as centre into a plane ε perpendicular to $O'A$, intersecting σ according to a line m normal to $O'A$; this plane ε must contain the centres of the spherical spaces of Sy_1 as it cuts all those spherical spaces at right angles. And farther, when inverting, the centre of a spherical space remains on the line connecting this

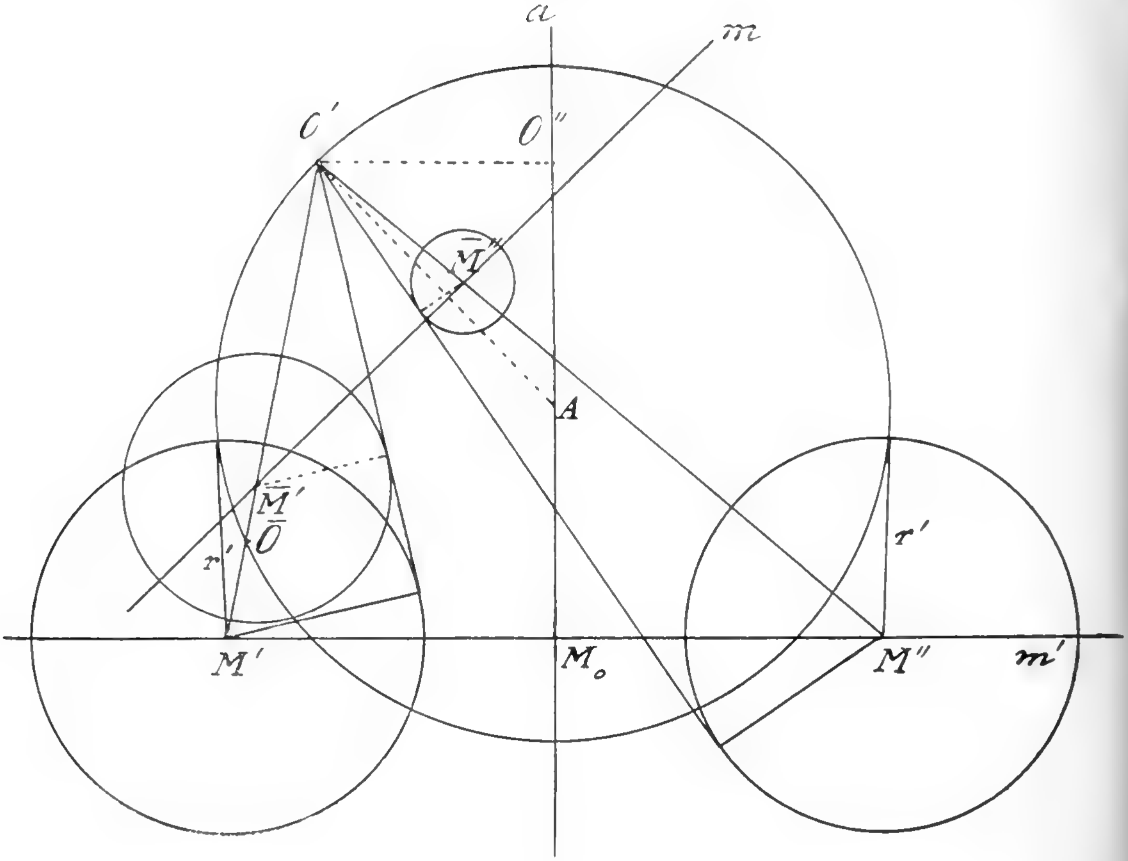

Fig. 2.

point with the centre O' of the inversion; so the oblique cone with O' as vertex and circle $C(M_0, r_0)$ as base must contain the centres of the spherical spaces of the series Sy_1, and the locus of those centres is the conic of intersection of this cone with the plane ε. Of this conic m is an axis of symmetry and the points $\overline{M}'$ and $\overline{M}''$, becoming the centres of the inverted spherical spaces $Sp''_n(M', r')$, $Sp''_n(M'', r')$ are vertices. This conic is an ellipse E, a parabola P or an hyperbola H, according to none, one or two of the spherical spaces Sp''_n of Sy'_1 passing through O', i. e. according to O' lying outside the two circles $C(M', r')$ and $C(M'', r')$, on one of those circles or inside one of them. Of these three cases fig. 2 represents the first and this will be furtheron exclusively under consideration.

If we suppose that the conic obtained is an ellipse E the inverse spherical spaces $Sp_n(M', r)$ and $Sp_n(M'', r'')$ of the spherical spaces $Sp''_n(M', r')$ and $Sp''_n(M'', r')$ will touch every spherical space $Sp_n(M, r)$ of the system Sy_{n-2} in the same kind. From the triangle $M\,M'\,M''$

then ensues, if we represent the radii vectores $M'M$ and $M''M$ of M with respect to the fixed points M' and M'' by u and v, that $u - v = \pm (r' - r'')$. So the locus of the centres of the spherical spaces $Sp_n(M, r)$ of the system Sy_{n-2} is the figure of revolution, which is generated when the hyperbola H with M' and M'' as foci and $\pm (\bar{r}' - \bar{r}'')$ as half real axis rotates round m in the space S_{n-1} through S_{n-2} and O'. And because each spherical space Sp_n of Sy_1 touches the spherical spaces of Sy_{n-1} having the vertices of the hyperbola H as centres, those vertices of the hyperbola H are reversely the foci of the ellipse E. Thus the theorem holds good:

"The spherical spaces Sp_n' touching n spherical spaces Sp_n given arbitrarily in S_n form 2^{n-1} singular infinite series. The spherical spaces of any of those series are connected by this that they intersect a definite spherical space $Sp'^{(0)}_n$ at right angles and that their centres lie on a definite conic (K'); the determining figures, the spherical space $Sp'^{(0)}_n$ and the conic (K'), change from seriés to series. To each series corresponds as envelope of its spherical spaces a definite curved space of order four, the n-dimensional cyclid of DUPIN. And if we confine ourselves to a single series, the system of n-given spherical spaces Sp_n can be extended to an $n-2$-fold infinite series of spherical spaces Sp_n, connected by the fact that they cut another spherical space $Sp^{(0)}_n$ at right angles and that their centres are situated on the surface of a figure of revolution generated by the rotation of a conic (K). These two conics (K) and (K') lie in mutually perpendicular planes in such a way that the foci of one are vertices of the other and reversely."

7. The inversion applied becomes impossible within the region of reality when the common power of the radical centre O of the n given spherical spaces Sp_n with respect to those spherical spaces is negative. In this case before inverting we can diminish the radii of the n given spherical spaces by a common quantity in such a way that the radius of one of those spherical spaces disappears. Then the power of the radical centre O of the new spheres is certainly positive. By operating now with the new system and after that, when the system Sy_1 has been found, by adding the assumed quantity to the radii of the spherical spaces of Sy_1, we arrive at the desired aim. As is evident we can even augment the radii of some of the given spherical spaces by the radius of the spherical space that is to become a spherical space reduced to a point if only the series of the tangent spherical spaces is chosen so as to correspond to this.

8. Are there not also non-linear systems Sy_k and Sy_{n-k-1} of spherical spaces Sp_n respectively k-fold and $n-k-1$-fold infinite situated in S_n in such a way that each spherical space of one system touches all the spherical spaces of the other?

This question must be answered in the affirmative as we shall prove here analytically.

If in a space S_{n-1} of S_n the spaces S_k and S_{n-k-1}, which have but the point O in common are perpendicular to each other in this point, if OP is the normal in O on S_{n-1}, OQ an arbitrary line through O in S_k, OR an arbitrary line through O in S_{n-k-1} and if we assume (fig. 3) in the planes OPQ and OPR an ellipse (E) with the half axes $OA=a$, $OB=b$ and an hyperbola (H) with the half axes $OC=c=\sqrt{a^2-b^2}$, $OD=b$, then by rotation of (E) round OP in the space $S_{k+1}=(OP, S_k)$ — when every point describes a spherical space Sp_k — a quadratic space of revolution $Q^{(2)}_{k+1}$ is generated, by rotation of (H) round OP in the space $S_{n-k}=(OP, S_{n-k-1})$ — when every point describes a spherical space Sp_{n-k-1} — a quadratic space of revolution $Q^{(2)}_{n-k}$ is generated.

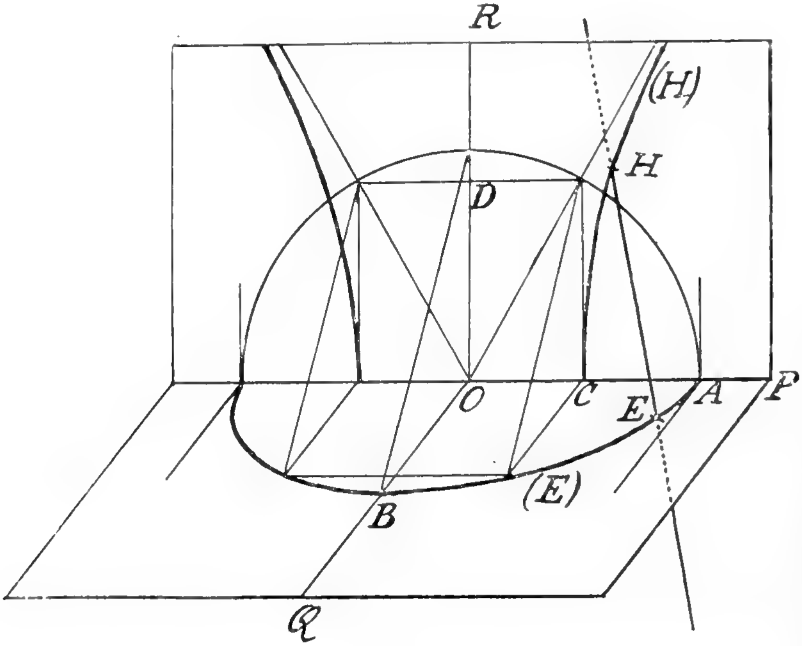

Fig. 3.

If now E and H are arbitrarily chosen points of those figures of revolution the distance EH can easily be calculated. If namely we use a rectangular system of coordinates with O as origin, OP as axis OX_1, the plane OPE as plane OX_1X_2, the plane OPH as plane OX_1X_3, then the coordinates of the points E and H are

$$E \dots . \; x_1 = a \cos \varphi, \quad x_2 = b \sin \varphi, \quad x_3 = 0 \quad , \quad x_4 = 0, \dots , x_n = 0,$$
$$H \dots . \; x_1 = c \sec \psi, \quad x_2 = 0 \quad , \quad x_3 = b \; tg \; \psi, \quad x_4 = 0, \dots , x_n = 0$$

and we find

$$EH = a \sec \psi - c \cos \varphi$$

From this ensues that the spherical spaces $Sp_n(E, c \cos \varphi + \varrho)$ and $Sp_n(H, a \sec \psi + \varrho)$, where ϱ represents an arbitrary constant, touch each other and that this contact is an external one or an internal one, according to $c \cos \varphi + \varrho$ and $a \sec \psi + \varrho$ having the same sign or not. Thus the theorem holds good:

"If we describe out of each point E of $Q^{(2)}_{k+1}$ with $a \cos \varphi$ as x_1 a spherical space $Sp_n(E, c \cos \varphi + \varrho)$ and out of each point H of $Q^{(2)}_{n-k}$ with $c \sec \psi$ as x_1 a spherical space $Sp_n(H, a \sec \psi + \varrho)$ where ϱ represents an arbitrary constant and φ and ψ assume all possible values, then two systems Sy_k, Sy_{n-k-1} of spherical spaces Sp_n are generated with the property that each spherical space of one system touches all spherical spaces of the other."

Both systems of spherical spaces are enveloped by the same curved space of order four. If namely of a rectangular system of coordinates with O as origin and OP as axis OX_1 the axes OX_2, OX_4, OX_5, . . . OX_{k+2} are situated in S_{k+1}, the axes OX_3, OX_{k+3}, OX_{k+4}, . . . OX_n in S_{n-k}, then the coordinates of two points E and H lying arbitrarily on $Q^{(2)}_{k+1}$ and $Q^{(2)}_{n-k}$ can be written in the form

E	H
$x_1 = a \cos \varphi$	$x_1 = c \sec \psi$
$x_2 = b \sin \varphi \cos \varphi_1$	$x_2 = 0$
$x_3 = 0$	$x_3 = b \; tg \; \psi \cos \psi_1$
$x_4 = b \sin \varphi \sin \varphi_1 \cos \varphi_2$	$x_4 = 0$
$x_5 = b \sin \varphi \sin \varphi_1 \sin \varphi_2 \cos \varphi_3$	$x_5 = 0$
. . . .	. . . .
$x_{k+1} = b \sin \varphi \sin \varphi_1 \sin \varphi_2 \dots \sin \varphi_{k-2} \cos \varphi_{k-1}$	$x_{k+1} = 0$
$x_{k+2} = b \sin \varphi \sin \varphi_1 \sin \varphi_2 \dots \sin \varphi_{k-2} \sin \varphi_{k-1}$	$x_{k+2} = 0$
$x_{k+3} = 0$	$x_{k+3} = b \; tg \; \psi \sin \psi_1 \cos \psi_2$
$x_{k+4} = 0$	$x_{k+4} = b \; tg \; \psi \sin \psi_1 \sin \psi_2 \cos \psi_3$
. . . .	. . . .
$x_{n-1} = 0$	$x_{n-1} = b \; tg \; \psi \sin \psi_1 \sin \psi_2 \dots \sin \psi_{n-k-3} \cos \psi_{n-k-2}$
$x_n = 0$	$x_n = b \; tg \; \psi \sin \psi_1 \sin \psi_2 \dots \sin \psi_{n-k-3} \sin \psi_{n-k-2}$

and

$$(x_1 - a\cos\varphi)^2 + (x_2 - b\sin\varphi\cos\varphi_1)^2 + x_3^2 + (x_4 - b\sin\varphi\sin\varphi_1\cos\varphi_2)^2 + \ldots$$
$$+ (x_{k+2} - b\sin\varphi\sin\varphi_1\sin\varphi_2\ldots\sin\varphi_{k-2}\sin\varphi_{k-1})^2 + x^2_{k+3} + \ldots + x_n^2 =$$
$$= (c\cos\varphi + \varrho)^2$$

is the equation of the spherical space $Sp_n(E, c\cos\varphi + \varrho)$. If we write this equation in the form.

$$\sum_{i=1}^{n} x_i^2 + b^2 - \varrho^2 =$$
$$= 2\{ax_1\cos\varphi + b\sin\varphi\,[x_2\cos\varphi_1 + x_4\sin\varphi_1\cos\varphi_2 + \ldots + x_{k+2}\sin\varphi_1\ldots\sin\varphi_{k-1}]\}$$

and underneath the k equations formed out of it by differentiation according to $\varphi, \varphi_1, \ldots \varphi_{k-1}$, then addition of the $k+1$ equations, after having squared them, furnishes us with

$$(\sum_{i=1}^{n} x_i^2 + b^2 - \varrho^2)^2 = 4[(ax_1 + c\varrho)^2 + b^2(x_2^2 + \sum_{i=4}^{k+2} x_i^2)]. \quad . \quad (1)$$

And this same equation is obtained in the form

$$(\sum_{i=1}^{n} x_i^2 - b^2 - \varrho^2)^2 = 4[(cx_1 + a\varrho)^2 - b^2(x_3^2 + \sum_{i=k+3}^{n} x_i^2)],$$

if we consider the spherical space of system Sy_{n-k-1}.

9. For a variable parameter ϱ equation (1) represents a system of parallel n-dimensional cyclids of DUPIN. Here we can then ask after the n numbers indicating successively how many of those cyclids pass through a point or touch a line, a plane, a space, etc. In this investigation the $k+(n-k-1)$-, i. e. the $n-1$-fold congruence of the right lines is in prominence, connecting an arbitrary point E of $Q^{(2)}_{k+1}$ with an arbitrary point H of $Q^{(2)}_{n-k}$; the case of $n = 3$ has been treated before in a small paper (*"Prace matematyczno-fizyczno"*, vol. 15, pages 83—85, 1904). And the more general case we do not touch here.

Mathematics. — *"On a special tetraedal complex."* By Prof. JAN DE VRIES.

1. By the equation

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = k^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

a system of similar ellipsoids is indicated.

The normal in a point P_1 on the ellipsoid containing this point is determined by

$$\frac{a^2(x-x_1)}{x_1}=\frac{b^2(y-y_1)}{y_1}=\frac{c^2(z-z_1)}{z_1},$$

or also by

$$x=\frac{a^2+u}{a^2}x_1\ ,\quad y=\frac{b^2+u}{b^2}y_1\ ,\quad z=\frac{c^2+u}{c^2}z_1\ . \quad . \quad . \quad (2)$$

For its orthogonal coordinates of rays, i. e. the quantities

$$p_1=x-x'\ ,\quad p_2=y-y'\ ,\quad p_3=z-z'\ ,$$
$$p_4=yz'-zy'\ ,\quad p_5=zx'-xz'\ ,\quad p_6=xy'-yx'\ ,$$

we find

$$p_1=\frac{u'-u}{a^2}x_1 \text{ etc.} \quad p_4=\frac{(b^2-c^2)(u'-u)}{b^2c^2}y_1z_1 \text{ etc.}$$

From this ensues that the ∞^3 normals of the system of ellipsoids form a quadratic complex with the equation

$$a^2p_1p_4+b^2p_2p_5+c^2p_3p_6=0. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

2. For the traces of the normal with XOZ and YOZ, we have successively $u''=-b^2$ and $u'=-a^2$, so

$$z''=\frac{c^2-b^2}{c^2}z_1 \text{ and } z'=\frac{c^2-a^2}{c^2}z_1.$$

Now follows from

$$z'':z'=(c^2-b^2):(c^2-a^2)$$

that the complex can be built up out of ∞^1 linear congruences, of which the directrices form two projective pencils of parallel rays situated in XOZ and YOZ having the direction OX and OY. So the complex is *tetraedral* and has as *principal points* O and the points X_∞, Y_∞, Z_∞ lying at infinity on the axes.

The trace of the ray of the complex with XOY is determined by $u'''=-c^2$. If we notice that the parameter u is proportional to the distance of the point P indicated by it to the point P_1, we see that out of

$$\frac{u'''-u'}{u'''-u''}=\frac{a^2-c^2}{b^2-c^2}$$

the characteristic anharmonic relation of the complex is obtained, namely

$$(P'\,P''\,P'''\,P^\infty)=(a^2-c^2):(b^2-c^2).$$

3. The footpoints P_1 of the normals let down out of P_0 lie evidently on the cubic curve

$$x=\frac{a^2x_0}{a^2+v},\ y=\frac{b^2y_0}{b^2+v},\ z=\frac{c^2z_0}{c^2+v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which passes through the points $P_0, O, X_\infty, Y_\infty, Z_\infty, (v=0, \infty, -a^2, -b^2, -c^2)$, and which is thus an orthogonal cubic hyperbola ω^3. Each of its points P_1 determines an ellipsoid, for which P_1P_0 is the normal in P_1.

Through a given point P_1 pass ∞^1 curves ω^3; their "*foci*" (Nullpunkte) P_0 are indicated by

$$a^2x_0 = (a^2+u)x_1, \; b^2y_0 = (b^2+u)y_1, \; c^2x_0 = (c^2+u)z_1; \quad . \quad (5)$$

so they lie on the normal having P_1 as footpoint.

These curves are all situated on the surface determined by the equations

$$x = \frac{(a^2+u)x_1}{a^2+v}, \quad y = \frac{(b^2+u)y_1}{b^2+v}, \quad z = \frac{(c^2+u)z_1}{c^2+v}, \quad . \quad . \quad . \quad (6)$$

or also by the equation obtained from these by elimination of u and v

$$\begin{vmatrix} a^2(x-x_1) & x & x_1 \\ b^2(y-y_1) & y & y_1 \\ c^2(z-z_1) & z & z_1 \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This same equation we obtain out of (3) if we express the coordinates of rays in the coordinates of points. *So the locus of the curves ω^3 passing through P_1 is the complex cone of P_1.*

Corresponding to this we find out of (6) for $v=$ const. a right line through P_1, whilst $u=$ const. indicates a curve ω^3 through P_1.

4. Out of the preceding ensues that all bisecants of a curve ω^3 are rays of the complex. This is further confirmed by the calculation of the coordinates of rays of the bisecant (v, v'). We find out of (4)

$$p_1 = \frac{a^2x_0(v'-v)}{(a^2+v)(a^2+v')}, \text{ etc.}$$

$$p_4 = \frac{b^2c^2y_0z_0(b^2-c^2)(v'-v)}{(b^2+v)(c^2+v)(b^2+v')(c^2+v')}, \text{ etc.}$$

from which ensues readily

$$a^2p_1p_4 + b^2p_2p_5 + c^2p_3p_6 = 0.$$

5. The planes of coordinates and the plane at infinity are the principal planes of the complex. The complex cone of a point lying in a principal plane must degenerate.

We truly find out of (7) for $z_1=0$ the planes $z=0$ and

$$(a^2-c^2)y_1x - (b^2-c^2)x_1y = (a^2-b^2)x_1y_1 \quad . \quad . \quad . \quad . \quad (8)$$

In connection with this the curve ω^3 consists now of the hyperbola

$$z=0, \qquad (a^2-b^2)xy + b^2y_1x - a^2x_1y = 0 \quad . \quad . \quad . \quad . \quad (9)$$

and the right line cut by it

$$(a^2-c^2)\,x = a^2 x_1 \quad , \quad (b^2-c^2)\,y = b^2 y_1 , \quad . \quad . \quad . \quad . \quad (10)$$

lying in the plane (8).

If in (7) we substitute $\lambda\varrho, \mu\varrho, \nu\varrho$ for x_1, y_1, z_1 and reduce it to the form

$$a^2\left(\frac{x}{\varrho}-\lambda\right)(\nu y-\mu z)+b^2\left(\frac{y}{\varrho}-\mu\right)(\lambda z-\nu x)+c^2\left(\frac{z}{\varrho}-\nu\right)(\mu x-\lambda y)=0,$$

then $\varrho=\infty$ furnishes the equation

$$(a^2-b^2)\,\lambda\mu z+(b^2-c^2)\,\mu\nu x+(c^2-a^2)\,\nu\lambda y=0, \quad . \quad . \quad (11)$$

which represents the plane containing the normals with the direction (λ, μ, ν). The footpoints of these normals lie evidently on the right line

$$x : \lambda a^2 = y : \mu b^2 = z : \nu c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

6. We determine with respect to the ellipsoid (k_0) the polar line of the normal n_1 having P_1 as footpoint.

For an arbitrary point P' of that normal we find the polar plane

$$\sum_3 \frac{a^2+u'}{a^4}\, x_1 x = k_0^{\,2}.$$

For all values of u' this plane passes through the line of intersection of the planes

$$\frac{x_1 x}{a^2}+\frac{y_1 y}{b^2}+\frac{z_1 z}{c^2}=k_0^{\,2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\frac{x_1 x}{a^4}+\frac{y_1 y}{b^4}+\frac{z_1 z}{c^4}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This line of intersection is the required polar line. When k_0 changes it displaces itself evidently parallel to itself.

Out of (13) and (14) we obtain the equation

$$\frac{(a^2-b^2)\,y_1 y}{b^4}+\frac{(a^2-c^2)\,z_1 z}{c^4}=k_0^{\,2},$$

which becomes identical with the equation

$$\frac{b^2 y}{y_2}-\frac{c^2 z}{z_2}=b^2-c^2$$

of a projecting plane of the normal n_2 with footpoint P_2, if the conditions are satisfied

$$\frac{(a^2-b^2)\,y_1}{k_0^{\,2} b^4}=\frac{b^2}{(b^2-c^2)\,y_2} \quad , \quad \frac{(a^2-c^2)\,z_1}{k_0^{\,2} c^4}=\frac{-c^2}{(b^2-c^2)\,z_2} .$$

From this we can deduce that the polar line of the normal n_1 with respect to the surface (k_0) is again a normal n_2; the footpoints P_1 and P_2 are connected with each other by the involutory relations

$$x_1\, x_2 = a^6\, k_0^2 : (a^2-b^2)\,(a^2-c^2),$$
$$y_1\, y_2 = b^6\, k_0^2 : (b^2-a^2)\,(b^2-c^2),$$
$$z_1\, z_2 = c^6\, k_0^2 : (c^2-a^2)\,(c^2-b^2).$$

By polarisation with respect to each of the ellipsoids the complex is thus transformed in itself. This agrees with a well known property of the tetraedal complex.

7. The footpoints of the normals are then arranged in an involutory quadratic correspondence, which transforms a right line into a twisted cubic, thus the tetraedal complex into a complex of twisted cubics which all pass through the points $O, X_\infty, Y_\infty, Z_\infty$. Let us now regard in general the transformation

$$xx' = \alpha^2 \;, \quad yy' = \beta^2 \;, \quad zz' = \gamma^2 \;. \quad . \quad . \quad . \quad . \quad (15)$$

It substitutes for the ray of the complex indicated by (2) the twisted curve

$$x' = \frac{a^2\,\alpha^2}{(a^2+u)\,x_1} \;, \quad y' = \frac{b^2\,\beta^2}{(b^2+u)\,y_1} \;, \quad z' = \frac{c^2\,\gamma^2}{(c^2+u)\,z_1} \;.$$

If we still put

$$\frac{\alpha^2}{x_1} = x_0 \;, \quad \frac{\beta^2}{y_1} = y_0 \;, \quad \frac{\gamma^2}{z_1} = z_0 \;, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

then this curve is indicated by

$$x' = \frac{a^2 x_0}{a^2+u} \;, \quad y' = \frac{b^2 y_0}{b^2+u} \;, \quad z' = \frac{c^2 z_0}{c^2+u} \;.$$

So it is the curve ω^3 belonging to the "*focus*" P_0, which corresponds in the transformation to the footpoint P_1 of the normal.

The complex of normals is thus transformed into the complex of the curves ω^3.

In connection with this the cone of the complex of P_1 passes into the locus of the curves ω^3 containing the point P_0, thus (§ 3) into the cone of the complex of P_0. Indeed the equation (7) does not change in form if we apply the relations (15) and (16).

8. If the vertex of the cone of the complex moves along the right line l represented by

$$x = \frac{\lambda_1\, x_1 + \lambda_2\, x_2}{\lambda_1 + \lambda_2} \;, \quad y = \frac{\lambda_1\, y_1 + \lambda_2\, y_2}{\lambda_1 + \lambda_2} \;, \quad z = \frac{\lambda_1\, z_1 + \lambda_2\, z_2}{\lambda_1 + \lambda_2},$$

then the cones form a system with index two represented by

$$\lambda_1^2\, U_1 + 2\,\lambda_1\,\lambda_2\, U_{12} + \lambda_2^2\, U_2 = 0,$$

where

$$U_1 = \sum_3 a^2 (x - x_1)(z_1 y - y_1 z) \quad , \quad U_2 = \sum_3 a^2 (x - x_2)(z_2 y - y_2 z).$$

$$2\, U_{12} = \sum_3 a^2 \{(x - x_2)(z_1 y - y_1 z) + (x - x_1)(z_2 y - y_2 z)\}.$$

The envelope of this system, at the same time the locus of the conics of the complex having l as chord, has for equation

$$U \equiv U_1 U_2 - U^2_{12} = 0.$$

The eight nodes which this biquadratic *surface of the complex* must possess are the points of intersection of the surfaces

$$U_1 = 0 \ , \quad U_{12} = 0 \ , \quad U_2 = 0 \ .$$

For we have

$$\frac{\partial U}{\partial x} = U_1 \frac{\partial U_2}{\partial x} + U_2 \frac{\partial U_1}{\partial x} - 2 U_{12} \frac{\partial U_{12}}{\partial x} \, .$$

so that $\frac{\partial U}{\partial x}$ disappears for each of those eight points of intersection.

To these nodes evidently belong the points $O, X_\infty, Y_\infty, Z_\infty$; the four other ones change their places with the right line l.

That l is double right line of the surface of the complex is immediately proved by the substitution $x = x_1 + \lambda\varrho$, $y = y_1 + \mu\varrho$, $z = z_1 + \nu\varrho$; on account of $z_1 y - y_1 z = \varrho\,(\mu z_1 - \nu y_1)$ we see that U then obtains the factor ϱ^2.

Mathematics. — "*On a group of complexes with rational cones of the complex.*" By Prof. JAN DE VRIES.

§ 1. In a communication included in the Proceedings of May 1903 [1]), I have treated a group of complexes of rays possessing the property that the cone of the complex of an arbitrary point is rational. In the following a second group will be indicated with the same particularity.

We consider a pencil (s) with vertex S in the plane σ, and in a second plane τ a system of rays $[t]_n$ with index n (thus the system of the tangents of a rational curve τ_n) and we suppose the rays t to be projectively conjugate to the rays s. The transversals of homologous rays form a complex, which will be investigated here.

Out of an arbitrary point P the pencil (S, σ) is projected on the plane τ in a pencil (S', τ), projective to $[t]_n$. Together these systems of rays generate a curve of order $(n+1)$ having in S' an n-fold point; for on an arbitrary ray s' through S' lies outside S' the point

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[1]) "On complexes of rays in relation to a rational skew curve." VI, p. 12—17.

of intersection of s' with the corresponding ray t; on the rays s' conjugate to the n rays t passing through S' this point of intersection falls in S', so that the locus of the point (s', t) must pass n times through S'; the curve is therefore of order $(n+1)$.

The cone (P) *of the complex is of order* $(n+1)$ *and of class* $2n$ *and has an n-fold edge* PS.

§ 2. If the point S' lies on the envelope τ_n two of the n rays t passing through S' coincide, so also two of the tangent planes through PS to the cone (P).

The locus of the points P *for which two tangent planes through the n-fold edge of the cone of the complex coincide is the cone* Σ *of order* $2(n-1)$ *projecting the envelope* τ_n *out of* S.

The $3(n-2)$ cuspidal edges of Σ contain the points P, for which three of the tangent planes of (P) coincide along the n-fold edge. The $2(n-2)(n-3)$ double edges of Σ form the locus of the points P, for which two pairs of tangent planes of P coincide along PS.

The cone Σ is a part of the *singular surface* of the complex; the remaining parts are planes.

To these belongs in the first place the plane σ. Each right line of σ is cut by n rays t, can thus be regarded n times as ray of the complex. Consequently σ is an *n-fold principal plane.* In connection with this the cone of the complex of a point P assumed in σ degenerates into n planes coinciding with σ and into the plane through P and the right line t corresponding to the ray s determined by P.

On the contrary τ is *single principal plane,* for each of its right lines rests on but one ray s. The cone of the complex of a point P lying in τ degenerates into τ and into the n planes through P and the n rays s corresponding to the n right lines t through P.

Finally there are still $(n+1)$ *principal planes* γ_k, $(k=1 \text{ to } n+1)$, each connecting two homologous rays s, t. For the points of the line of intersection of σ and τ are arranged by the projective systems (s) and $[t]_n$ in a $(1, n)$ correspondence; in each of the $(n+1)$ points of coincidence C_k two homologous rays meet. In connection with this the cone of the complex of a point P assumed in one of these principal planes degenerates into the combination of this principal plane with a cone of order n, for of the projective systems (s') and $[t]_n$ lying in τ two homologous rays coincide.

§ 3. The *curve of the complex* (π) in the arbitrary plane π is of class $(n+1)$ and has the line of intersection $(\sigma\pi)$ as n-fold tangent;

so it is of order $2n$. Its points of contact with $(\sigma\,\pi)$ are determined on $(\sigma\,\pi)$ by the n rays s corresponding to the n rays t through the point $(\sigma\,\tau\,\pi)$.

If π passes through one of the $2\,(n-1)$ points of intersection of σ with the envelope τ_n two of the points of contact of $(\sigma\,\pi)$ coincide. Regarded as locus of points (π) then consists of a curve of order $(2n-1)$ and the right line $(\sigma\,\pi)$.

The planes containing curves of the complex for which two points of contact of the multiple tangent coincide form $2(n-1)$ *sheaves having their vertices on the line of intersection of* σ *and* τ.

If π passes through a ray s_1, then (π) as envelope consists of a pencil having its vertex in the trace of the homologous ray t_1 and of the pencil (S, π) of which each ray belongs n times to the complex, because it is intersected by n rays t. As locus of points (π) is here the line connecting the vertices of the pencils counted $2n$ times.

If π contains a ray t_1 the envelope (π) consists of a pencil having the trace S_1 of the homologous ray s_1 as vertex and of a curve of class n for which $(\sigma\,\pi)$ is an $(n-1)$-fold tangent. As figure of order $2n$ the curve (π) breaks up into a curve of order $2(n-1)$, its $(n-1)$ fold tangent and the tangent which can moreover be drawn to it out of S_1.

If one brings π through one of the coincidences C_k, then (π) breaks up in the same way into a pencil with vertex C_k and a curve of class n.

The complex possesses an n-fold principal point S and $(n+1)$ *single principal points* C_k.

§ 4. Let us now consider the surface of the complex Δ of an arbitrary right line l, thus the envelope of the rays of the complex resting on l. The rays in a plane π brought through l envelop a curve (π) of order $2n$ (§ 3). If π is one of the $2n$ tangent planes through l to the cone of the complex of the point P lying on l, then two of the tangents drawn out of P to (π) coincide, so that P is a point of (π). So each point of l belongs to $2n$ curves of the complex; consequently l is a $2n$-fold right line of Δ.

The surface of the complex is of order $4n$.

In the planes connecting l with the principal points C_k the curve (π) breaks up into a curve of order $2\,(n-1)$ and two right lines. This also takes place when π passes through one of the n rays t resting on l. In the plane through l and S the curve (π) degenerates into a right line to be counted $2n$ times.

In each of the planes connecting l with the points of intersection of τ_n and σ the curve (π) consists of a curve of order $(2n-1)$ and a right line (§ 3).

On Δ lie besides the 2n-fold right line and a 2n-fold torsal right line 6n single right lines more.

The plane σ contains $2(n-1)$ right lines of Δ and touches Δ in the points of a curve of order $(n+1)$, which is the locus of the points where the curve of the complex (π) touches its n-fold tangent $(\sigma\pi)$. For, if the ray s_0 resting on l corresponds to the ray t_0 cutting σ in T_0, then one of the points of contact of the curve of the complex of the plane $(l T_0)$ with σ lies in the trace L_σ of l; consequently the indicated points of contact lie on a curve of order $(n+1)$. This curve is generated by the pencils (L_σ) and (S) arranged in a $(1, n)$ correspondence; so it has in S an n-fold point.

The plane τ touches Δ according to a curve of order $(n+1)$ which is the locus of the points of contact of the curves (π), in planes π through l, with the traces $(\pi\tau)$. This curve has an n-fold point in the trace L_τ of l on τ; the tangents in this multiple point are the traces of the planes π cutting $(\sigma\tau)$ on the n rays s conjugate to the rays t drawn out of L_τ.

The plane τ has farthermore the envelope τ_n in common with Δ. For, while a point P of the right line $(\pi\tau)$ bears in general n tangents of the curve of the complex (π) determined by the rays s corresponding to the n rays t drawn through P, two of those tangents coincide as soon as P lies on the envelope τ_n; then however P belongs to the curve (π), thus to the surface of the complex Δ.

Microbiology. — "*An obligative anaerobic fermentation Sarcina.*"

By Prof. M. W. Beijerinck.

The following simple but yet delicate experiment gives rise to a vigorous fermentation, caused by a sarcine, wherein microscopically no other microbes are perceptible and which, when rightly performed, can produce a real pure culture of this fermentation organism. The simplicity of the experiment is the result of many previous investigations, partly made conjointly with Dr. N. Goslings, which have gradually rendered clear the conditions of life of the examined microbe.

Bouillon with 3 to 10 $^0/_0$ glucose, or malt wort, is acidified with phosphoric acid to an acidity of 8 cc. normal per 100 cc. of culture liquid and introduced into a bottle, which is quite filled with it and fitted with a tube to remove the gas. The infection is done with an *ample quantity*[1]) of garden soil, from which the heaviest and roughest portion has been removed, but in which so much solid substance is left behind that in the nutrient liquid it forms a muddy deposit from 5 to 7 or more millimeters thick. The culture is effected in a thermostat at 37° C. After 12 hours already the liquid is in a strong fermentation, which lasts from 24 to 36 hours, and whereby the surface is covered with a rough scum, produced by gas bubbles mounting up from the depth. Whilst the liquid itself remains wholly free from microbes, the microscopical image of the deposit shows a luxuriant, pure or almost pure culture of a sarcine, of which the elementary cells measure for the greater part about 3.5 μ, so that the species belongs to the largest forms known, and the multicellular sarcine-packages are easily visible to the naked eye. The cells are colorless and transparent and the packages present irregular sides. Here and there, but much less generally, a brownish intransparent form is seen, with more regularly cubical packages of which the cells measure 2 to 2,5 μ.

The scum floating on the fermenting fluid consists of slime in which the evolved gas remains for a time imprisoned. This slime is produced by the outer side of the sarcine cells, whose walls for the rest consist of cellulose, which becomes violet-blue by zinc-chloride and jodine. This reaction was discovered in 1865 in the stomacal sarcine by SURINGAR[2]), who on this account argued the vegetal nature of this organism, which fully corresponds to the small-celled fermentation sarcine. The large-celled form more resembles the figures which LINDNER[3]) gives of his *Sarcina maxima*, found, as he expresses it, in "Buttersäuremaischen", hence, in wort wherein a spontaneous butyric fermentation. I am not, however, convinced that both these forms do really belong to two different species of sarcine, as it is well known that in this genus of microbes great morphological differences may occur in the same species.

The gas is a mixture of about 75 % carbonic acid and 25 % hydrogen; methan is not present. Besides, a moderate quantity of acid is formed, which for example, in a nutrient liquid with an acidity of 6 cc. per 100, may mount to 12 cc., a percentage only found back in the technical lactic fermentations. Furthermore a peculiar odor originates, reminding of the ordinary lactic-acid fermentation, by

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[1]) With *little soil for infection*, the experiment becomes doubtful.

[2]) W. F. R. SURINGAR, De sarcine (*Sarcina ventriculi* GOODSIR), pag. 7, Leeuwarden 1865. Here very good figures are to be found.

[3]) Mikroskopische Betriebscontrolle in den Gärungsgewerben, 3e Aufl. p. 432, 1901.

Lactobacillus. If, as is probable, this acid will prove to consist entirely, or for the greater portion, of lactic acid, the fermentation sarcine may be considered as the most differentiated lactic-acid ferment hitherto known.

When using a sufficient quantity of soil for the infection, that is a relatively great number of sarcines, which thereby, in the given circumstances, may compete with advantage with, and conquer all other microbes, the experiment described succeeds within very wide limits. Thus the sarcine fermentation may *in this case be obtained as well in an open flask as in a closed bottle,* whence it follows that the sarcine can suffer a moderate quantity of oxygen; and it will appear below, that a slight quantity is even wanted under all circumstances. Notwithstanding this, the name of obligative anaerobic remains applicable as the cultivation at full atmospheric pressure is impossible. The acid may further be varied between 3 and 11 cc. normal phosphoric acid per 100 cc.. The phosphoric acid may be replaced by lactic and even by hydrochloric acid, if the acidity of the latter is not taken higher than 6 to 7 cc. per 100 cc., but not by nitric acid.

Instead of glucose cane sugar may be used, but with milk sugar and mannite the experiment does not succeed. As source of nitrogen only peptone can be used, such as found in malt-wort or bouillon; simpler nitrogen sources, like asparagin, ureum, ammonia and saltpeter, are unfit for the nitrogen nutrition of the sarcine. The limits of the temperature are wide and may vary between 28° C. and 41° C.

Although the experiment may thus be modified in many respects, the first described arrangement is recommendable, as it is best adapted to the optimum of the different conditions of life of the organism.

A property peculiarly important for this research is the readiness with which the function of fermenting, that is the power of evolving gas, gets lost under the influence of a secretion product, probably the acid, and through which all transports with old material become perfectly useless. Hence it is necessary to transport cultures still in fermentation to insure the success of further experiments.

That some aeration enhances the life-functions of this obligative anaerobic and that access of a little air is even necessary in the long run, is evident from the fact that the most vigorous fermentations are obtained in a closed bottle, with the deposit got in an open flask, whereas renewing of the nutrient liquid formed above the deposit in a closed bottle will after few repetitions give rise to diminuation or cessation of the fermentation.

For the continuation of the culture by inoculating *slight quantities* of material of a rough fermentation into the same nutrient liquid, two precautions should be taken. First, the inoculation should be done into the medium, freed from air by boiling, the bottle being entirely filled with the hot liquid, so that on cooling no air can dissolve. Second, an acidity of less than 7 proves not sufficient, hence this should be 8 or 10 cc., as otherwise the lactic acid ferments might prevail and supplant the sarcine.

From the necessity of expelling the air we see that the fermentation sarcine undoubtedly belongs to the ordinary anaerobies, which, considering the success of the rough accumulation experiment *with aeration*, might perhaps not have been expected; but the fact holds good in the same way for the butyric acid ferment, generally accepted as an obligative anaerobic, so that, also with respect to the fermentation sarcine, there should be spoken of "microaerophily." Further examination shows that in deep test-tubes with maltwort-agar, very easily pure cultures may be obtained, whereby the sarcine is recognisable by the obvious size and the remarkably rapid development of its colonies. On the other hand, on maltwort, or broth-bouillon-glucose-agar-plates with or without acid at 37° C., with access of air, no growth at all of the sarcine takes place, as might be expected. Of course the packages can also be seen on the plates without growing and be removed in a pure condition. When we make use of little acid for the rough accumulation, colonies of lactic acid ferments, belonging to the physiological genus *Lactobacillus*, will develop on the plates at the air, which can grow as well with as without air, but whose other life conditions correspond to those of the sarcine. In this case the experiment shows at the same time that everywhere in garden soil real lactic acid ferments are present, whereof the proof had not been given until now.

When using much acid, for example 10 cc. or more normal acid per 100 cc. of culture fluid, through which the vital functions of the sarcine, such as rapidity of growth and the faculty of assimilating oxygen, are lessened, certain alcohol ferments, proper to garden soil, come to development, but they can, together with some of the other impurifications of the rough accumulations, as moulds, *Mucor* and *Oidium*, be checked and expelled by exclusion of air, hence, by culture in closed bottles. To this end however, it is necessary to render the conditions for the sarcine as favorable as possible and not allow a temperature below 37° C.

The staying out of the butyric acid fermentation (caused by *Granulobacter saccharobutyricum*), which so readily originates with exclusion of air in glucose-bouillon and maltwort, is due to the acidity of about 8 cc. or more, whereby this fermentation becomes impossible.

Although it is evident from the foregoing, that the growth of the sarcine is less inhibited by the acid than that of the lactobacilli and of the butyric ferment, it may still be easily proved that already 7 cc. acid per 100 cc., are less favorable than 3 or 5 cc., also for the development of the sarcine itself, so that the higher amount of acid in the accumulation only serves to render competition with the said ferments possible. If by timely transports into maltwort with more than 8 cc. phosphoric acid, or by separation in solids, real pure cultures are at disposal, the further transfers, with entire omission of the acid, show that then also vigorous growth and fermentation may occur. We thus see how wide the limits are of the life conditions of the sarcine, as soon as competition with all other microbes is quite out of question.

The discovery of this certainly unexpected fermentation has sprung from the working out of the general question which organisms of the soil can develop in a sugar-containing culture fluid in presence of an acid and with imperfect aeration. At temperatures of about 30° C. and lower, alcoholferments, *Mucor racemosus* and *Oidium* prove to be the strongest, but then already a few sarcines are observed. At about 40° C. most alcoholferments of garden soil, besides *Mucor* and *Oidium* can no more compete with the sarcine and the lacto bacilli, which then become predominant. This being fixed the last steps which led to the culture of the fermentation sarcine alone, were the recognition of the obligative anaerobiosis, and of the superiority of the resistence of the sarcine with respect to anorganic acids compared with that of *Lactobacillus* and the butyric ferments.

Above, already, I pointed to the perfect correspondence of the small-celled form of the fermentation sarcine to the description which SURINGAR gives of the stomacal sarcine, and I suppose that in the cases of non-cultivable *Sarcina ventriculi*, of which, for instance, DE BARY speaks[1]), there should really be thought of the fermentation sarcine. This view is supported by different observations in the older literature, cited by SURINGAR. But still more convincing is my accumulation experiment, which proves that the conditions for the existence of this sarcine are just of a nature to render its life in the stomach possible.

It will be easy to obtain certainty thereabout by a repetition of

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[1]) Vorlesungen über Bacterien, 1e Aufl. pg. 96, 1887.

this experiment, not with garden soil for infection material, but by using the stomacal contents of such a case of stomacal sarcine. The "not cultivability" of DE BARY may mean the same as anaerobiosis, for it is well known how difficult it is, even at the present time, to cultivate anaerobics if the particulars of their life conditions are not exactly known.

For the rest I do not doubt of the precision of FALKENHEIM's [1]) and MIGULA's [2]) observations, who have seen aerobic colonies of micrococci originate from stomacal sarcine. It is true that I for my part have not succeeded in confirming this observation with regard to the fermentation sarcine, but for other species of *Sarcina* I have, with certainty, stated the transition into micrococci, and with various anaerobics, although not belonging to the genus *Sarcina*, I have seen now and then colonies originate of facultative anaerobics, which in all other respects, corresponded to the obligative anaerobics used for the cultures. Therefore this modification also seems possible for some individuals of the fermentation sarcine. Accumulation or transfer experiments with stomacal contents will however only then give positive results, if these are used when still in fermentation; with long kept material nothing can be expected.

Already the older observers [3]) as SCHLOSSBERGER (1847), SIMON (1849) and CRAMER (1858) have tried, although in vain, by a kind of accumulation experiments, to cultivate the stomacal sarcine, wherefore they prepared, as nutrient liquid, artificial gastric juice with different additions. Remarkable, and illustrating the biological views of those days, is the fact, that for the infection they did not use the stomacal contents themselves, but beer yeast, supposing, that the sarcine might originate from the yeast cells, which somewhat resemble it, and are always found in the stomach together with the sarcine itself.

Physics. — "*The motion of electrons in metallic bodies.*" II. By Prof. H. A. LORENTZ.

(Communicated in the meeting of January 28, 1905).

§ 11. By a mode of reasoning similar to that used in the last §, we may deduce a formula for the intensity i of the current in a *closed* thermo-electric circuit. For this purpose we have only to suppose the ends P and Q, which consist, as has been said, of the

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[1]) Archiv f. experiment. Pathologie und Pharmacologie. Bd. 10, pg. 339, 1885.

[2]) System der Bacteriën. Bd. 2, pg. 259, 1900.

[3]) Cited from SURINGAR (l. c.).

same metal and are kept at the same temperature, to be brought in contact with each other. The potentials φ_P and φ_Q will then become equal, but the stream of electrons ν will no longer be 0. We shall have on the contrary, denoting by Σ the normal section, which may slowly change from point to point, as has already been observed,

$$i = e\,\nu\,\Sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Taking this into account and using (23), we get from (21) and (30)

$$\frac{d\varphi}{dx} = -\frac{1}{e}\frac{dV}{dx} - \frac{m}{e}\frac{d}{dx}\left(\frac{1}{h}\right) - \frac{m}{2eh}\frac{d\log A}{dx} - \frac{1}{\sigma\Sigma}\,i.$$

We shall integrate this along the circuit from P to Q. Since i has the same value everywhere and

$$\varphi_P = \varphi_Q\,, \quad V_P = V_Q\,, \quad h_P = h_Q,$$

we find

$$-\frac{m}{2e}\int_P^Q \frac{1}{h}\frac{d\log A}{dx}\,dx - i\int\frac{dx}{\sigma\Sigma} = 0.$$

Here, the first term is reduced to the form (34), if we integrate by parts. Hence, if we put

$$\int\frac{dx}{\sigma\Sigma} = R\,,$$

the result is

$$F = i\,R, \quad i = \frac{F}{R},$$

as was to be expected. Indeed, σ being the coefficient of conductivity, R is the resistance of the circuit.

§ 12. We shall now proceed to calculate the heat developed in a circuit in which there is an electric current i, or rather, supposing each element of the wire to be kept at a constant temperature by means of an external reservoir of heat, the amount of heat that is transferred to such a reservoir per unit time. Let us consider to this effect the part of the circuit lying between the sections whose positions are determined by x and $x + dx$ and let $w\,dt$ be the work done, during the time dt, by the forces acting on the electrons in this element. $W\Sigma$ being the quantity of heat traversing a section per unit time, we may write

$$\frac{d}{dx}(W\,\Sigma)\,dx$$

for the difference between the quantities of heat leaving the element at one end and entering it at the other, and the production of heat is given by

$$q = w - \frac{d}{dx}(W\Sigma)\,dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (37)$$

In order to determine w, we observe in the first place that the work done, during the time dt, by the force acting on a single electron is

$$m\,X\,\xi\,dt$$

and that, by the formula (1), the element Σdx contains

$$f(\xi, \eta, \zeta)\,\Sigma\,dx\,d\lambda$$

electrons having their velocity-points within the element $d\lambda$ of the diagram of velocities. Taking together the forces acting on all these particles, we find for their work

$$m\,X\,\Sigma\,dx\,dt\,.\,\xi f(\xi, \eta, \zeta)\,d\lambda\,,$$

an expression that has yet to be integrated over the whole extent of the diagram. On account of (4), the result becomes

$$m\,X\,\mathbf{v}\,\Sigma\,dx\,dt\,,$$

so that, by (36)

$$w = \frac{miX}{e}\,dx\,.$$

Now, the value of X may be taken from (21). Substituting

$$\mathbf{v} = \frac{i}{e\Sigma}$$

and using at the same time (23), we find

$$X = \frac{1}{2h}\,\frac{d\,log\,A}{dx} + \frac{d}{dx}\left(\frac{1}{h}\right) + \frac{e\,i}{m\sigma\Sigma}, \quad . \quad . \quad . \quad . \quad . \qquad (38)$$

so that

$$w = w_1 + w_2\,,$$

if we put

$$w_1 = \frac{mi}{e}\left[\frac{1}{2h}\,\frac{d\,log\,A}{dx} + \frac{d}{dx}\left(\frac{1}{h}\right)\right]dx. \quad . \quad . \quad . \quad . \quad . \qquad (39)$$

and

$$w_2 = \frac{i^2}{\sigma\Sigma}\,dx.$$

The expression (22) may likewise be transformed by introducing into it the value (38), or, what amounts to the same thing, the value of

$$2\,h\,A\,X - \frac{dA}{dx}\,,$$

that may be drawn from (21). One finds in this way

$$W = W_1 + W_2\,,$$

if

$$W_1 = \frac{2\pi m l A}{3h^3} \frac{dh}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

and

$$W_2 = \frac{m}{h} \mathfrak{r} = \frac{mi}{e \Sigma h}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

§ 13. The expression (37) for the amount of heat produced in the element dx may now be divided into *three* parts.

The first of these

$$w_2 = \frac{i^2}{\sigma \Sigma} dx$$

corresponds to JOULE's law. Indeed $\frac{dx}{\sigma \Sigma}$ is the resistance of the part of the circuit extending from (x) to $(x + dx)$.

The second part

$$- \frac{d}{dx} (W_1 \Sigma) dx$$

is entirely independent of the current, as appears from (40). It may therefore be considered to be due to ordinary conduction of heat. This is confirmed by comparing it with what has been said in § 9.

It remains to consider the quantity of heat

$$q' = w_1 - \frac{d}{dx} (W_2 \Sigma) dx,$$

or, if (39) and (41) are taken into account,

$$q' = \frac{m\, i}{2\, e\, h} \frac{d \log A}{dx} dx.$$

This expression, proportional to the current and changing its sign if the latter is reversed, will lead us to formulae for the PELTIER-effect and the THOMSON-effect. Reduced to unit current, it becomes

$$q'_{i=1} = \frac{m}{2eh} \frac{d \log A}{dx} dx \quad . \quad . \quad . \quad . \quad . \quad (42)$$

a. I shall suppose in the first place that, between two sections of the circuit, there is a gradual transition from the metal I to the metal II, the temperature and consequently h being the same throughout this part of the circuit. Then, reckoning x from the metal I towards II, and integrating (42), I find for the heat produced at the "place of contact" by a current of unit strength flowing from I towards II,

$$\frac{m}{2\, e\, h} \log \left(\frac{A_{II}}{A_I} \right) = \frac{2\, \alpha\, T}{3\, e} \log \left(\frac{A_{II}}{A_I} \right).$$

Hence, if we characterize the Peltier-effect by the *absorption* of heat $\Pi_{I,\,II}$ taking place in this case,

$$\Pi_{I,\,II} = \frac{2\,\alpha\,T}{3\,e}\,log\left(\frac{A_I}{A_{II}}\right) = \frac{2\,\alpha\,T}{3\,e}\,log\left(\frac{N_I}{N_{II}}\right) \quad . \quad . \quad . \quad (43)$$

b. In the second place, substituting again for h the value (14), we shall apply (42) to a homogeneous part of the circuit. We have then to consider $log\,A$ as a function of the temperature T, so that we may write

$$q'_{i=1} = \frac{2\,\alpha\,T}{3\,e}\,\frac{d\,log\,A}{dT}\,dT$$

for the heat developed between two points kept at the temperatures T and $T + d\,T$, if a current of unit strength flows from the first point towards the latter. What Kelvin has called the "specific heat of electricity" (Thomson-effect) is thus seen to be represented by

$$\mu = -\frac{2\,\alpha\,T}{3\,e}\,\frac{d\,log\,A}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

§ 14. An important feature of the above results is their agreement with those of the well known thermodynamic theory of thermo-electric currents. This theory leads to the relations

$$\mu_{II} - \mu_I = T\,\frac{d}{dT}\left(\frac{\Pi_{I,\,II}}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

and

$$F = -\int_{T'}^{T''} \frac{\Pi_{I,\,II}}{T}\,dT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

in which μ_I and μ_{II} are the specific heats of electricity in the metals I and II, at the temperature T, whereas F denotes what we have calculated in § 10, viz. the electromotive force in a circuit composed of these metals and whose junctions are kept at the temperatures T' and T'', the force being reckoned positive if it tends to produce a current which flows from I towards II through the first junction.

The values (44), (43) and (35) are easily seen to satisfy the equations (45) and (46).

Instead of verifying this, we may as well infer directly from (42) that our results agree with what is required by the laws of thermodynamics. On account of the first of these we must have

$$\Sigma\,q'_{i=1} = -F$$

and by the second

$$\Sigma \frac{q'_{i=1}}{T} = 0,$$

the sums in these formulae relating to all elements of the closed circuit we have examined in § 11. Now, by (42), these formulae become

$$F = -\frac{m}{2e}\int_P^Q \frac{1}{h}\frac{d \log A}{dx}\, dx$$

and

$$\int_P^Q \frac{1}{hT}\frac{d \log A}{dx}\, dx = 0.$$

The first of these equations is identical with (34) and the second holds because hT has everywhere the same value.

It must also be noticed that the formula (35) implies the existence of a *thermo-electric series* and the well known law relating to it. This follows at once from the fact that the value (35) may be written as the difference of two integrals depending, for given temperatures of the junctions, the one on the properties of the first and the other on those of the second metal. Denoting by III a third metal, we may represent by $F_{I,\,II}$, $F_{II,\,III}$, $F_{III,\,I}$ the electromotive forces existing in circuits composed of the metals indicated by the indices, the junctions having in all these cases the temperatures T' and T'' and the positive direction being such that it leads through the junction at the first temperature from the metal indicated in the first towards that indicated in the second place. Then it is seen at once that

$$F_{I,\,II} + F_{II,\,III} + F_{III,\,I} = 0 \, . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (47)$$

Strictly speaking there was no need to prove this, as it is a consequence of the thermodynamic equations and our results agree with these.

§ 15. In what precedes we have assumed a *single* kind of free electrons. Indeed, many observations on other classes of phenomena have shown the negative electrons to have a greater mobility than the positive ones, so that one feels inclined to ask in the first place to what extent the facts may be explained by a theory working with only *negative* free electrons.

Now, in examining this point, we have first of all to consider the absolute value of the electromotive force F. If we suppose the temperatures T' and T'' to differ by one degree and if we neglect the variability of N_I and N_{II} in so small an interval, we may write for (35)

$$F_1 = \frac{2\,a}{3\,e} \log \frac{N_{II}}{N_I},$$

$$\log \frac{N_{II}}{N_I} = \frac{3\,e}{2\,a} \, . \, F_1 \, .$$

The value of the first factor on the righthand side may be taken from what, in § 9, we have deduced from the electrochemical aequivalent of hydrogen [1]. We found for $T = 291$

$$\frac{aT}{e} = 38 \times 10^5 .$$

so that

$$\log \frac{N_{II}}{N_I} = 0{,}00011 \, F_{1°} .$$

In the case of bismuth and antimony, $F_{1°}$ amounts to 12000, corresponding to

$$\log \frac{N_{II}}{N_I} = 1{,}32 \quad ; \quad \frac{N_{II}}{N_I} = 3{,}7$$

I see no difficulty in admitting this ratio between the number of free electrons in two metals wide apart from each other in the thermo-electric series [2].

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[1] The numbers of that § contain an error which, however, has no influence on the agreement that should be established by them. The value of $3\,p$ and that of $\frac{\alpha T}{e}$ deduced from the measurements of Jaeger and Diesselhorst are not 38 and 47, but

$$3\,p = 38 \times 10^5$$

and

$$\frac{aT}{e} = 47 \times 10^5 .$$

[2] Let n be the mean value of $\log \frac{N_{II}}{N_I}$ between the temperatures T' and T''. Then the equation (35) may be put in the form

$$Fe = \frac{2}{3}\, n\, a\, (T'' - T') .$$

This may be expressed as follows: The work done by the electromotive force in case one electron travels around the circuit is found if we multiply by $\frac{2}{3}\,n$ the increase of the mean kinetic energy of a gaseous molecule, due to an elevation of temperature from T'' to T'''.

The question now arises whether it will be possible to explain all observations in the domain of thermo-electricity by means of suitable assumptions concerning the number of free electrons. In order to form an opinion on this point, I shall suppose the PELTIER-effect to be known, at one definite temperature T_0, for all combinations of some standard metal with other metals and the THOMSON-effect to have been measured in all metals at all temperatures. Then, after having chosen arbitrarily the number N_0 of free electrons in the standard metal at T_0, we may deduce from (43) the corresponding values for the other conductors, and the equation (44) combined with (13) and (14), will serve to determine, for all metals, the value of N at any temperature we like. Now, the numbers obtained in this way, all of which contain N_0 as an indeterminate factor, will suffice to account for all other thermo-electric phenomena, at least if we take for granted that these phenomena obey the laws deduced from thermodynamics. Indeed, these laws leading to the relation

$$\Pi_{I,II} + \Pi_{II,III} + \Pi_{III,I} = 0,$$

similar to (47), the values of N we have assumed will account not only for the PELTIER-effect at the temperature T_0 for all metals combined with the standard metal, but also for the effect, at the same temperature, for any combination. Finally, we see from (45) that the value of $\Pi_{I,II}$ at any temperature may be found from that corresponding to T_0, if we know the THOMSON-effect for all intermediate temperatures and from (46) that the values of the electromotive force are determined by those of Π.

There is but one difficulty that might arise in this comparison of theory with experimental results; it might be that the assumptions we should have to make concerning the numbers N would prove incompatible with theoretical considerations of one kind or another about the causes which determine the number of free electrons.

As to the conductivities for heat and electricity, it would always be possible to obtain the right values from (24) and (27), provided only we make appropriate assumptions concerning the length l of the free path between two encounters [1]).

It must be noticed, however, that, whatever be the value of this length, the foregoing theory requires that the ratio $\frac{k}{\sigma}$ shall be the

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[1]) If the electric conductivity were inversely proportional to the absolute temperature, as it is approximately for some metals, and if we might neglect the variations of N, the formula (24) would require that l is inversely proportional to $\sqrt{T}$. I am unable to explain why N should vary in this way.

same for all metals. The rather large deviations from this law have led DRUDE to assume more than one kind of free electrons, an hypothesis we shall have to discuss in a sequel to this paper. For the moment I shall only observe that one reason for admitting the existence not only of negative but also of positive free electrons lies in the fact that the HALL-effect has not in all metals the same direction.

(March 22, 1905).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday March 25, 1905.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 25 Maart 1905, Dl. XIII).

CONTENTS.

The following papers were read:

Mathematics. — *"On moments of inertia and moments of an arbitrary order in spaces of arbitrary high rank."* By Prof. Dr. R. Mehmke at Stuttgart. (Communicated by Prof. P. H. Schoute).

In the "Mathematische Annalen" Vol. 23 (1884) pages 143—151 I have pointed out a manner of calculating the moments of inertia, leading easily and quickly to the purpose and being independent of the number of dimensions. As an instance I chose the case of a figure filled with a homogeneous matter in the space of $(n-1)$ dimensions, analogous to the tetrahedron, thus according to the well-known expression of Mr. Schoute a simplex S_n. Without being acquainted with this Mr. Schoute has lately treated this case in another way in the "Rendiconti del Circolo Matematico di Palermo", Vol. XIX (1905) and has arrived at the same result. Instead of contenting myself with the reference to these facts I wish to communicate how in the same way moments of any higher order than the second can be found. It is true this problem has been prepared in the above mentioned place, pages 146—147, for a simplex so far, that but a slight step would have been necessary to bring about its solution.

Let us presuppose a flat space of $(n-1)$ dimensions, a space of "rank" ("Stufe") n as GRASSMANN expressed it as early as 1844, or of "point-value" n as Prof. SCHOUTE has said in his excellent textbook on polydimensional geometry. The moment M_ν of order ν of an arbitrary material figure belonging to this space with respect to a space E of rank $(n-1)$ (thus $n-2$ dimensions) contained in the same space is

$$M = \int r^\nu \, dm,$$

where r indicates the distance of a central point p in an element of that figure from E, dm the mass of the element. According to GRASSMANN however

$$r = [E\,p],$$

i. e. equal to the "outer" product of E and p, when we assign both to E and p the numerical value 1, consequently

$$M_\nu = \int [E\,p]^\nu \, dm \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

I assume that ν is a positive integer. If ν is an even number and if the moment is to be calculated with respect to a space A of a rank smaller than $(n-1)$, if thus it is e. g. a case of a moment of inertia with respect to an axis $(\nu=2)$, then according to GRASSMANN

$$r^2 = [Ap \mid Ap],$$

where the symbol $\mid$ denotes the "inner" multiplication, and we arrive at

$$M_\nu = \int [Ap \mid Ap]^{\frac{\nu}{2}} \, dm. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad b)$$

The integrals appearing in a) and b) can be evaluated by one and the same integration, if we make use of the very useful notion of the "gap-expressions" introduced by GRASSMANN. If namely we place the point p appearing in $[Ep]^\nu$ or in $[Ap \mid Ap]^{\frac{\nu}{2}}$ symbolically outside the brackets and if with PEANO we indicate every gap thus formed by $*$, we arrive at

$$r^{\nu} = [E*]^{\nu} . p^{\nu} \quad \text{resp.} \quad r^{\nu} = [\Delta * | \Delta *]^{\overset{\nu}{2}} . p^{\nu}$$

or

$$r^{\nu} = Lp^{\nu},$$

where the expression L (furnished with ν gaps) is equal to $[E*]^{\nu}$ in the first case and to $[\Delta * | \Delta *]^{\overset{\nu}{\overline{2}}}$ in the second. The expression L remaining constant in the integration it can be placed before the symbol $\int$ of the integral, so that we get

$$M_{\nu} = L . \int p^{\nu} \, dm = Lp^{(\nu)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

This has reduced our problem to the determination of the "point-quantity of order ν"

$$p^{(\nu)} = \int p^{\nu} \, dm, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

belonging to the given material figure. (The ν^{th} power of a point p we have to imagine as the ν-fold point p. The algebraic product of ν different points is the total of these points, where on account of the interchangeability of the factors of an algebraic product the order of succession of the points is arbitrary. The sum of an arbitrary number of such like quantities has primarily but a formal meaning, but then it may be represented geometrically by a figure of order ν, the analogon of the ellipsoid of inertia). The integral 2) is dependent only on the form and the distribution of the mass of the given material figure, and whilst when treating our problem in the usual way with the aid of cartesian coordinates the space E or Δ may have a very disturbing influence upon the integration this influence is here entirely done away with. Various other problems lead to a similar integral as 2). If inter alia we wish to calculate the kinetic energy T of an (invariable or affinitely variable) continuously moving system of masses for an arbitrary epoch, then

$$2\,T = \int v^2 dm,$$

where v denotes the velocity of a central point p in the element dm. But v^2 is equal to the "inner" square of the vector $\frac{dp}{dt}$ representing the velocity of p according to length and direction, i.e.

$$r^2 = \frac{dp}{dt} \mid \frac{dp}{dt},$$

and when the symbol $\mathfrak{A}$ denotes a certain affinity the momentaneous system of velocities of the system of masses is indicated by

$$\frac{dp}{dt} = \mathfrak{A}p;$$

hence we have

$$T = Lp^{(2)},$$

$$L = \tfrac{1}{2}\,[\mathfrak{A}* \mid \mathfrak{A}*],\quad p^{(2)} = \int p^2 dm.$$

The evaluation of the static sum of the forces of inertia of an arbitrary order called forth during the motion of the system of mass at any epoch and the evaluation of the energies of higher species inter alia considered by J. SOMOFF also lead to the integral $p^{(2)}$.

It does not raise the slightest difficulty to find the integral $p^{(\nu)}$ for a simplex of constant denseness with the vertices $a_1, a_2, \ldots, a_n$. We can put

$$p = \lambda_1 a_1 + \lambda_2 a_2 + \ldots + \lambda_n a_n,$$

where all points inside the simplex are obtained, when to the numerical quantities $\lambda_1, \lambda_2, \ldots, \lambda_n$ are given all positive values compatible with the condition

$$\lambda_1 + \lambda_2 + \ldots + \lambda_n = 1$$

If we think the simplex broken up into elements of the shape of the parallelotop, i. e. of the $(n-1)$ dimensional analogon to the parallelepiped of our space, and with edges parallel to the edges of the simplex starting from a_1, then a slight calculation to be found (l. c.) on page 147 gives us

$$dm = (n-1)!\, M\, d\lambda_2\, d\lambda_3 \ldots d\lambda_n,$$

where M indicates the mass of the entire simplex. Hence we find

$$p^{(\nu)} = (n-1)!\, M \int (\lambda_1 a_1 + \lambda_2 a_2 + \ldots + \lambda_n a_n)^\nu d\lambda_2\, d\lambda_3 \ldots d\lambda_n.$$

The polynomial theorem gives

$$(\lambda_1 a_1 + \lambda_2 a_2 + \ldots + \lambda_n a_n)^\nu = \sum \frac{\nu!}{\nu_1!\nu_2!\ldots\nu_n!} \lambda_1^{\nu_1} \lambda_2^{\nu_2} \ldots \lambda_n^{\nu_n} a_1^{\nu_1} a_2^{\nu_2} \ldots a_n^{\nu_n}$$

with

$$\nu_1, \nu_2, \ldots \nu_n = 1, 2, \ldots n\ ,\ \nu_1 + \nu_2 + \ldots + \nu_n = n.$$

On the other hand we find according to a wellknown theorem of LIOUVILLE under the above conditions for $\lambda_1, \lambda_2, \ldots \lambda_n$:

$$\int \lambda_1^{\nu_1} \lambda_2^{\nu_2} \,..\, \lambda_n^{\nu_n} d\lambda_2\, d\lambda_3 \ldots d\lambda_n = \frac{\nu_1!\, \nu_2! \ldots \nu_n!}{(\nu_1 + \nu_2 + \ldots + \nu_n + n-1)!} =$$

$$= \frac{\nu_1!\, \nu_2! \ldots \nu_n!}{(\nu + n-1)!} ,$$

hence

$$p^{(\nu)} = \frac{\nu!\,(n-1)!}{(\nu + n-1)!} M \sum_{\nu_1, \nu_2 \ldots \nu_n = 1}^{n} a_1^{\nu_1} a_2^{\nu_2} \ldots a_n^{\nu_n} \quad . \quad . \quad . \quad (3)$$

with

$$\nu_1 + \nu_2 + \ldots + \nu_n = \nu .$$

The sum to the right could evidently be arrived at out of $(a_1 + a_2 + \ldots + a_n)^{\nu}$ by developing it according to the polynomial theorem and by suppressing all the polynomial coefficients. The factor

$$\frac{\nu!\,(n-1)!}{(\nu + n-1)!}$$

is nothing else but the reciprocal of the number of terms. By introducing in 1) the obtained value of $p^{(\nu)}$, we find, when the distance of the vertex a_i of the simplex from the space E or A is indicated by y_i,

$$M_\nu = \frac{\nu!\,(n-1)!}{(\nu + n-1)!} M \sum y_1^{\nu_1} y_2^{\nu_2} \ldots y_n^{\nu_n} ,$$

$$(\nu_1 + \nu_2 + \ldots + \nu_n = \nu).$$

For $\nu = 2$ I have deduced (l. c.) the sum in 3) to a sum of $(n+1)$ respectively n squares, in other words I have substituted for the simplex a system of $(n+1)$ resp. n single material points, which is equivalent to it with respect to all questions connected with the moments of inertia. For $\nu > 2$ a similar reduction seems to be less easily effectible.

Stuttgart, March 1905.

Physiology. — "*On the branchings of the nerve-cells in repose and after fatigue.*" By Dr. S. J. DE LANGE. (Communicated by Prof. C. WINKLER.)

In the laboratory of MATTHIAS DUVAL some experiments have been made by MANOUÉLIAN in order to ascertain whether it is possible to demonstrate modifications in the dendrites of the ganglion-cells in cases of sleep through fatigue. His results have been published in the "Comptes Rendus de la Société de Biologie, 28 Févr. 1898" and subsequently.

The animals he made use of for his experiments were mice, and he proceeded in the following manner: For the space of an hour together a mouse was driven to and fro in a cage, without granting it any rest: after that the exhausted animal fell asleep or at any rate remained perfectly quiet. The control-animal was kept in perfect repose. Both animals were then killed, and small pieces of the brain were immediately fixed after the method of GOLGI. He obtained manifest results already when only feebly magnifying: the collaterals of the dendrites have vanished, instead of these the dendrites have globular tumefactions, retracted branchings which seem to have loosened themselves from the neighbouring end-arborisations.

MANOUÉLIAN writes:

"On pense, en présence de ces images, à celle d'une sangsue vue comparativement dans l'état d'élongation et dans l'état de rétraction en boule."

Previous to these experiments, RABL-RÜCKHARDT had published a theory on the amoeboid motion in the cells of the central nerve-system, a theory not founded however on microscopical data. (Neurolog. Centralblatt 1890, p. 199). The investigations of WIEDERSHEIM who experimented on a living Crustacea, Leptodora hyalina, and those of PERGENS and others on the retina of Leuciscus rutilus, seemed to confirm the conjectures of RABL-RÜCKHARD.

WIEDERSHEIM has been able to follow the motion of the processes of the nerve-cells with the microscope and arrives equally at the conclusion: "dasz die centrale Nervensubstanz nicht in starre Formen gebannt, sondern dasz sie activer Bewegungen fähig ist."

J. DEMOOR injected dogs with lethal dozes of morphia, and studied a small piece of the cortex cerebri, which he extirpated before the death of the animal. He too, and likewise STEFANOWSKA, after injecting mice with ether, found similar changes as observed by MANOUÉLIAN: the branchings having become smaller and shaped like a string of beads.

Two american authors however, FRANK and WEIL, did not obtain these results on animals under narcosis.

In order to obtain some certitude whether any differences might in reality be observed, I tried a few experiments in the laboratory of Professor WINKLER.

Firstly I did repeat the experiments of STEFANOWSKA and DEMOOR, albeit the methods employed were not in every respect the same as theirs.

The mice were brought under narcosis by means of chloroform instead of ether: immediately after death they were decapitated, the head was caught into a liquid, prepared after the method of GOLGI

S. J. DE LANGE. "On the branchings of the nerve-cells in repose and after fatigue."

Nerve-cells of the cornu Ammonis from a mouse, exhausted by incessantly running in a turning cage for four hours together.

modified by Cox, whilst the brain was prepared directly in the liquid. For the control another mouse, not having been put under narcosis, was treated in the same manner. No differences whatever were to be observed in the microscopical preparations, obtained by means of the freezing-microtome.

Neither did I observe any differences in the case of mice, injected in the manner used by Demoor with repeated doses of morphia until death ensued.

Thinking these results might have been impaired by the fact that the animals were decapitated only after death, I next tried with the utmost accuracy a repetition of the experiments of Manouélian.

A mouse was put into a turning cage, being therefore constrained to run incessantly, whilst the cage was kept in continual motion by means of a small motor driven by water. The motion was continued for four hours together, the animal experimented upon being therefore perfectly exhausted. Meanwhile the control animal had been kept in darkness, enveloped in wadding. The four hours having elapsed, both animals were very quickly decapitated, the heads being caught into the fixation-liquid, and the brain being further prepared in it.

After ten weeks the preparations were impregnated with celloidine and section-series in frontal direction were made of both brains. In this way it became possible to obtain a comparable material.

For further control another pair of mice was sacrificed, for the purpose of demonstrating by means of the method of Nissl the presence of the well-known modifications in the easily tinctured parts of the protoplasma of the nerve-cells.

For whilst under normal conditions the elective tincturing part of the protoplasma of the ganglion-cells is divided into small granula, in case of fatigue these granula tend to dissolving more and more, the tincturing of the cellular body thus becoming homogeneous.

These modifications are clearly to be observed in the ganglion-cells of the exhausted animal experimented upon: the fatigue therefore must have been exquisite.

The preparations, made after the method of Golgi modified by Cox, offer however beautiful arborisations as well in the case of the non-fatigued animal, as in that of the exhausted one used for the experiment, the annexed photographical reproduction of the exhausted animal presenting no trace of retracted branchings, or of globular tumefactions, neither of being shaped like a string of beads.

I have therefore not succeeded in demonstrating after this method modifications in the branching system of the nerve-cells of the cortex cerebi, caused by intense fatigue.

Astronomy. — Prof. J. A. C. Oudemans presents as a first communication on his journey to Réunion for observing the transit of Venus: "*A short account of the determination of the longitude of St. Denis, (Island of Réunion), executed in* 1874."

In our ordinary meeting of October 30, 1875 I communicated a few details on the state of the computation of the observations at St. Denis on the transit of Venus of December 9, 1874. The purport substantially was, that the computations had been carried out as far as was possible at that moment.

Several circumstances, independent of my will, were the cause that this state of things remained the same till the middle of last year, and that the computations could not earlier be taken in hand again.

What I communicated then has been inserted in the Proceedings of that meeting. Passing by all that refers to the heliometer measures, which I hope to take up at some later time, I will only mention the fact that the necessity was pointed out of determining with precision the longitude of the place of observation.

For this purpose we, viz. Mr. Ernst van de Sande Bakhuyzen, Mr. Soeters and myself, have observed a number of occultations, not so much of the brighter stars, announced in the Nautical Almanac, as rather of fainter stars, of the 8th or 9th magnitude, the positions of which were not yet known with precision at that time. These had to be determined therefore by meridian observations; our honoured president readily undertook the task of having these determinations made at the observatory under his direction.

As a rule at least four determinations have been made of each star. Though the added epochs show that this was done between the years 1879 and 1884, it lasted a considerable time, till November 1901, before the reductions of those determinations had proceeded so far that the results could be communicated to me.

At the same time my attention was called to the fact that most of these stars had been since also observed at other observatories.

It thus became necessary, in my opinion, to look for all these determinations in the several Annals and to reduce them to the same epoch, (of course 1874), in order to make allowance for proper motion, wherever necessary. In many cases it proved sufficient to retain the Leiden determination unchanged.

But besides, the errors of the lunar tables, that is to say of the positions published in the Nautical Almanac, had to be derived from observations. For this purpose the observations at the meridian-circles of Paris, Greenwich and Washington and those at the Altazimuth of Greenwich have been used.

It is true that, in a remarkable paper, *Investigation of corrections to* HANSEN's *Tables of the moon, with tables for their application*, NEWCOMB brought together the corrections to be applied to the formulae by means of which HANSEN calculated his tables of the moon. The paper contains the terms which had to be added according to the state of science in that year, and also an empirical correction determined by the most recent observations.

Moreover a table of corrections for 1874 was given, founded on these data. But after having made a diagram representing, both the corrections found by direct observation and those furnished by NEWCOMB's table, I came to the conclusion that the former was to be preferred [1]).

As for the longitude of St. Denis, I will remark, that it has been determined by the French naval officer GERMAIN in 1867 and 1868 by means of 13 culminations of the first and 12 of the second limb. In the *Connaissance des Temps* of 1871 a short report of that determination is to be found. Though the 25 results there given, agree tolerably well, this kind of determinations is always liable to the drawback that the difference in the constant error, made in observing the culmination of the moon's limb and of the comparison stars, enters into the result, about thirty times magnified. There is no fear of such an injurious influence in a determination of longitude by occultations [2]). If the voyage to reach the isle of Réunion did not last so long, and if the Indian Ocean were not so wild and bois-

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[1]) The present state of science requires a correction of one of the tables of NEWCOMB. He points out (page 9) that the parallactic equation of HANSEN is founded on the value 8".916 of the solar parallax, whereas the value which he derived in 1867 from all the available materials is but 8".848, which is less by 0".068. Further that later determinations require rather a diminution than an increase of that number. At present 8".800 is generally adopted as being the most probable value of the solar parallax, which is less than NEWCOMB's value by 0".048. The parallactic correction of NEWCOMB must therefore be increased 1,7 fold; in other words: three terms have to be added, viz.:

$$+ 0''.67 \sin D + 0''.05 \sin (D-g) - 0''.09 \sin (D + g'),$$

where D represents the mean elongation of the moon from the sun, g the mean anomaly of the moon and g' that of the sun.

[2]) NEWCOMB says at the beginning of his paper above mentioned: "Determi-"nations of longitude from moon occultations are found by experience to be "subject to constant errors which it is difficult to determine and allow for. It "was therefore a part of the policy of the American Commission to depend on "occultations rather than upon culminations for the determinations of longitudes, etc."

terous, these voyage would also present an occasion of determining the longitude by transport of chronometers. Unfortunately the results given by the different chronometers were so diverging as to be of no value whatsoever.

The report above mentioned of GERMAIN's determination is accompanied by a plan showing his place of observation. We see from this plan that west of the town the river St. Denis runs nearly in a north-north-westerly direction towards the sea and that the place of observation of GERMAIN was still on the west of the river.

A brick pillar, on which stood his transit instrument in 1867 and 1868, was still extant during our stay in 1874.

The result of GERMAIN's determination of longitude and latitude was given by him as follows:

Longitude of the place of observation east of Paris	$3^h32^m25^s,7$
Reduction to the flag-staff, east of the Barachois (*i. e.* of the little creek which protects the sloops in landing)	$+ 1,07$
Longitude of the flag-staff east of Paris, (*sic.*:) . .	$3^h32^m26^s,8$

Southern latitude of the place of observation determined by 4 northern and 3 southern stars	20°52′ 2″,0
Reduction to the flag-staff	− 23 ,7
Southern latitude of the flag-staff	20°51′38″,3

Our observations of occultations took place at different points, the relative position of which was accurately determined by Mr. SOETERS.

Taking the difference of longitude of Paris and Greenwich $= 9^m20^s63$ from the Nautical Almanac of 1874, (as given at that time both in the C. d. T. and in the N. A.), we got from the numbers just mentioned, for the flag-staff $3^h41^m47,43$ east of Greenwich.

Corresponding therewith:

Place of observation:	Long. E. of Gr.	Latitude
1st on the ground of the harbour office	$3^h41^m47^s,32$ —	20°51′40″,6
2nd „ „ „ „ our dwelling house, N°. 51 Rue du Conseil	48 ,11	46 ,1
3rd Near or in the pavilion of the heliometer on the battery	47 ,81	35 ,3

The calculation of the longitude from the occultations has been carried out on printed forms, arranged according to the method which I developed in the *Astronomische Nachrichten* N°. 1763.

In this method the declination of the moon is taken from the astronomical almanac, using an adopted longitude; the parallax is then computed for that point of the moon's limb, where the star has disappeared and which therefore has the same right ascension and declination as the star. We then have to add or to subtract two terms to or from the right ascension of the star, to get that of the moon's centre, and finally we find from the almanac the Greenwich time corresponding with that right ascension.

The longitude of the place of observation, then found, is the right one, if it agrees with the adopted longitude. If it does not agree, we have only to repeat a small part of the calculation with a modified longitude of the place, to derive the true longitude from the two differences.

This method corresponds with the method, which was customary in the 18th century (which we find inter alia explained in the well known treatise of BOHNENBERGER : *Anleitung zur geografischen Ortsbestimmung*) with this distinction that then the whole computation was carried out in longitude and latitude, whereas we use the right ascension and declination. Further, that for BOHNENBERGER c. s. there is no question of any second hypothesis.

I will readily grant that BESSEL's method of computing ecliptic phenomena and thus also for the prediction of occultations and for the calculation of the longitude from an observed occultation, is justly considered to be the classic method. It is also the only one explained in most of the textbooks. But it seemed to me that the method indicated by myself is more expeditive and only in a few cases inferior to that of BESSEL in point of accuracy. The drawback of this last method consists in the troublesome preparatory calculations, which it requires. Any one may convince himself of the truth of this statement by consulting the wellknown textbook of CHAUVENET : *A manual of spherical and practical Astronomy*, Philadelphia 1874, vol I, p. 550 [1]).

The horizontal equatorial parallax of the moon could be derived from the Nautical Almanac, without any correction. As for the apparent semidiameter of the moon, I myself made a determination of this quantity, based on an elaborate investigation in 1859, (vid. *Verslagen en Mededeelingen der Natuurkundige Afdeeling*, Vol. VI, p. 25 seqq.)

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[1]) I have calculated a single example by this method ; the result differed only by $0^s,1$ from that obtained by the other method ; in the first however 57 logarithms had to be taken out, against 37 in the latter. Thinking the matter over, however, I believe that the method of BESSEL will probably admit of a modification by which this difference will be materially diminished. I hope shortly to investigate this more thoroughly.

which furnished 0.27264 for the proportion of the mean moon's semidiameter and that of the earth's equator (at least this is the result of the occultations discussed). After mature consideration, however, I now adopted the value 0.2725 × hor. equ. parallax + 0″04. This leads approximately to the same value as when we take the sine of the moon's apparent semidiameter =0.272525 of the sine of the equatorial horizontal parallax.

This factor is the mean of those which were derived from occultations during total eclipses of the moon by LUDWIG STRUVE in 1888 and by J. PETERS in 1895 (0.272535 and 0.272518). The Nautical Almanac, which used both the semidiameter and the parallax as given in the Tables of HANSEN, gave a value larger by 1″4 to 1″6. This difference has remained the same up to the present time.

About the observed occultations we may communicate the following particulars. They were mostly observed by myself, partly with the Fraunhofer telescope, (aperture 11 cm.) mounted on a stand, which Mr. STOOP of Amsterdam had kindly lent to the commission for the observation of the transit of Venus, partly with the telescope of the heliometer (aperture $7^1/_2$ cm.). At a later epoch, when the assistance of Mr. ERNST BAKHUYZEN was not so constantly required, as in the beginning, for the experiments of Dr. KAISER with the photoheliograph, he also took part in the observation of the occultations, as also did Mr. SOETERS in one case.

Altogether 35 disappearances and 4 reappearances were observed; but 12 disappearances and 1 reappearance had to be rejected. There thus remained 23 disappearances and 3 reappearances, that is altogether 26 observations, which furnished useful results.

The reason of the rejection lay partly in the fact that, already in recording the observation, the remark "uncertain" had been added, an addition due to the faintness of the star as it approached the moon's limb, or to passing clouds.

For another part the correction of the longitude determined by GERMAIN and adopted by myself, came out so extravagantly large that some mistake or other seemed probable. There seemed to be reason to suspect that a wrong star had been taken for the occulted one. In five of the cases I succeeded to find out the right star by means of star catalogues, but in four other cases all my endeavours proved in vain. Ultimately there remained five cases in which the correction to the adopted longitude was found so considerable (— 21^s, — 20^s, —28^s, — 24^s and + 33^s), that there was no escape from the conclusion that either a mistake, however improbable in itself, had been committed in writing down the time, or that the

Results for the longitude of St. Denis-Réunion, (flag-staff), obtained by occultations, without making a difference between disappearances and reappearances.

1874		Observer	Star, Name or apparent place.	Disapp. or reapp.	Limb	$\triangle L$ = Corr. Germain	G	$G \triangle L$	ε	$G\varepsilon^2$
Sept.	19	O.	Arg. Z. 223, No. 75	*D*	*D*	$+2^s.26$	0.70	$+1^s.58$	$+3^s.18$	7.08
»	»	O.	Cordoba III.1589	*D*	*D*	+6.64	0.74	+4.91	+7.56	37.29
»	»	O.	» XVIII.124	*D*	*D*	+8.21	0.60	+4.93	+9.12	49.90
»	22	O.	33 Capricorni	*D*	*D*	+1.00	0.29	+0.29	+1.92	1.07
»	»	O.	Arg. Z. 255, No. 27	*D*	*D*	—6.10	0.50	—3.15	—5.18	13.42
»	»	O.	» » » » 32	*D*	*D*	—1.54	0.63	—0.97	—0.62	0.24
»	»	O.	» » » » 34	*D*	*D*	—1.51	0.89	—1.34	—0.59	0.31
»	»	O.	» » » » 35	*D*	*D*	—5.75	0.97	—5.57	—4.83	22.63
»	26	O.	73 Piscium	*R*	*D*	+3.11	0.91	+2.83	+4.03	14.78
October	2	O.	53 Geminorum	*R*	*D*	+1.27	0.28	+0.36	+2.49	1.34
»	4	O.	$\left(\alpha = 9^h0^m39^s.60\right)$ $\left(\delta = +22°57'38'',7\right)$	*R*	*D*	+4.39	1.00	+4.39	+5.31	28.20
»	16	B.	Arg. Z. 223, No. 47	*D*	*D*	—3.91	1.00	—3.91	—2.99	8.94
»	»	B.	»	*D*	*D*	+9.67	0.40	+3.87	+10.59	44.86
»	»	O. B.	» » » 49	*D*	*D*	—5.99	0.95	—5.69	—5.07	24.42
»	»	O. B.	» » » 52	*D*	*D*	+3.84	0.51^5	+1.98	+4.76	11.67
»	»	O. B.	» » » 51	*D*	*D*	+4.65	0.49	+2.28	+5.57	15.20
»	»	S. B.	$\left(\alpha = 18^h6^m41^s.75\right)$ $\left(\delta = -28°0'56'',8\right)$	*D*	*D*	—4.26	0.99	—4.22	—3.34	11.05
»	»	B.	Gould 24851	*D*	*D*	+5.84	0.87	+5.08	+6.76	39.76
»	17	O.	$\left(\alpha = 19^h2^m35^s.76\right)$ $\left(\delta = -27°54'17''75\right)$	*D*	*D*	+5.39	0.19	+1.03	+6.31	7.57
»	»	O.	Arg. Z. 241, No. 9	*D*	*D*	—5.10	0.58	—2.96	—4.18	10.13
»	»	O.	» » 231, » 12	*D*	*D*	+1.45	0.35	+0.40	+2.07	1.50
»	»	O.	» » » » 11	*D*	*D*	—4.73	0.62	—2.93	—3.81	9.00
»	18	B.	» » 239, » 103	*D*	*D*	—5.10	0.95	—5.07	—4.18	16.60
»	19	B.	» » 247, » 99	*D*	*D*	—2.62	0.98	—2.57	—1.70	2.83
»	»	B.	χ Capricorni	*D*	*D*	—4.22	0.97	—4.09	—3.30	10.56
»	»	B.	$\left(\alpha = 21^h2^m24^s.71\right)$ $\left(\delta = -21°33'15'',1\right)$	*D*	*D*	—8.95	0.94	—8.41	—8.03	60.61
							18.30^5	+33.93	$25\,m^2 =$	450.96
								—50.78	$m^2 =$	18.04
								—16.85	$m =$	$\pm 4^s25$

$$\triangle L = -\frac{16.85}{18.305} = -0^s.92 \pm 0^s.99,$$

Results for the longitude of St. Denis-Réunion, reappearances and disappearances separately.

The 3 reappearances give: $\Sigma G = 2.19$ $\Sigma G \Delta L = + 7.58$ therefore $\Delta L = + 3^{s}.462$
The total sum was: 18.30^{5} -16.85
Therefore the disappearances separately give: 16.11^{5} -24.43 „ $\Delta L = - 1.516$
Mean: $+ 0^{s}.97$

ε	ε^2	G	G^2
Disapp.			
$+3^{s}.78$	14.29	0.70	10.00
+8.16	66.59	0.74	49.28
+9.73	94.67	0.60	56.80
+2.52	6.35	0.29	1.84
−4.58	20.98	0.50	10.49
−0.02	0	0.63	0
+0.01	0	0.89	0
−4.23	17.89	0.97	17.35
−2.39	5.71	1.00	5.71
+11.19	125.22	0.40	50.09
−4.47	19.98	0.95	18.98
+5.36	28.73	0.51^{5}	14.80
+6.17	38.07	0.49	18.65
−2.74	7.51	0.99	7.43
+7.36	54.17	0.87	47.13
+6.91	47.75	0.19	9.07
−3.58	12.82	0.58	7.32
+2.67	7.13	0.35	2.50
−3.21	10.30	0.62	6.39
−3.58	12.82	0.95	12.18
−1.10	1.21	0.98	1.19
−2.70	7.29	0.97	7.07
−7.43	55.20	0.94	51.89
Reapp.			
$-0^{s}.35$	0.12	0.91	0.11
−2.19	4.80	0.27	1.34
+0.93	0.86	1.00	0.86

N.B. As there is no reason to suppose that a reappearance at the dark limb should be so much more accurate than a disappearance at the dark limb, I have combined them.

$22\, m^2 = 406.16$
$m^2 = 18.06$
$m = \pm 4^{s}.34$
(not used)

$2\, m^2 = 2.31$
$m^2 = 1.155$
$m = \pm 1^{s}.08$
(not used)

Together:
$24 m^2 = 408.47$
$m^2 = 17.02$
$m = \pm 4^{s}.13$

$\frac{m^2}{16.115} = 1.056$ $\sqrt{\ } = \pm 1^{s}.03,$

$\frac{m^2}{2.19} = 7.78$ $\sqrt{\ } = \pm 2.79.$
8.84
4 2.21 $\sqrt{\ } = \pm 1.49.$

occultation had taken place at a point considerably elevated above the rest of the limb. In the following lines we will only communicate the results of those observations which have been retained.

We remark that the weights *G*, which have been added, were taken equal to $\sin^2 \psi$, 2ψ being the arc, of which the star would describe the chord behind the disk of the moon, were this disk at rest; (according to the notation of CHAUVENET this would become $\cos^2 \psi$). This quantity could be easily derived from the numbers occurring in the computation.

The calculations have been all made in duplicate; the first by myself, the other by Mr. KRESS, amanuensis at the observatory of Utrecht.

We thus find:

Taking disappearances and reappearances together:

Correction to GERMAIN's longitude: $-0^s,92 \pm 0^s,99$ (m. err.)

Treating them separately: $+0,97 \pm 1,49$ „ „)

We thus come to the conclusion that the occultations observed by us leave undecided whether the longitude of St. Denis, according to the determination of GERMAIN in 1867 and 1868, must be increased or diminished; in other words they confirm his result.

Only one of these days I noticed, that since 1886 the *Connaissance des Temps* gives a longitude for that place, which is larger by 1^s2 or 18″; in the last column of the table of the geographical positions

M. T. Greenwich	From meridian observations.		Newcomb.		N. — Merid.	
	s	″	s	″	s	″
Sept. $19^1/_8$	—0.52	—4.3	—0.39	+0.3	+0.13	+4.6
$22^1/_6$	—0.51	—1.9	—0.49	—2.4	+0.02	—0.5
$22^5/_{12}$	—0.51	—2.1	—0.49	—2.6	+0.02	—0.5
$26^1/_6$	—0.73	—5.9	—0.70	—5.8	+0.03	+0.1
Oct. $2^1/_2$	—0.79	+1.7	—0.95	+0.6	—0.16	—1.1
$4^1/_2$	—0.75	0.0	—0.77	+2.9	—0.02	+2.9
$16^1/_5$	—0.35	—4.1	—0.47	+0.4	—0.12	+4.5
$17^1/_4$	—0.43	—2.0	—0.46	—0.4	—0.03	+2.4
$18^1/_3$	—0.35	—1.2	—0 45	—1.3	—0.10	—0.1
$19^1/_3$	—0.34	—2.5	—0.44	—2.0	—0.10	+0.5
					s	″
				Mean:	—0.03	+1.3

we find: GERMAIN corr. 86; the reason for the correction is however not stated. I have therefore written to Paris asking for information.

Moreover I will observe that the difference of longitude Paris—Greenwich above used, must be increased according to the determination executed by French and English observers in 1902. The result obtained by the English observers was $9^m20^s,932 \pm 0{\cdot}006$; by the French observers $9^m20^s,974 \pm 0{\cdot}008$. Mean $9^m20{\cdot}953$. (Monthly Notices of the R. A. S. Jan. 1905).

Finally we subjoin a comparison of the corrections to the moon's ephemeris of the Naut. Alm. of 1874, furnished by the meridian observations on the one hand, and by NEWCOMB's formulae on the other.

It might be worth while to ascertain, whether the agreement of the results is improved, if we adopt the corrections according to NEWCOMB.

As for the meridian observations, some have been made at other observatories (Leiden, Pulkowa etc.). I hope to investigate this more closely; it is not probable however that the result will be greatly altered.

A last remark in conclusion. According to the "*Post en Telegraafgids*" the isle of Mauritius is already connected telegraphically with Europe. There is reason therefore to expect that the same will shortly be the case for Réunion also. In that case the "Bureau des Longitudes" will no doubt endeavour to obtain a telegraphically determined longitude of St. Denis.

Utrecht: 1905 March 24.

Physiology. — "*On the presence of fibringlobulin in fibrinogen solutions.*" By Dr. W. HUISKAMP. (Communicated by Prof. C. A. PEKELHARING).

After HAMMARSTEN had proved that in fibrinogensolutions, which had been coagulated either by heat to 55° or by means of fibrinferment, a proteid, afterwards called fibringlobulin, appears which coagulates at 64°, there existed several possibilities with regard to the formation or appearance of this proteid.

Firstly the original fibrinogensolution might already have contained the fibringlobulin as an admixture; in the second place it was possible that at the heat-coagulation or by means of fibrinferment, the fibrinmolecule was disintegrated, and that in such a way that an insoluble substance, fibrin, is formed, along with a soluble one, fibringlobulin; and lastly the fibringlobulin might perhaps be an altered fibrinogen, which has remained in solution, a sort of soluble fibrin.

Against the first of these possibilities HAMMARSTEN[1] has raised serious objections, and by his later researches he came more and more to the conviction that fibringlobulin must be a somewhat changed soluble fibrin.

A research of CALUGAREANU [2]) was the occasion for experiments to be made in this direction. The author inter alia demonstrates that natriumfluoride, in strong concentration, greatly increases the effect quantities of fibrinferment. CALUGAREANU prepared horseoxalateplasma, which contained a quantity of fibrinferment so small, that the plasma remained fluid for a considerable time.

If this plasma was mixed with natrium fluoride to a quantity of about $3^0/_0$, either by addition of a saturated solution of NaFl or also of finely powdered NaFl, then there ensued an almost immediate coagulation. That the formed precipitate really is fibrin, CALUGAREANU derives from the fact, that it is like fibrin insoluble in diluted salt solutions. Further CALUGAREANU discovered that horseoxalateplasma, if it was only perfectly free from ferment, did not coagulate by addition even of several volumina $3^0/_0$ Na Fl. When therefore no ferment is present the natriumfluoride remains inactive, from which CALUGAREANU concludes that the Na Fl exercises its influence on the fibrinferment but not on the fibrinogen.

When the experiments of CALUGAREANU were repeated I obtained results which partly differed from his.

It namely appeared that perfectly fermentfree solutions containing fibrinogen gave a precipitate with natriumfluoride; this precipitate is in case horsefibrinogen is used gelatinous and in consequence reminds one more or less of coagulation; if however oxenfibrinogen or oxenbloodplasma is used, the precipitate is flocculent and does therefore not, outwardly at least, resemble coagulation.

In the second place it appeared that the precipitate formed by Na Fl could be easily dissolved, when treated properly, and that these solutions coagulated with fibrinferment.

Some experements I will describe here in detail.

A rabbit was injected in the vena jugularis with 65 ccm. leech-extract, next the blood out of the Carotis was received in a centrifugalglass covered with paraffine and the corpuscles where centrifugalised off. Plasma in this way prepared contains no ferment as PEKELHARING [3]) has demonstrated; the plasma, meant here, remained

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[1]) Pflügers Archiv., Bd. 22, p. 431.

[2]) Arch. internat. de Physiol. Vol. II, p. 12.

[3]) Untersuchungen über das Fibrinferment. Verhand. Kon. Akad. van Wet. Amsterdam 1892.

fluid for a number of days, as long as it was kept, yet by addition of three times the volume of saturated natriumfluoridesolution a flocculent precipitate was slowly formed; a fibrinogensolution prepared from the plasma could also be precipitated by the addition of saturated natrium fluoride solution; by saturating with solid natrium fluoride a precipitate ensued immediately.

Other experiments were taken with horsefibrinogen. The fibrinogen solutions used, which were prepared by three times precipitating with salt from oxalateplasma showed even after being preserved for several days, no trace of clotting; by addition of $Ca\,Cl_2$ no clotting was caused either at 37° or at the temperature of the room. In such a fibrinogen solution a thick precipitate is then immediately formed[1]) by addition of the double volume of saturated natrium fluoride solution; this gelatinous precipitate can be easily wound round a glass rod and in this state be taken out of the liquid for further research. The precipitate washed by water showed the following properties. It did not dissolve perceptibly at the temperature of the room in 3—5 % salt, more easily the solving succeeded in this way, at the temperature of the body, or still better at 40—45°. On cooling, the precipitate does not return. The surest way to obtain a complete solution is to make use of $^1/_{20}$ % ammonia as solvent; if the precipitate is divided with a glass rod, rather concentrated solutions can easily be prepared in this way. Such a solution can after addition of salt, to a quantity of 3—5 % be neutralised without a precipitate forming anew (only when the concentration of the solution was very great, a part of the dissolved substance precipitated often again after some time; this precipitate was solved however at 37°). Such a solution may be precipitated again in the same way, with the double volume saturated natrium fluoride solution and may be dissolved in $^1/_{20}$ % ammonia. Such neutral solutions containing 3—5 % salt and prepared by being once or twice precipitated with Na Fl possessed all the properties of fibrinogen; by addition of an equal volume saturated salt solution, a great precipitate was formed; acetic acid caused a precipitate soluble in excess; the coagulation temperature was at 54°; the solutions coagulated quickly and completely with fibrinferment for which I mention the following experiments as example.

5 ccm. fibrinogen solution of 0.342 % + 1 ccm. fibrinferment solution; the coagulation begins at 37° after half an hour; the tube further coagulates completely.

5 ccm. of the same fibrinogen solution + 5 drops of oxenblood-

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[1]) The mixture contains then not much more than 3 % Na Fl.

serum, the coagulation begins (at 37°) after ten minutes; after an hour a solid clot was formed.

Placed at 37° a tube with 5 ccm. of the same solution, without ferment for control, remained perfectly fluid.

The above mentioned experiments were now repeated with horse-oxalateplasma, which was not perfectly free from ferment, as was obvious from the partial clotting of the received blood; the results were in general the same; the precipitate obtained with Na Fl dissolved only with somewhat more difficulty; the solution of this precipitate meanwhile possessed the properties of a fibrinogen solution and coagulated with fibrinferment.

Further experiments were taken with fermentfree oxenfibrinogen prepared after the method of HAMMARSTEN. It was stated that to precipitate this fibrinogen with NaFl more natrium fluoride solution was needed than for horsefibrinogen. The flocculent precipitate obtained with Na Fl dissolved at 37° more easily in a diluted salt solution than the horsefibrinogen precipitated with NaFl; on the contrary less easily in $^1/_{20}$ % ammonia; rather great quantities dissolved already at the temperature of the room in 3—5 % NaCl. The coagulation temperature of the neutral solution, containing about 3 % salt was at 53—54°; addition of acetic acid caused a precipitate which dissolved in excess; by half saturating with Na Cl the fibrinogen could be precipitated. That the solution coagulates with fibrinferment appears from the following experiment.

5 ccm. of the solution in 3 % NaCl + 5 drops of oxenbloodserum. Complete clotting after two hours.

Although it might seem after the above mentioned experiments that the fibrinogen remains unaltered on being precipitated with Na Fl, a closer inquiry brings to light a remarkable alteration. If namely a solution of fibrinogen precipitated with Na Fl is heated to 55—58°, very little fibringlobulin is found in the liquid filtered off from the coagulum; if the fibrinogen is precipitated twice with natrium fluoride, no or only few traces of fibringlobulin can be obtained from the solution as appears from the following experiments.

I. A solution of fibrinogen prepared after the method of HAMMARSTEN was partly precipitated twice with Na Fl; the last precipitate was dissolved in $^1/_{20}$ % ammonia and the solution was neutralised after addition of salt; 8 ccm. of this solution, which contained 0.445 % fibrinogen were heated for five minutes to 55—60°, then it was filtered; the clear filtrate was heated to 72°, by which only a small opalescence ensued, which did not increase perceptibly after the liquid had been made slightly acid and afterwards boiled.

For comparison the fibrinogen from 8 ccm. of that part of the fibrinogen solution which had not been prepared with NaFl, was in the same way first coagulated and afterwards the fibringlobulin in the filtrate; although the fibrinogen solution used for this experiment contained 0,565°/₀ fibrinogen and so had been but little more concentrated than the solution prepared with Na Fl the quantity fibringlobulin found was remarkably larger, as there was formed abundance of flocculent precipitate by heating to 70°.

Another experiment gave the following results.

II. The solution of the fibrinogen not precipitated with Na Fl contained 0,634°/₀ fibrinogen, that of the fibrinogen precipitated with Na Fl 0,452°/₀. after this the fibrinogen being removed from the two solutions by heating to 55—58° and by filtering off of the coagulum, 5 ccm. of each of the filtrates were mixed with $1^1/_2$ ccm. of a saturated solution of picric acid. In the filtrate of the fibrinogen treated with Na Fl there was formed only an opalescence which after some time passed into a very slight precipitate; in the filtrate of the fibrinogen not precipitated with Na Fl there was immediately a considerable flocculent precipitate.

III. A solution of oxenfibrinogen was precipitated by four times the volume of a saturated natrium fluoride solution; afterwards the precipitate was centrifugalised off, washed with water and dissolved in 4°/₀ salt; the solution contained 0,232°/₀ fibrinogen; after its having been removed by heating to 55—58° and filtering off of the coagulum the filtrate remained perfectly clear on being boiled, and so contained no fibringlobulin, although the original fibrinogensolution had been precipitated with Na Fl only once.

So it appears that by means of natrium fluoride fibrinogensolutions may be obtained, which by heating produce no fibringlobulin or only traces of it.

This confirms the opinion that the fibringlobulin was present already in the original, not heated fibrinogensolution either combined with fibrinogen or simply as admixture, and that consequently fibringlobulin is not formed by alteration of the fibrinogen during the heating; in the last case it could not be explained why the fibrinogen, prepared with Na Fl should not be altered as well in the same degree by heating in fibringlobulin. If however the fibringlobulin was present already in the fibrinogensolution, every thing may be explained in this way that on being treated with Na Fl the fibringlobulin passes into the filtrate at any rate for the greater part, while the fibrinogen proper precipitates. The possibility that the fibringlobulin does not precipitate also appears from the following experiment. In a solution of horsefibrinogen prepared after the method of HAMMARSTEN the fibrinogen was coagulated by heating to 60° and filtered off; to the filtrate was added a double volume of saturated natrium fluoride solution; the liquid remained perfectly clear.

The question whether the fibringlobulin passes into the filtrate when the fibrinogen is precipitated with Na Fl cannot be answered immediately by examining the filtrate, while the fibrinogen with Na Fl does not precipitate completely, so a certain quantity of fibrinogen exists still in the filtrate, and when, after heating, fibringlobulin is still found, the possibility exists, that all this fibringlobulin proceeds from the quantity of fibrinogen present in the filtrate; only the quantitative research can decide here; if on precipitating with Na Fl the fibringlobulin passes into the filtrate it must be possible to prepare from this filtrate nearly as much fibringlobulin as from the original fibrinogensolution. As the fibrinogen precipitated with Na Fl is not perfectly free from fibringlobulin, an accurate agreement is not to be expected. In the first place I subjoin the results of such an experiment.

a) 100 ccm. of a pure horsefibrinogensolution, prepared after HAMMARSTEN's method were precipitated with 200 ccm. saturated natrium fluoride solution. The precipitate was taken with a glass rod out of the liquid, pressed out firmly, dried to constant weight and weighed, the substance was burnt carefully, the weight of the ashfree substance proved to be 0,2435 gram. After the precipitate obtained with Na Fl had been removed a clear liquid remained, which was neutralised with some drops of diluted acetic acid, as the reaction of the solution of NaFl used was faintly alkaline, which mostly is the case. The liquid (285 ccm.) was heated afterwards for a quarter of an hour in a waterbath to 55—60°; the coagulated fibrinogen was filtered off on a weighed, ashfree filter, with a diluted saltsolution and after that washed with water, dried to constant weight and weighed together with the filter; the filter and the substance was carefully burnt. It proved, that 0.2262 gram ashfree fibrinogen had been present on the filter; this quantity was obtained from 285 ccm.; so in the original 300 ccm. there would have been found 0.2381 gram.

In order to determine the quantity of fibringlobulin 250 ccm. liquid filtered off of the coagulated fibrinogen were heated during a quarter of an hour to 67—69° in a waterbath. The liquid remained perfectly clear till 64°; to obtain a coagulation as perfect as possible 5 ccm. 1°/₀ of a sulphas cupri solution were added as soon as the liquid became turbid; by this the coagulum became roughly flocculent and could easily be filtered off. The weight of the filtered fibringlobulin was afterwards determined in the same way as was done with the coagulated fibrinogen and amounted to 0.1141 gram ashfree substance; so from 300 ccm. filtrate would have been gained 0.1369 gram. In the liquid filtered off from the fibringlobulin no proteid could be demonstrated.

b). For comparison it was determined how much fibringlobulin the fibrinogen solution used gave without treatment with Na Fl. Therefore 100 ccm. of this solution was again mixed with 200 ccm. $4\frac{3}{4}$% salt through which volume and salt quantity in this experiment was made equal with that of experiment *a*). By heating for a quarter of an hour to 55–60° the fibrinogen was coagulated and was treated further as mentioned above; the weight of the fibrinogen amounted to 0,4548 gram ashfree substance. 250 ccm. of the liquid filtered off from the coagulated fibrinogen were heated for a quarter of an hour to 67—69; the liquid remained perfectly clear till 64°, just as in experiment *a*); here also 5 ccm. 1% $CuSO_4$ were added as soon as the first turbidness became visible.

The coagulated fibringlobulin was filtered off and treated as mentioned above; the weight of the fibringlobulin amounted to 0,1354 gram; in the liquid filtered off from the coagulated fibringlobulin no proteid could be shown.

Taking together the results of these experiments we find, that in experiment *a*) after the removal of the precipitate obtained with Na Fl, 0,2381 gram fibrinogen and 0,1369 gram fibringlobulin were present; and in experiment *b*) 0,4548 gram fibrinogen and 0,1625 gram fibringlobulin. So the quantity of fibrinogen was in experiment *a*) reduced to $\frac{52}{100}$ through precipitation with Na Fl while the quantity of fibringlobulin only showed reduction to $\frac{85}{100}$. Consequently there must have passed a considerable quantity of fibringlobulin into the filtrate after precipitation with Na Fl. The difference of 0,0256 gram between the quantities of fibringlobulin, found in both experiments, must be attributed, apart from any errors of determination to the fact that the fibrinogen which was not precipitated with Na Fl is not perfectly free from fibringlobulin; the weight of this precipitate amounted to 0,2435 gram; if we abstract from this 0,0256 gram as being fibringlobulin, this precipitate contained to 100 mg. at 55° coagulable fibrinogen 11,7 mg. fibringlobulin; in experiment *b*) 35,7 mg. fibringlobulin was found to 100 mg. at 55° coagulable fibrinogen and in experiment *a*) after removal of the precipitate obtained with Na Fl 57,5 mg. fibringlobulin to 100 mg. at 55° coagulable fibrinogen. By precipitating with Na Fl the fibrinogensolution was consequently divided into a precipitate, which contained relatively little and a filtrate which contained relatively much fibringlobulin.

In experiment *a*) about half of the fibrinogen was precipitated with Na Fl; the liquid poured off from this precipitate was clear; if however such a liquid is left standing for some time it becomes turbid and a new precipitate has formed itself after 24 hours, in the filtrate of this precipitate a new turbidness forms again etc., till at last after some days all the fibrinogen has precipitated. It may me expected after the above mentioned experiments, that, as more fibrinogen precipitates, relatively (that is to say with regard to the quantity of fibrinogen which was not precipitated) more fibringlobulin will be present in the filtrate; this supposition is confirmed by the two following experiments.

1. 100 ccm. horsefibrinogensolution of 0.642 $^0/_0$ were precipitated with 200 ccm. saturated natrium fluoride solution; the precipitate was removed with a glass rod and the liquid remained standing after that twice 24 hours. When the fibrinogen, precipitated after that time, also was removed by filtering, the quantity of fibrinogen and fibringlobulin in 250 ccm. filtrate was determined in the same way as in the above mentioned experiment *a*). It appeared that in these 250 ccm. 0.0742 gram fibrinogen and 0.1113 gram fibringlobulin were present.

2. 100 ccm. of the same fibrinogensolution were precipitated with 200 ccm. saturated natrium fluoride solution; after removal of the precipitate the liquid remained standing for eight days; putridity did not occur from this on account of the quantity of Na Fl, the new formed precipitate was filtered off, the filtrate became again turbid and after 24 hours a slight precipitate had again formed, that was filtered off. The filtrate was neutralised with a few drops of diluted acetic acid; by heating of the neutral liquid to 55—60° there followed only an exceedingly slight opalescence; the fibrinogen was therefore precipitated almost completely by the Na Fl; when the opaline liquid was filtered a considerable flocculent precipitate was formed by heating the filtrate to 67—69°.

While in experiment *a*) after the removal of the precipitate obtained with Na Fl still $1^3/_4$ times more fibrinogen than fibringlobulin was present in the filtrate, the analogous filtrate in experiment 1) contained only $^2/_3$ times as much fibrinogen as fibringlobulin, while in experiment 2) with a considerable quantity of fibringlobulin only a small quantity of fibrinogen was present.

The results of the above described experiments lead to the conclusion that at the coagulation of the fibrinogen, the fibringlobulin does not proceed from the fibrinogen, but that this proteid was already present in the fibrinogensolution, for it could not be explained, that on one hand, the fibrinogen precipitated with Na Fl produces no or but little fibringlobulin, and that on the other hand the liquid filtered off from this precipitate contains fibringlobulin in such greater quantity.

It here is necessary to discuss still a few objections that might be raised against this conclusion.

Firstly — on account of the fact that the fibrinogen precipitated with NaFl, dissolves with more difficulty in diluted saltsolution than the usual fibrinogen, and that the solution does not produce any fibringlobulin by heating — it might be asked whether the substance precipitated with NaFl might not be a kind of soluble fibrin, as for instance the "fibrine concrète pure" described by Denis. The latter also principally dissolved in diluted saltsolution at 40°; while the dissolution went very slowly at the temperature of the room. Against the opinion that the substance precipitated with NaFl is a soluble fibrin speaks first the coägulation temperature which was found by Denis for the dissolved "fibrine concrète pure" at 60—65°, while in every case it is not higher than 55° for the substance precipitated with NaFl. The strongest argument against the opinion that this last is fibrin, namely the power of this substance to clot with fibrinferment, I have already stated several times; if we further take into consideration that the fibrinogen prepared with NaFl behaves with respect to acetic acid, half saturation with salt etc. quite as common fibrinogen, the opinion that this substance is fibrin may be considered as having been refuted.

As to the slight solubility of the fibrinogen precipitated with NaFl and in diluted salt solution, this peculiarity may be explained in this way, that on being heated with NaFl it forms a slight soluble fluorine-compound of the fibrinogen, which dissolves only very slowly in saltsolution; by the great abundance of chlorine-ions then present, this dissolving will probably be accompanied by an exchange of the fluorine by chlorine. It is still rendered more probable that a fluorine-compound is formed, when we consider that the slight quantity of the natrium fluoride solution cannot be put on one line with the precipitating of proteid by the saturating of the solution with a neutral salt.

It might be imagined that the fibrinogen, it is true, is precipitated as such by natrium fluoride, but that also (especially as natrium fluoride solutions usually react slightly alkaline) part of the fibrinogen is changed into fibringlobulin; by which the presence of fibringlobulin in the filtrate would be explained.

Apart from this that then it would not be explained why the fibrinogen precipitated with NaFl does not produce any fibringlobulin by heating, it would have to be expected according to this view that, if the fibrinogen were precipitated with NaFl for the second or third time also a part of it would be changed into fibringlobulin, which ought to be found in the filtrate. This however is not the case; under these circumstances only very little or no fibringlobulin is found in the filtrate.

So, when it should be assumed, that the fibringlobulin is present in the fibrinogen solutions beforehand already, the question remains, whether this proteid is combined with the fibrinogen or must be considered as a simple admixture.

For a compound plead some experiments of HAMMARSTEN [1]), in which is demonstrated that from concentrated fibrinogen solutions after heating to 56—60° and filtering off of the coagulum, relatively less fibringlobulin is obtained than from the same solutions after their having been diluted. If the fibringlobulin were only an admixture it would be expected that the relation between the quantities of fibrinogen and fibringlobulin would always be the same; on the other hand, if the fibringlobulin is combined with the fibrinogen the results of HAMMARSTEN could be explained thus, that in diluted fibrinogen solutions the fibringlobulin is more easily disintegrated. To a compound also points the fact, that when a fibrinogen solution is precipitated for the first time with NaFl a not inconsiderable quantity of fibringlobulin is precipitated also.

Against a compound speaks however that by precipitating with NaFl the fibringlobulin passes into the filtrate, at least for the greater part, for it is difficult to believe, that addition of alkali salt, as NaFl up to a quantity of about 3°/₀ would have for its result a splitting off of fibringlobulin. The following observation may perhaps give some light.

100 ccm. of horsefibrinogensolution were precipitated with the double volume of saturated natrium fluoride solution; the solution of NaFl used reacted almost neutral by exception; with litmuspaper the alkaline reaction was hardly perceptible. Part of this natrium fluoride solution was now made weakly alkaline by addition of 0.8 ccm. normal sodium hydrat with 200 ccm. of the natrium fluoride solution; with this 100 ccm. of the same fibrinogen solution were precipitated twice in the same way.

From the precipitates obtained with neutral and with alkaline NaFl two fibrinogen solutions of equal concentration were prepared.

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[1]) Loc. cit.

The fibrinogen was in both cases coagulated and filtered off by heating to 55—60°. The filtrate of the fibrinogen prepared with slight alkaline natrium fluoride solution gave a slight precipitate by heating to 70° or by addition of picric acid, while the precipitate of fibringlobulin in the other filtrate was clearly greater, perhaps twice or three times.

From this it would follow that the supposed splitting off of fibringlobulin is not brought about by Na Fl but by the alkaline reaction of the natrium fluoride solutions; for this disintegration however exceedingly small quantities of alkali are already sufficient, for also that fibrinogen solution which was prepared with almost neutral Na Fl produced much less fibringlobulin than a fibrinogen solution of the same concentration, not prepared with Na Fl. The supposition that water also, in particular at a rising temperature could bring about the splitting off of fibringlobulin is obvious; if this is the case there would be present in a fibrinogen solution a compound of fibringlobulin with fibrinogen, which is disintegrated more or less by hydrolysis and this idea is, as appears to me, most easily reconciled with the facts. The disintegration will in this case with raised temperature e.g. at 55—60° be rather complete; from diluted solutions relatively more fibringlobulin may however be obtained than from concentrated solutions, because in the first case the disintegration will be more complete owing to the greater excess of water. That not all the fibringlobulin passes into the filtrate by the precipitation with Na Fl, becomes clear if only a partly hydrolytic disintegration is accepted.

If the fibringlobulin is mixed simply with the fibrinogen in consequence of hydrolysis, be it then for a part only, it cannot be expected, — with a view to this, that by half saturation with salt as is usual with the preparation of fibrinogen, no complete precipitation of the fibringlobulin takes place, — that in every fibrinogensolution the relation between the quantities of fibrinogen and fibringlobulin will be the same; this may perhaps lead to the explanation of some observations of HAMMARSTEN [1]) from which it appeared that fibrinogensolutions prepared from different plasma produce, it is true, relatively different quantities of fibringlobulin, that however a diluted solution does not always produce relatively more fibringlobulin than a concentrated solution.

In conclusion I will discuss some facts here, relating to clotting by means of ferment.

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[1]) loc. cit. p. 456.

Of the indentity of the fibringlobulin which is obtained by the coagulation by ferment and that which is found in filtrate after the heat-coagulation of the fibrinogen, there is no doubt, on account of the conformity in composition, coagulation temperature etc. When however it must be assumed that the fibringlobulin is already beforehand present in the fibrinogensolutions, then for the present falls away every ground to assume that by the clotting by ferment the fibringlobulin should be formed still in another way e.g. by transformation of fibrinogen, the more so, as the quantity of fibringlobulin which is obtained by clotting with ferment certainly is comparatively not larger than that which can be prepared by heating from a fibrinogensolution. HAMMARSTEN [1]) found, it is true, that in weak alkaline solutions relatively little fibrin was formed by ferment and so relatively much proteid remained dissolved; this may partly be explained by the fact that the fibringlobulin was disintregrated very completely by the alkaline reaction, partly also, as HAMMARSTEN himself observes, by the fact, that under these circumstances part of the fibrin remained dissolved as "soluble fibrin".

From the fact that a solution of fibrinogen, from which the fibringlobulin is removed by means of NaFl, clots with fibrinferment, must be deduced that by removal of the fibringlobulin the fibrinogen proper is not, as might be expected from the formula given by SCHMIEDEBERG and defended a short time ago by HEUBNER [2]) changed into fibrin, and that in general the fibringlobulin does not play a considerable part in the clotting. So the clottingprocess must consist in an alteration of the fibrinogenmolecule itself. That fibringlobulin is present in the serum of coagulated fibrinogensolutions can be easily explained from this, that fibringlobulin was found already in free condition in greater or smaller quantities in the fibrinogensolution, so the supposition, that the ferment causes a splitting off of fibringlobulin is superfluous as may be deduced from this.

Physics. — "*The transformation of a branch plait into a main plait and vice versa.*" By Prof. J. D. VAN DER WAALS.

If for a binary mixture the temperature is raised above the critical temperature of one of the components, the ψ-surface has a plait, which does not occupy the whole breadth from $x = 0$ to $x = 1$, but which is closed on the side of the component for which T_k lies below the chosen value of T. In normal cases such a plait

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[1]) Pflügers Archiv, Bd. 30, p. 479.

[2]) Arch. f. exp. Pathol. u. Pharmakol. Bd. 49, p. 229.

which is closed on one side, does not present any special particularities, and starting from the open side a bitangent plane may be rolled regularly over the binodal curve as far as the plaitpoint. There are, however, also cases where we meet with complications, and already in my "Théorie moléculaire" I have allowed in my description of the ψ-surface, for the possibility of the existence of a branch plait by the side of the main plait. If two plaits exist simultaneously over a very great range of temperature, we may properly speak of a transverse plait and a longitudinal plait, and the non-miscibility in the liquid state may be ascribed to the longitudinal plait. But if these two plaits occur only over a small range of temperature, it is better to speak of a main plait and a branch plait; I have chosen these names, because really in such cases one of the plaits may be considered as main plait, and the other only as branch plait. But, what has not been observed as yet, the circumstance may occur, that at a certain temperature these two plaits reverse their parts. What was a branch plait, becomes a main plait, and the main plait is reduced to a branch plait.

In saying this I have chiefly in view the description of the modifications to which the ψ-surface is subjected with change of the value of T, to account for the observations of KUENEN on the critical phenomena of mixtures of ethane and some alcohols.

These mixtures have, for a value of T only little greater than T_k of ethane, a plait on the ψ-surface with a continuous course without any complication. But with rise of T, besides the plaitpoint on the ethane side, a new plaitpoint appears lying more to the side of the alcohol. So from this temperature T_1 we may speak of a three-phase-pressure. With further rise of T the new plait extends, and at a certain higher value of $T = T_2$, the first plaitpoint disappears. Then the three-phase-pressure vanishes, and from that moment the plait has resumed its simple form. Between T_1 and T_2 we have, therefore, a plait with two plaitpoints. If referring to a plait we speak of a base and a top, we have between T_1 and T_2 a plait with one base and two tops. Beyond the limits of T equal to T_1 and T_2, the plait has only one base and one top. But whereas just above T_1 the top which has newly appeared, extends but little beyond the binodal curve of the original plait, at a higher value of T this top will extend further; the top on the ethane side contracts, and disappears altogether at T_2, and as we shall show, disappears as a branch plait.

As therefore the plait appearing at T_1, is originally a branch plait, a transformation must take place with increasing value of T

which converts this branch plait into a main one. On the other hand that part of the plait, which at T_1 was situated in the neighbourhood of the existing plaitpoint lying below T_1, and which was then a main plait, must have been reduced to a branch plait for values of T slightly below T_2.

That the distinction between a main plait and a branch plait is not arbitrary, but essential, appears when we determine which of the two tops which occur between T_1 and T_2 belongs to the base of the plait, and when this is ascertained, examine in what way the binodal curve of the other top must be completed.

So the question is, when the bi-tangent plane is rolled over the binodal curve from the base part of the plait, which of the two occurring tops will be reached by continued rolling.

If we consult fig. 1, it is easily seen that a rolling tangent plane which comes from the right side, and which has reached the two points of contact A' and A'', has obtained a new point of contact in A, lying on the same isobar and in this way has become a plane touching in three points. At the assumed temperature we have therefore a three-phase-pressure. In this case there are two tops of a plait viz. P and Q. But there cannot be any doubt as to which of these two tops belongs to the base part lying right of $A'A''$. If viz. we continue to roll the tangent plane when it has the line AA' as nodal line, the binodal line on the side of the small volumes between the points A'' and A is completed by the curve $A''BCA$, the configuration $A'B'C'A'$ giving on the other hand the completion on the side of the larger volumes. This harmonizes with the diagram in my Théorie Moléculaire. (Cont. II p. 23). So when continuing to roll we reach P as top of the plait. We are therefore justified in considering the part of plait $A'PA$ as belonging to the main plait. There lies, however, on and by the side of the main plait, a second configuration, of which AQA'' is a part. If a rolling tangent plane is moved over it, starting from Q, the binodal curve described in this way does not end in the points A and A'', but if the plane has reached those points and has therefore again assumed the position of the three-phase-triangle, we may roll it continuously further till it has reached a point of the spinodal curve. This curve is denoted by D in fig. 1. The binodal curve under consideration has then obtained a minimum pressure; the conjugate point D' is then a cusp [1]).

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[1]) For a proof of these and similar properties consult Cont. II, fig. 3. Further the very important papers of KORTEWEG on the theory of plaits.

When the plane is rolled further the binodal curve passes the part DE' on the left side and the part $D'E$ on the right side, where the spinodal curve is again met with. For this part there is a maximum pressure, while there is now a cusp in E'. And finally this plait, which has its top in Q, is closed by the portion $E'RE$ of its binodal curve. If we consider also unstable phases as realisable, states between E' and R coexist with conjugate ones between E and R on this part. The point R closes this branch plait as unrealisable plaitpoint.

There is not the slightest doubt that for the above mentioned mixtures of ethane and alcohol just above T, the newly appearing plaitpoint Q on the alcohol side leads to the diagram of fig. 1 and that Q is then the top of a branch plait. If the points A and A'' are still very close together, then the distances from these points to points of the spinodal line must, a fortiori, be extremely small, and we have justly assumed that the tangent plane in $A'A''$ when rolled further, passes through the spinodal curve on the side of A''.

That on the other hand at temperatures just below T_2 the plait the top of which is P, must be considered as a branch plait, is beyond doubt for the same reasons. Above T_2 namely, only the top Q is found, and the whole plait does not present the slightest complication. Only with decrease of temperature below T_2 an extremely small bulging out appears in the beginning at P (i. e. in the position which that point has at that temperature) and the same reasons which led us to consider the point Q as top of a branch plait just above T_1, must lead us now to consider P as top of a branch plait. Fig. 3 represents the binodal lines in this case. Only we have assumed there that the temperature has fallen already so much below T_2, that the branch plait has got such an extension, that at first sight it is not to be distinguished from a part of a main plait.

Both in fig. 1 and in fig. 3 there is asymmetry between the two binodal curves of the tops P and Q. But when T is gradually changed from T_1 to T_2 or vice versa, fig. 1 will gradually pass into fig. 3 or vice versa. This transition requires a value of T, at which the asymmetry between the two tops P and Q has vanished. What the shape of the binodal curves must be at the transition temperature, is represented in fig. 2. Then we have one plait with one base, but with two heads.

If we compare fig. 1 and fig. 2, the only difference is that the points B' and E' have coincided, which involves that the node belonging to B' and that belonging to E', so the points B and E, also coincide. From fig. 2 we derive fig. 1 by separating again the parts which have run together, at the points which have coincided, and which is denoted by B' and E', and by doing the same with the point $B\,E$. In the same way fig. 2 leads to fig. 3. But the way in which this separation must take place is different for these two transitions. What happens in one case in the left-hand point, takes place in the other case in the right-hand point.

The coinciding of the points B' and E' is represented in fig. 2 on the spinodal curve; also the coinciding of the points B and E. The spinodal line is namely the curve which is denoted thus — — — —, and which runs through the points $B'E'\,P\,D\,R\,C\,Q\,BE$. That the coinciding must take place on the spinodal curve might be anticipated from the characteristic which we have used to distinguish between main plait and branch plait. We had to consider Q as top of a branch plait, if the rolling tangent plane, arrived at the position $A'A''$, reached the spinodal curve on the side of A'' when rolled further, so in the space lying within the top Q. On the contrary P was the top of a branch plait when this happened on the other side. For the case that there is symmetry between the two tops P and Q, the meeting of the spinodal curve must take place on both sides simultaneously. But we might also have taken as criterion for the main plait, that the main plait is such a plait for which the points B' and E' are separated [1]). The comparison of these two criteria leads to the fact that the coincidence of the points B' and E' must take place on the spinodal curve. But as long as the two tops P and Q are present, whatever the character of these tops may be, there is a third plaitpoint, viz. the point R, belonging to a composition of the binary mixture which lies between the compositions belonging to the points P and Q.

In the figs. 4, 5 and 6 the complete (p, x) curves have been given for the coexisting phases. Fig. 4 for a temperature which is little higher than T_1, and at which Q is still the top of the branch plait, and fig. 6 for temperatures below T_2, at which P is still the top of the branch plait. Fig. 5 represents the transition temperature. I may assume as known that the differential equation for this (p,x) curve is:

$$v_{21}\,dp = (x_2 - x_1)\frac{\partial^2\zeta}{\partial x_1{}^2{}_{pT}}\,dx_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Whenever that the (p,x) curve has a point in common with the spinodal curve $\left(\frac{\partial^2\zeta}{\partial x^2{}_{pT}} = 0\right)$, p is a maximum or a minimum. This

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[1]) Cf. Wiskundige opgaven enz. IV^{de} deel, 5de stuk, Vraagstuk CXXXIX, where it is also demonstrated, that the branches of the binodal curve which touch in $B'\,E'$, have the same curvature. Also the conjugate ones, which touch in BE.

is the case in the plaitpoints, but also in the other points, in which a phase coexisting with an other, passes through the spinodal curve. In fig. 5 there must therefore be maxima or minima at P, Q, $B'E'$, BE, D, C, R. If from the differential equation we calculate the value of $\frac{d^2p}{dx_1^2}$ for the points $B'E'$ and BE, it appears, that for the two branches which meet, this value is the same there. If we differentiate equation (a), we get:

$$v_{21}\frac{d^2p}{dx_1^2}+\frac{dp}{dx_1}\frac{d(v_{21})}{dx}=(x_2-x_1)\left\{\frac{\partial^3\zeta}{\partial x_1^3}_{pT}+\frac{d^2v}{dx^2}_{pT}\frac{dp}{dx_1}\right\}+\frac{\partial^2\zeta}{\partial x_1^2}_{pT}\frac{d(x_2-x_1)}{dx_1}.$$

$\frac{dp}{dx_1}$ and $\frac{\partial^2\zeta}{\partial x_1^2}_{pT}$ being 0, this equation is simplified to:

$$v_{21}\frac{d^2p}{dx_1^2}=(x_2-x_1)\left(\frac{\partial^3\zeta}{\partial x_1^3}\right)_{pT}.$$

The quantities v_{21}, (x_2-x_1) and $\left(\frac{\partial^3\zeta}{\partial x_1^3}\right)_{pT}$ are the same for the two branches, and so also $\frac{d^2p}{dx_1^2}$. In fig. 5 this has not been fulfilled in the tracing of the branches in the neighbourhood of the points $B'E'$. Better in the neighbourhood of the points BE. Also in the cusps an inaccuracy in the proper curvature of the branches may be detected here and there. But the figs. should be considered as only schematical. The properties that the two curves in fig. 2 which touch have the same curvature, and that this is also the case with the two curves which touch in fig. 5, are of course closely allied. From

$$\frac{dp}{dx}=\left(\frac{\partial p}{\partial x}\right)_{vT}+\left(\frac{\partial p}{\partial v}\right)_{xT}\frac{dv}{dx}$$

and

$$\frac{d^2p}{dx^2}=\frac{\partial^2p}{\partial x^2}_{vT}+2\frac{\partial^2p}{\partial x\,\partial v}_{T}\left(\frac{dv}{dx}\right)+\frac{\partial^2p}{\partial v^2}_{xT}\left(\frac{dv}{dx}\right)^2+\frac{\partial p}{\partial v}_{xT}\frac{d^2v}{dx^2}$$

follows for two curves, passing through the same point, and for which, therefore, $\frac{\partial^2p}{\partial x^2}$, $\frac{\partial^2p}{\partial x\,\partial v}$, $\frac{\partial^2p}{\partial v^2}$ and $\frac{\partial p}{\partial v}$ is the same, and which touch in that point, and for which also $\left(\frac{dv}{dx}\right)$ is therefore the same, that the equality of $\frac{d^2v}{dx^2}$ involves also the equality of $\frac{d^2p}{dx^2}$ and vice versa. KORTEWEG's thesis, which has also been proved by KLUYVER, might therefore also be proved by the method followed here.

Mathematics. — "*A group of algebraic complexes of rays*". By Prof. JAN DE VRIES.

§ 1. Supposing the rays a of a pencil (A, α) to be projective to the curves b^n of order n, passing through n^2 fixed points, B_k, of the plane β, we shall regard the complex of the rays resting on homologous lines. For $n = 1$ we evidently find the *tetrahedral complex*.

Out of any point P we project (A, α) on β in a pencil (A', β), generating with the pencil (b^n) a curve c^{n+1}. So we have a *complex of order* $(n+1)$.

Evidently the curve c^{n+1} does not change when the point P is moved along the right line AA'; so the intersections of the ∞^3 cones of the complex (P) with the plane β belong to a system ∞^2. It is easy to see that they form a *net*.

For, if such a curve c^{n+1} is to contain the point X and if b^n_X is the curve through B_k and X, and a_X the ray conjugate to it through A, the point A' must be situated on the right line connecting X with the trace of a_X on the plane β. In like manner a second point through which c^{n+1} must pass, gives a second right line containing A'. The curve c^{n+1} being determined as soon as A' is found, *one* curve c^{n+1} can be brought through two arbitrary points of β.

On the right line $\alpha\beta$ the given pencils determine a $(1, n)$-correspondence; its $(n+1)$ coincidences C_k are situated on each c^{n+1}. So the net has $(n^2 + n + 1)$ fixed base-points [1]).

§ 2. When A' moves along a right line a' situated in β and cutting the plane α in S, the curve c^{n+1} will always have to pass through the n points D_k which a' has in common with the curve b^n conjugate to the ray AS. It then passes through $(n+1)^2$ fixed points, so it describes a pencil comprised in the net.

To the $3\,n^2$ nodes of curves belonging to that pencil must be counted the n points of intersection of $\alpha\beta$ with that c^n passing through the points B_k and D_k. Hence a' contains, besides S, $(3\,n^2 - n)$ points A' for which the corresponding curve c^{n+1} possesses a node.

If A' coincides with one of the base-points B_k then the projective pencils (A') and (b^n) generate a c^{n+1} possessing in that point B a node. According to a well known property B is equivalent to two of the nodes appearing in the pencil (c^{n+1}) which is formed

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[1]) To determine this particular net one can choose arbitrarily but $\frac{1}{2}\,n(n+3) - 1$ points B and three points C.

when A' is made to move along a right line a' drawn through B.

From this ensues in connection with the preceding:

The locus of the vertices of cones of complex possessing a nodal edge is a cone Δ *of order* $n\,(3n-1)$ *having* A *as vertex and passing twice through each edge* AB_k.

§ 3. If P moves along the plane α then the cone of the complex (P) consists of the plane α and a cone of order n cut by α along the right lines AC_k. So α is a *principal plane* and at the same time part of the singular surface.

The plane β belongs to this too. For, if P lies in β then the rays connecting P with the points of the ray a corresponding to the curve b^n drawn through P belong to the complex. All the remaining rays of the complex through P lie in β. So β is an *n-fold principal plane* and *the singular surface* consists of a simple plane, an n-fold plane and a cone Δ of order $n\,(3n-1)$.

The complex possesses (n^2+n+2) single *principal points*, namely the point A, the n^2 points B_k and the $(n+1)$ points C_k.

§ 4. The nodes of curves c^p belonging to a net lie as is known on a curve H of order $3\,(p-1)$ the Hessian of the net, passing twice through each base-point of the net. This property can be demonstrated in the following way.

We assume arbitrarily a right line l and a point M. The c^p touching l in L, cuts ML in $(p-1)$ points Q more. As the curves passing through M form a pencil, so that $2\,(p-1)$ of them touch l, the locus of Q passes $2\,(p-1)$ times through M; so it is of order $3\,(p-1)$. Through each of its points of intersection S with l one c^p passes having with each of the right lines l and MS two points in common coinciding in S; so S is a node of this c^p.

Consequently the locus of the nodes is a curve of order $3\,(p-1)$.

If l passes through a base point B of the net then the pencil determined by M cuts in on l an involution of order $(p-1)$. This furnishing $2\,(p-2)$ coincidences L, the locus of Q is now of order $(3p-5)$ only. So B represents for each right line drawn through that point two points of intersection with the locus of the nodes, consequently it is a node of that curve.

If l touches in B_1 the curve $c_1{}^p$ having a node in B_1 and if one chooses M arbitrarily on this curve, then the curves of the pencil determined by M have in B_1 a fixed tangent and B_1 is one of the coincidences of the involution of order $(p-1)$. The locus of the nodes has now in B_1 three coinciding points in common with l; consequently it has in B_1 the same tangents as $c_1{}^p$.

For the net N^{n+1} of the curves c^{n+1} lying in the plane β the locus of the nodes H breaks up into the right line $\alpha\beta$ and a curve of order $(3n-1)$. For, $\alpha\beta$ forms with each curve b^n a degenerated curve c^{n+1}.

The locus of the nodal edges of the cones of the complex is a cone with vertex A of order $(3n-1)$ having the n^2 right lines AB_k as nodal edges.

§ 5. The tangents in the nodes of a net N^p envelop a curve Z of class $3(p-1)(2p-3)$[1], the curve of ZEUTHEN. It breaks up for the net N^{n+1} indicated above; for, the tangents to the curves b^n in their points of intersection with $\alpha\beta$ envelop a curve, which must be a part of the curve Z. The pencil (b^n) is projective to the pencil of its polar curves p^{n-1} with respect to a point O; the points of intersection of homologous curves form a curve of order $(2n-1)$; in each of its points of intersection S with $\alpha\beta$ a curve b^n is touched by OS; so these tangents envelop a curve Z' of class $(2n-1)$.

So for N^{n+1} the curve of ZEUTHEN consists of the envelope Z' and a curve Z'' of class $3n(2n-1)-(2n-1)=(3n-1)(2n-1)$.

The pairs of tangents in the nodes of the genuine curves of N^{n+1} determine on a right line l a symmetric correspondence with characteristic number $(2n-1)(3n-1)$. To the coincidences belong the points of intersection S of l with the curve H; to such a point S are conjugated $(2n-1)(3n-1)-2$ points distinct from S; so S is a double coincidence. The remaining $4(n-1)(3n-1)$ coincidences evidently originate from cuspidal tangents.

The locus of the vertices of cones of the complex, possessing a cuspidal edge consists of $4(n-1)(3n-1)$ edges of the cone Δ.

A general net of order $(n+1)$ contains $12(n-1)n$ cuspidal curves, thus $4(n-1)$ more; therefore each of the $2(n-1)$ figures consisting of the right line $\alpha\beta$ and a curve b^n touching it is equivalent to two curves c^{n+1} with cusp. Evidently the nodes of these figures form with the point C_n the section of $\alpha\beta$ with the curve H.

§ 6. On the traces of a plane π with the planes α and β the pencils (a) and (b^n) determine two series of points in $(n, 1)$-correspondence; the envelope of the right lines connecting homologous points is evidently a curve of class $(n+1)$ touching $\alpha\pi$ in its point of intersection with the ray a conjugate to the curve b^n through

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[1] This has been indicated in a remarkable way by Dr. W. BOUWMAN (Ueber den Ort der Berührungspunkte von Strahlenbüscheln und Curvenbüscheln, N. Archief voor Wiskunde, 2nd series, vol. IV, p. 264).

the point $\alpha\beta\pi$, whilst it touches $\beta\pi$ in its points of intersection with the curve b_0^n for which the corresponding ray passes through $\alpha\beta\pi$.

The curve of the complex of the plane π has the right line $\beta\pi$ for n-fold tangent, so it is rational.

If the curve b_0^n touches the intersection $\beta\pi$, then the multiple tangent is at the same time inflectional tangent.

We now pay attention to the tangents r out of the point $S \equiv \alpha\beta$ to the curve b^n corresponding to a. The envelope of these tangents has the right line $\alpha\beta$ as multiple tangent; its points of contact are the $2(n-1)$ coincidences of the involution, determined by the pencil (b^n) on $\alpha\beta$. As S evidently sends out $n(n-1)$ right lines r the indicated envelope is of class $(n-1)(n+2)$.

The planes containing a curve of the complex of which the n-fold tangent is at the same time inflectional tangent envelop a plane curve of class $(n-1)(n+2)$.

§ 7. The curve (π) can break up in three different ways.

First the point $\alpha\beta\pi$ may correspond to itself, so that (π) breaks up into a *pencil* and into a *curve of class n*. This evidently takes place when π passes through one of the principal points C_k.

Secondly the involution on $\beta\pi$ may break up, so that all its groups contain a fixed point; then also a pencil of rays of the complex separates itself. This will take place, when π passes through one of the principal points B_k.

Thirdly the curve π may contain the principal point A. Then the curve b^n corresponding to the ray $a \equiv \alpha\pi$ determines on $\beta\pi$ the vertices of n pencils, whilst also A is the vertex of a pencil. The curve π is then replaced by $(n+1)$ *pencils*.

In a plane through $\alpha\beta$, thus through all principal points C_k, the curve (π) consists of course also of $(n+1)$ *pencils*.

A break up into *two pencils* with a curve of class $(n-1)$ takes place when the plane π contains two principal points B_k or a point B_k and a point C_k.

§ 8. To obtain an analytical representation of the complex we can start from the equations

$$x_3 = 0 \quad , \quad x_1 + \lambda x_2 = 0 ;$$
$$x_4 = 0 \quad , \quad a_x^n + \lambda b_x^n = 0 .$$

Here a_x^n and b_x^n are homogeneous functions of x_1, x_2, x_3, of order n.

For the points of intersection X and Y of a ray of the complex with α and β we find

$$x_1 : p_{13} = x_2 : p_{23} = x_4 : p_{43},$$

$$y_1 : p_{14} = y_2 : p_{24} = y_3 : p_{34}.$$

After substitution, and elimination of λ, we find an equation of the form

$$p_{23}\,(a_1\,p_{14} + a_2\,p_{24} + a_3\,p_{34})^n = p_{13}\,(b_1\,p_{14} + b_2\,p_{24} + b_3\,p_{34})^n,$$

by which the exponent between brackets reminds us that we must think here of a *symbolical* raising to a power.

If in $p_{k4} = x_k\,y_4 - x_4\,y_k$ we put the coordinate x_4 equal to zero, we find for the intersection of the cone of the complex of Y on β the equation

$$(y_3\,x_2 - y_2\,x_3)\,(a_1\,x_1 + a_2\,x_2 + a_3\,x_3)^n = (y_3\,x_1 - y_1\,x_3)\,(b_1\,x_1 + b_2\,x_2 + b_3\,x_3)^n,$$

or shorter

$$y_1\,x_3\,b^n_x - y_2\,x_3\,a^n_x + y_3\,(x_2\,a^n_x - x_1\,b^n_x) = 0.$$

This proves anew, that the intersections of the cones of the complex form a net.

Mathematics. — *“On nets of algebraic plane curves”*. By Prof. Jan de Vries.

If a net of curves of order n is represented by an equation in homogeneous coordinates

$$y_1\,a^n_x + y_2\,b^n_x + y_3\,c^n_x = 0$$

to the curve indicated by a system of values $y_1 : y_2 : y_3$ is conjugated the point Y having y_1, y_2, y_3 as coordinates and reversely.

A homogeneous linear relation between the parameters y_k then indicates a right line as locus of Y, corresponding to a pencil comprised in the net.

To the Hessian, H, passing through the nodes of the curves belonging to the net, a curve (Y) corresponds of which the order is easy to determine. For, the pencil represented by an arbitrary right line l_Y has $3\,(n-1)^2$ nodes. So for the order n'' of (Y) we find $n'' = 3\,(n-1)^2$.

If one of the curves of a pencil has a node in one of the base-points, it is equivalent to two of the $3\,(n-1)^2$ curves with node belonging to the pencil. Then the image l_Y touches the curve (Y) and reversely.

Let us suppose that the net has b fixed points, then H passes twice through each of those base-points; so it has with the netcurve c^n_Y indicated by a definite point Y yet $(nn'-b)$ single points in common; here $n'=3(n-1)$ represents the order of H. The curve c^n having a node in D, determines with c^n_Y a pencil represented by a tangent of the curve (Y). From this ensues that the class of (Y) is indicated by $k''=3n(n-1)-2b$.

The genus g'' of this curve is also easy to find. As the points of (Y) are conjugated *one* to *one* to the points of H these curves have the same genus. So we have

$$g''=\tfrac{1}{2}(n'-1)(n'-2)-b=\tfrac{1}{2}(3n-4)(3n-5)-b.$$

We shall now seek the number of nodes and the number of cusps of (Y). These numbers δ'' and $\varkappa''$ satisfy the relations

$$2\delta''+3\varkappa''=n''(n''-1)-k'',$$

$$\delta''+\varkappa''=\tfrac{1}{2}(n''-1)(n''-2)-g''.$$

From this ensues after some reduction

$$\delta''=\tfrac{3}{2}(n-1)(n-2)(3n^2-3n-11)+b,$$

$$\varkappa''=12(n-1)(n-2).$$

The curve (Y) has nodes in the points Y_B which are images of the curves c^n_B possessing a node in a base-point of the net. For, to each right line through a point Y_B a pencil corresponds, in which c^n_B must be counted for two curves with node.

Each of the remaining nodes of (Y) is the image of a curve c^n, possessing two nodes.

So a net N^n *contains* $\tfrac{3}{2}(n-1)(n-2)(3n^2-3n-11)$ *curves with two nodes.*

To a cusp of (Y) will correspond a curve replacing in each pencil to which it belongs two curves with node. According to a well-known property that curve itself must have a cusp. For a definite pencil its cusp is one of the base-points; this pencil has for image the tangent in the corresponding cusp of (Y).

So a net N^n *contains* $12(n-1)(n-2)$ *curves with a cusp.*

The two properties proved here are generally indicated only for a net consisting of polar curves of a c^{n+1}. We have now found that they hold good for every net, independent of the appearance of fixed points B.

We can now easily determine the class z of the envelope Z of the nodal tangents of the net.

Through an arbitrary point P of a right line l pass z of these tangents. If we add the second tangent in the corresponding node to each of these tangents, these new set of z tangents intersects the right line l in z points P'. The coincidences of the correspondence (P,P') are of two kinds. They may originate in the first place from cuspidal tangents, in the second place from the points of intersection of l with the curve H; each of these latter points of intersection however is to be regarded as a double coincidence. Thus $2z = 12(n-1)(n-2) + 6(n-1) = 6(n-1)(2n-3)$.

The curve of Zeuthen *is of class* $3(n-1)(2n-3)$.

ERRATA.

Page 504, line 13, for members read member.
,, 504, ,, 15, ,, not wanting read wanting.
,, 509, ,, 24, ,, blewish read bluish.

(April 19, 1905).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday April 22, 1905.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 22 April 1905, Dl. XIII).

CONTENTS.

The following papers were read:

Chemistry. — "*On the different forms and transformations of the boundary-curves in the case of partial miscibility of two liquids.*" By J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of March 25, 1905).

1. In a preceding communication[1]) I showed, that when one of the two components of a binary mixture is *anomalous*, the T, x-representation of the spinodal curve, and consequently also that of the connodal curve, the so-called saturation- or boundary-curve $x = f(T)$, can assume different forms, which are indicated there. It depends principally only on the value of the *critical pressure* of the normal component, with regard to that of the anomalous component, which of the different forms may occur with a definite system of substances.

An affirmation of the theory, developed by me, that is to say of the cases and transformations deduced by me from the general equations, is found in the circumstance, that these cases and transformations may be realised *in quite the same succession with one and the same substance*, and this by *external pressure*. In the same way as with *different* normal substances as second component the form drawn in fig. 7 l.c., presents itself at relatively *low* critical pressures (with regard to that of the anomalous component), and that of fig. 2 l.c. at relatively *high* critical pressures — the form of fig. 7 may be realised at relatively *low* external pressure, and that of fig. 2 at relatively *high* external pressure, whereas at intermediate pressures all the transitional cases again will return in just the same succession.

2. For that purpose we but have to look at the p, T-diagram of the critical curve for ethane and methylalcohol, as projected by KUENEN[2]) in consequence of his experimental determinations (compare fig. 1). We see, namely, immediately from the form of the curve, departing from C_2 (the higher critical temperature, that of CH_3OH), which indicates the pressures, at which for different temperatures the two coexistent phases coincide, and above which we have consequently perfect homogeneity, that according to the value of the pressure *one* critical point a may occur (at the pressures 1 and 2), *two* viz. a and b, c (at 3), *three*, viz. a, b and c (at 4), again *two*, that is to say (a, b) and c (at 5), and finally again *one*, viz. c (at 6). (also compare fig. 2).

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[1]) These Proceedings of 28 Jan. 1905.

[2]) Phil. Mag. (6) **6**, 637—653, specially p. 641 (1903).

All this is rendered still more conspicuous, when we project a *space*-representation, in connexion with fig. 1 and of some successive p, x-sections. In fig. 1 D_1 and D_2 represent the vapourpressure-curves of the two components; LM is the threephasepressure-curve, which terminates abruptly in M, where the gaseous phase 3 coincides with the liquid phase 1 (which consists for the greater part of ethane), because it meets there the critical curve C_1C_2, that is to say the curve of the plaitpoints P. Beyond M there is coexistence only between the *fluid* phase 3,1 and the phase 2, which consists principally of alcohol. It is the equilibrium between these latter phases, of which in fig. 2 the T, x-representation is projected at different pressures. (The dotted boundary-curve 0 corresponds with a pressure inferior to the critical pressure of the second component, and superior to that of the first one). The T, x-representation of fig. 3 corresponds, at the (variable) threephase-pressure, with the threephase-equilibrium unto M. In fig. 4 the indicated space-representation is drawn, which will be clear now without the least difficulty [1]). For the different higher pressures the corresponding T, x-sections are drawn in that representation.

Remark. From C_2 (see fig. 1) to the maximum at 126°, where a and b coincide, and also from the minimum at 26°, where b and c coincide, to the lowest temperatures, increase of pressure will *lower* the critical temperature Q, and these critical points will be *upper* critical points in the T, x-sections at constant pressure (see fig. 2). On the other hand, from the maximum at 126° to the minimum at 26° increase of pressure will *raise* the critical temperature, and the designed critical points will be *lower* critical points.

That increase of pressure *favours* the mixing, as is clear from fig. 1 and from the p, x-representations — as well in the case of an upper critical point, as of that of a lower one — is also in agreement with the T, x-representation of fig. 2. For in the case of an *upper* critical point (see also fig. 5) a point A, situated *within* the boundary-curve will come — when the pressure is increased, by which T_0 will be removed to the lower point T_1 (for $\frac{dT}{dp}$ is *negative*, as we saw above) — *without* the new boundary-curve. And the same will be obviously the case for a *lower* critical point, where $\frac{dT}{dp}$ is *positive*.

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[1]) This space-representation (without the T, x-sections) has been already projected independently by Mr. BÜCHNER; but is not inserted in his communication. (These Proceedings of 28 Jan. 1905).

To the considered type also belongs $SO_2 + H_2O$, $C_2H_6 + H_2O$, and equally *ether* and *water*. This latter mixture only with this difference, that the composition of the vapour-phase is here continually *between* that of the two liquid phases (see fig. 3^a). KUENEN [1]) found, that at 201° the vapour-phase coincides with that liquid phase, which consists for the greater part of ether. The threephase-pressure is then 52 atm. (At C_1 we have $T_1 = 195°$, $p_1 = 38$ atm.).

The p, x-diagrams would now show a *maximum-vapourpressure*, if the two liquid phases 1 and 2 could become identical. In connexion with this the threephase-pressure will be *higher* (here only some mM) than the vapourpressures of each of the components, and it follows immediately from fig. 1, that the critical curve C_1C_2, or rather C_1M, will at first run back from C_1, that is to say will present a *minimum* critical temperature. In the case of $C_2H_6 + CH_3OH$, where the composition of the vapour-phase is *without* that of the liquid layers, the threephase-pressure will always be *between* the vapourpressures of the components.

3. Now, as to the representation of the so-called transversal- and longitudinal plait on the ψ-surface at different temperatures (in its projection on the v, x-surface) in the case of $C_2H_6 + CH_3OH$, it will be obvious, that the critical point Q, considered above, of the longitudinal plait always lies at the side of the *small* volumes. For increase of pressure finally favours (see above) the mixing.

The successive transformations of the transversal- and of the longitudinal plaits are further represented *schematically*, in agreement with the p, x-sections, in fig. 6. The longitudinal plait, occurring here, is regarded by VAN DER WAALS [2]) — and this equally in the case to be considered presently — as a *transformed* transversal plait. Many questions however, connected with these plaits, lose — as has been remarked already by VAN DER WAALS [3]) — much of their weight, and become of *secondary* interest, as soon as we succeed *in connecting with other properties* of the components of the mixture the often so complicated transformations, which may occur at the different plaits. And to do this an attempt is made in my preceding communication. There I showed, that the *ordinary* theory of the association is capable of representing the different possible forms of the boundary-curves qualitatively, and in many cases even quantitatively.

4. We will now consider the *second* of the *three* principal types,

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[1]) Z. f. Ph. Ch. **28**, 342—365, specially p. 352 (1899).

[2]) These Proceedings **7**, p. 467 (1899).

[3]) Id. 25 Oct. 1902, p. 399.

indicated in a recent communication of BAKHUIS ROOZEBOOM and BÜCHNER [1]), the *first* of which is amply considered above.

Fig. 7 gives the p,T-representation of it; fig. 8 the T,x-diagram of some sections at constant pressure (the dotted boundary-curves are relative to pressures between that of M'' and C_2, and to that below M').

The series of p,x-diagrams, and also the space-representation (also projected already by BÜCHNER) are omitted here. We find that case with mixtures of *ethane* and *ethyl-*, *propyl-*, *isopropyl-* and *normal butylalcohol*, all examined by KUENEN [2]). Also *triethylamine* + *water*, and some other mixtures [3]) with a *lower* critical point (this lies at 18°,3 C in the last mentioned case) belong to that type. Indeed, it is obvious from fig. 8 and from the p,x-diagrams, that M' is at present a lower critical point, contrary to M in fig. 1, which was an upper critical point. For, whereas in M (fig. 1) the threephase-pressure *ends*, this pressure *commences* in M'. Farther however, in M'', the gaseous phase coincides again with the first liquid phase (rich in ethane) (because the threephasepressure-curve $M'M''$ anew meets the critical curve C_1C_2), after which the further course is the same as with the preceding type. The T,x-representation with variable threephase-pressure, that is to say between M' and M'' (fig. 9*a*), is in agreement with it.

It appears that, as little as with the preceding type, there exists here a properly-said upper critical point. For in both cases 1 and 3 coincide, when the threephase-pressure comes to an end, and not 1 and 2 (see fig. 3*a* and 9*a*). The vapour-phase becomes identical with the upper liquid layer and vanishes, but then there remain still two phases, the lower liquid layer 2 and the fluid phase 1,3. These however always pass into each other with further increase of the temperature, as is plainly indicated by the space-representations (see e. g. fig. 4), at the vapourpressure-curve of the second component at $x_{13} = x_2 = 1$ (also compare the dotted boundary-curves in fig. 2 and 8). So, if we begin with a mixture of a definite composition, then *with increase of temperature we come finally* beyond the bourdary-curve 1,3 at the moment, that the liquid layer 2 has entirely vanished. So we have demonstrated more exactly at the same time what I have said in my preceding communication, namely that the existence of a lower critical point involves necessarily that of a higher upper one. It is however not, as we have seen, a *critical* point proper.

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[1]) Id. 28 Jan. 1905, p. 531—537.

[2]) Z. f. Ph. Ch. 28, p. 358—363 (1899).

[3]) Among others β-collidine, and the bases of the pyridine- and chinoline-series with H_2O.

From the series of p,x-diagrams we might still see, that the boundary-curve of the two liquid phases with the plaitpoint Q below the temperature, where 1 and 2 coincide (in M'), does not come *within* the boundary-curve vapour-liquid, as KUENEN [1]) thinks, but has *entirely vanished.* In fact, there is no reason to suppose, that in M' decrease of pressure should cause again permanent separation (if that state were realisable), as apparently KUENEN thought that he had "undoubtedly" to expect with mixtures of triethylamine and water [2]). What he has observed in another case with propane and methylalcohol [3]), must be ascribed in my opinion to this, that the expansion just above the (upper) critical point has caused the temperature to fall a little, so that he came on the (metastable) part of the two liquid curves, which lies below the threephase-pressure. But when the cusp was reached, the metastable equilibrium became immediately stable, and by further expansion homogeneous liquid and vapour reappeared.

Because increase of pressure in this case too favours the mixing, as appears from fig. 7 and from the p,x-diagrams, the plait on the ψ-surface will have turned its plaitpoint Q also to the side of the *small* volumes. Fig. 10 gives a schematical representation of the successive transformations of the two plaits, or rather of the transversal plait, for we can regard again with VAN DER WAALS the longitudinal plait as a transformed transversal one.

In fig. 7 we see, that increase of pressure raises the critical points Q, at least in the beginning, if the curve $M'C_2$ should present a maximum; and from the p,x-diagrams, that these critical points will be again in that case *lower* critical points, just as in fig. 1 between the minimum and the maximum in the curve of the critical points Q.

Equally in the case of the second general type the threephase-pressure may be either *between* the vapourpressures of the two components, as in the case of C_2H_6 and the mentioned alcohols, in which case the composition of the vapour-phase will be *not between* that of the liquids — or may be *higher* than that of the components. Then there is again a *maximum*-vapourpressure after the coinciding of the two liquid phases below the lower critical point, and the composition of the vapourphase is *between* that of the liquid layers [4]).

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[1]) Phil. Mag. l. c. p. 645.

[2]) Id. p. 652.

[3]) Id. p. 646.

[4]) That at the coinciding of the two liquid phases 1 and 2 in M' the vapour-phase does not necessarily coincide with 1 and 2, has been already remarked by KUENEN, and still earlier has been deduced by me theoretically for an analogous case

(see fig. 9*b*). It is a matter of course, that in fig. 7 the critical curve C_1C_2, or rather C_1M'', again turns back in that case, consequently presents a *minimum*; equally the critical curve $M'C_2$ will not seemingly cut C_1C_2 between C_1 and M'' in this case, but remain on the left of C_1. This case occurs e. g. with mixtures of *water* and *triethylamine*, where in consequence of the almost complete unmiscibility of the two components above the lower critical point the threephase-pressure will be but very little smaller than the *sum* of the vapourpressures of the two components. So KUENEN found, that at 93° C. the threephase-pressure was 142,6 cm., whereas the vapourpressures of triethylamine and water were resp. nearly 86 c.m. and 58,6 cm., consequently together 144,6 cm.

5. It is worth remarking, that the region of the threephase-pressure continually shrinks the more we ascend to *higher alcohols* (KUENEN). In the case of $C_2H_6 + C_2H_5OH$ the temperatures in M' and M'' were resp. 31°,9 (46 atm.) and 40°,7 (55 atm.); in that of $C_2H_6 + C_3H_7OH$ these are 38°,7 and 41°,7; in that of C_2H_6 + isopropylalcohol ? and ± 44°; in that of *n*-butylalcohol 38°,1 and 39°,8 (55 atm.). Finally with isoamylalcohol three phases were no longer realisable, so that the critical points Q coincide there with the critical points P, one continuous critical curve being formed from C_1 to C_2 (General type III).

In agreement with this is the fact, that the anomaly of the alcohols decreases, as these are higher. In fact, we approach then more and more the case of mixtures of *normal* substances, where only at *very low* temperatures (see my preceding communication) a formation of two liquid layers can present itself. KUENEN found indeed, that C_2H_6 + ether mix in all proportions, whereas $C_2H_6 + H_2O$ again present a threephase-equilibrium.

The influence of the fact that the *alcohol* is higher is also sensible in the case of mixtures of CS_2 and different alcohols. So we find for the upper critical points of CS_2 with CH_3OH, C_2H_5OH, C_3H_7OH and C_4H_9OH successively +40°,5 (ROTHMUND), —10°,6 (KUENEN) —52° (K.) and —80° (K.).

Equally the influence of the hydrocarbon was examined by KUENEN. While, as we saw above, the separation between type I and II in the case of C_2H_6 + different alcohols was between CH_3OH and

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(equilibrium between two solid phases and one liquid phase). This will obviously also be the case with an upper critical point, as appeared from the experiments of SCHREINEMAKERS with *water* and *phenol*. We will return to this question in § 8.

C_2H_5OH, and that between II and III between *n*-butyl- and isoamylalcohol, the separation between I and III in the case of CH_3OH + different hydrocarbons is lying now between C_2H_6 and C_3H_8. Propane and the following hydrocarbons + CH_3OH belong consequently, just as C_2H_6 + isoamylalcohol, and the greater part of the mixtures with an *upper* critical point, examined by GUTHRIE, ALEXEJEW and ROTHMUND, to the *third* general type, which we will briefly consider now.

6. The *third* general type is principally characterised by this, that the threephasepressure-curve meets *no* longer the critical curve $C_1 C_2$, but has come to an end already before (fig. 11). This third type may proceed either from the second type (see fig. 7), the threephasepressure-curve $M' M''$ shrinking more and more, and finally vanishing, as is the case with the transition from C_2H_6+C_4H_9OH to C_2H_6 + $C_5H_{11}OH$ (see above) — or from the first type, when ΔM ends already before $C_1 C_2$. In the first case (e.g. with C_2H_6+$C_5H_{11}OH$, C_2H_6 + ether) there exists no threephase-equilibrium at all — or it should be at very low temperatures, which even may be expected according to the theory (see my preceding communication), so that the question arises, whether also in the case of fig. 7 there exists at low temperatures a new threephasepressure-curve, and we will return to that question at the end of this communication — in the second case there exists a threephase-pressure from the beginning, which vanishes at a definite temperature (*upper* critical point). To this latter case belong the mixtures of CH_3OH with C_3H_8, etc., H_2O + CO_2, CS_2 + different alcohols (KUENEN), and also the greater part of the mixtures formerly examined (see above).

But in the case of this third type there exists still another difference. Firstly the threephasepressure-curve again may lie either between or without the vapourpressure-curves of the two components, with all the consequences, connected with it in the p, x-diagrams, etc. (see above). As to the mixtures of CH_3OH with C_3H_8, C_5H_{12}, C_6H_{14}, with all these is found (KUENEN, l. c.), that the threephase-pressure is *higher* than the vapourpressures of the hydrocarbons, contrary to C_2H_6 + CH_3OH, which belongs to type I, where the threephasepressure is lower than that the vapourpressure of C_2H_6. Equally with phenol and water (SCHREINEMAKERS, V. D. LEE), H_2O + CS_2 (REGNAULT) — where, according to the exceedingly small miscibility, the threephase-pressure is again a little smaller than the sum of the vapourpressures of the components — H_2O + Br_2 (BAKHUIS ROOZEBOOM), H_2O + isobutylalcohol (KONOWALOW), CS_2 + CH_3OH and C_2H_5OH (KUENEN), H_2O + aniline (KUENEN), etc. we find everywhere the threephase-pressure higher than the vapourpressures of each of the components. Only of $H_2O + SO_2$ (Bakhuis Roozeboom), and of some systems more ($S +$ Xylol and Toluol, $CO_2 + H_2O$) we know with certainty, that the threephase-pressure is between the vapourpressures of the two components.

There exists, however, still another, important difference. Wheras in the case of type I (fig. 1) the critical curve QC_2 presents alternately positive and negative $\frac{dT}{dp}$, and in that of type II (fig. 7) $\frac{dT}{dp}$ is of course positive in the beginning in M' (indeed, the point Q just appears in M') — in the case of type III the initial course of MQ may be as well to the left as to the right.

Is this course to the *left*, that is to say is $\frac{dT}{dp}$ negative, then — just as in fig. 1 between C_2 and the maximum and between the minimum and the lowest temperatures — increase of pressure will *lower* again the critical temperature in the case of these upper critical points, and the plait on the ψ-surface in its v, x-projection will again have turned the plaitpoint Q to the side of the *small* volumes. (This is equally the case with $C_2H_6 +$ isoamylalcohol, where no threephase-equilibrium could be stated, but where the plaitpoint Q, which has become here identical with P, has removed strongly to the x-axis, just as in the case of mixtures of C_2H_6 and the *lower* alcohols). We find this e.g. with $C_3H_8 + CH_3OH$.

But when the initial course of MQ is to the *right*, as in the case of $C_5H_{12} + CH_3OH$, $C_6H_{14} + CH_3OH$, and of phenol and water, then increase of pressure will *raise* the point Q, and the mentioned plait will now have turned the plaitpoint Q for the first time to the side of the *large* volumes.

The question, whether the longitudinal plait, as in the case of phenol and water, will present still a second plaitpoint at very small volumes, consequently at very high pressures — in other terms, whether the coexistent liquid phases, after diverging initially, will reapproach afterwards in composition, has not yet been answered theoretically with certainty. It however appears to me, that where in the case of $C_3H_8 + CH_3OH$ the plait has turned the plaitpoint Q to the side of the *small* volumes, whereas C_5H_{12} and C_6H_{14}, equally with CH_3OH, have turned this point to the side of the *large* volumes, there must exist a *continuous* transition between the two kinds of longitudinal plaits, and that also the latter (as long as it has not yet detached itself from the liquid curve of the transversal plait, that is to say below the upper critical point) must be regarded as an appendix of the transversal plait. Only when the longitudinal plait has detached itself entirely from the liquid curve of the transversal plait above the critical temperature of mixing, it can be regarded in my opinion as a *separate* plait by the side of the transversal one. This is in full agreement which what we find e. g. for the boundary-curves in the T,x-representation (see fig. 2).

As long as the two parts of the boundary-curve, for instance N°. 2, are not yet separated, we can hardly speak of two boundary-curves: it remains one continuous boundary-curve; only beyond the transitional case N°. 3, e. g. N°. 4, we have a right to speak of two isolated boundary-curves.

As to the values of the different critical temperatures, we still mention, that with $C_3H_8 + CH_3OH$ the upper critical point was found at 21° C., with C_5H_{12} + id. at 19°,5, and with C_6H_{14} + id. at circa 40°. With $C_6H_{14} + C_2H_5OH$ the latter temperature immediately falls down to — 65°.

7. Resuming all that precedes, we have the following summary. (p_3 designs the threephase-pressure, p_1 and p_2 the vapour-pressures of the two components).

Type I (fig. 1).
- p_3 between p_1 and p_2
  - $\underline{C_2H_6 + CH_3OH}$
  - $C_2H_6 + H_2O$
  - $SO_2 + H_2O$
- $p_3 > p_1$ and p_2
  - $\underline{\text{Ether} + H_2O}$

Type II (fig. 7).
- p_3 between p_1 and p_2
  - $\underline{C_2H_6 + C_2H_5OH}$, C_3H_7OH, iso-id., n. C_4H_9OH.
- $p_3 > p_1$ and p_2
  - $\underline{\text{Triethylamine} + H_2O}$

Type III (fig.11).
- p_3 between p_1 and p_2
  - $CO_2 + H_2O$
  - S + Xylol, Toluol
- $p_3 > p_1$ and p_2
  - $\underline{C_3H_8 + CH_3OH}$ $({}^{dp}/_{dT}\, -)$
  - C_5H_{12} and C_6H_{14} + id. $({}^{dp}/_{dT}\, +)$
  - $C_6H_{14} + C_2H_5OH$
  - H_2O + Phenol $({}^{dp}/_{dT}\, +)$
  - H_2O + Aniline; id + isobutylalcohol.
  - $Br_2 + H_2O$; $CS_2 + H_2O$, CH_3OH, C_2H_5OH, C_3H_7OH, C_4H_9OH.

8. We saw above, that when the composition of the vapour-phase is *between* that of the two liquids — which is the case, when the threephase-pressure is *higher* than the vapourpressures of each of the components — there must be a *maximum*-vapourpressure *after* the coinciding of the liquid phases 1 and 2. That maximum may however still be present *before* the coinciding of these liquid phases, which is connected with the fact, that this maximum, which appeared originally at lower temperatures as a minimum (see fig. 12) in the metastable region, has become gradually a maximum, and has moved outwards before the coinciding of 1 and 2. The vapour-phase 3, which was lying at lower temperatures always between 1 and 2, as to its composition, remains not necessarily between these till the moment of coinciding of 1 and 2, as was thought formerly, but may have come outwards long before (see also fig. 9*b*). It would be very accidental on the contrary, when 3 coincided in the same time as 1 and 2 to one phase. In the case of *phenol* and *water* SCHREINEMAKERS has in fact shown experimentally this moving outwards [1]).

In what manner the moving outwards takes place, has first been clearly shown and considered quantitatively by me [2]) in a series of figures, and this in the case of coexistence of two solid solutions and one liquid phase, whereas we have here — what of course is quite the same [3]) — the coexistence of two liquid and one gaseous phase. The figures 9—14, drawn in the indicated communication (which refer to meltingcurves, and consequently are T,x-representations) are to be turned upside down, and the figs. 12, reproduced here, are obtained (fig. 12 of the mentioned communication is omitted). It will be remembered, that the case, which is realised with respect to liquid-vapour with phenol and water, is realised with respect to solid-liquid with $AgNO_3 + NaNO_3$ (only the maximum of fig. 14*b* l.c. at *D* has been already vanished there).

Some months after the publication of my communication KUENEN [4]) came independently of me also to entirely the same view. What is described on the pages 471 and 472 of his communication, is quite identical with that, which I have described and represented on the pages 184—186 of the designed communication.

Z. f. Ph. Ch. **35**, p. 462—470 (1900).

[2]) K. A. v. W. 27 June 1903.

[3]) The calculations were based on the equation of state of VAN DER WAALS, so that the results of it are à fortiori applicable in the case of two liquid phases and one gaseous phase.

[4]) K. A. v. W. 31 Oct. 1903.

9. Now, that we have sufficiently characterised the three general types, and have brought some harmony into the multiplicity of the phenomena, the question arises, whether there is a still farther synthesis, a still higher unity. More than once the occasion presented itself in the treatment of the different general types to remark striking agreements and continuous transitions, often accompanied with great differences. Equally the fact, that with a higher alcohol or a higher hydrocarbon, suddenly a quite different type often appears, must certainly draw attention in a high degree. All this induces us to look for the *one* fundamental type, of which the three types, treated above, are special cases.

Also the *analytical* consideration of the question suggests that idea to us. Indeed, the coexistence of two liquid phases and one gaseous phase, or of two liquid phases, or finally of one liquid phase and one gaseous phase, is determined by one and the same equation of state, and it must consequently always be possible to reduce all the different cases, which may occur to *two* fundamental proportions: that of the *critical temperatures* and that of the *critical pressures* of the two components — entirely in the same way as I have formerly deduced *all* the different types in the case of mixed crystals, where appear two solid phases by the side of one liquid phase, from *two* fundamental proportions: that of the *meltingtemperatures* and that of the *latent heats of melting* of the two components.

In a following communication it will be shown theoretically, that the three types may be deduced from the ordinary equation of state of Prof. VAN DER WAALS, even in the case of *normal* components. In connexion with this we must not forget, that in the neighbourhood of the critical points of each of the components the influence of anomaly vanishes nearly always. In the case of $C_2H_6 + H_2O$ for instance the water will be in the neighbourhood of 365° C. already normal long before, and in the neighbourhood of 32° C. the liquid phase, which consists nearly entirely of ethane, will contain the water in such a dilute state, that this will be passed for the greater part into the state of simple molecules.

Chemistry. — "*An exact expression for the course of the spinodal curves and of their plaitpoints for all temperatures, in the case of mixtures of normal substances.*" By J. J. VAN LAAR. (Communicated by Prof H. A. LORENTZ).

(Communicated in the meeting of March 25, 1905.)

1. It is well-known, that the points of the ζ-surface, corresponding to points of the spinodal curve on the ψ-surface, are given by the simple relation

$$\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{p,T} = 0,$$

which corresponds with the condition $\frac{\partial^2 \psi}{\partial x^2}\frac{\partial^2 \psi}{\partial v^2} - \left(\frac{\partial^2 \psi}{\partial x \partial v}\right)^2 = 0$,[1]) when instead of the thermodynamic potential the free energy is used, and not x, p and T, but x, v and T are the independent variables.

As we have further in the case of normal components e. g.

$$\mu_1 = \frac{\partial \zeta}{\partial n_1} = \zeta - x\frac{\partial \zeta}{\partial x},$$

we have also $\frac{\partial \mu_1}{\partial x} = - x\frac{\partial^2 \zeta}{\partial x^2}$, and the above-mentioned condition may be replaced by

$$\frac{\partial \mu_1}{\partial x} = 0.$$

Now

$$\mu_1 = C_1 - \left(\omega - x\frac{\partial \omega}{\partial x}\right) + RT \log (1-x),$$

where C_1 is a pure function of the temperature, whereas ω is given by

$$\omega = \int p dv - pv.$$

The condition $\frac{\partial \mu_1}{\partial x} = 0$ is therefore identical with

$$x\frac{\partial^2 \omega}{\partial x^2} - \frac{RT}{1-x} = 0,$$

or

$$RT = x(1-x)\frac{\partial^2 \omega}{\partial x^2}, \quad \ldots \ldots \ldots \quad (1)$$

from which I also started in my preceding communication[2]).

Now the difficulty arises, that the exact calculation of $\frac{\partial^2 \omega}{\partial x^2}$ leads to rather complicated expressions, so that VAN DER WAALS contented himself most times with approximations. These consisted in this, that in the liquid state at sufficiently low temperatures 1st p was omitted by the side of $\frac{a}{v^2}$, 2nd terms of order $v-b$ were neglected against those of order v.

Starting namely from the equation of state of VAN DER WAALS

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[1]) Compare VAN DER WAALS, Cont. II, p. 137.

[1]) These Proc. 28 Jan. 1905.

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT,$$

where b will be regarded as *independent* of v and T, then we find for ω:

$$\omega = RT\ log\,(v-b)+\frac{a}{v}-pv \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we write now $\frac{RT}{p+{}^a/_{v^2}}$ for $v—b$, and omit p, then we obtain:

$$\frac{\partial\omega}{\partial x}=-RT\frac{\partial}{\partial x}\,log\,\frac{a}{v^2}+\frac{\partial}{\partial x}\left(\frac{a}{v}\right),$$

in which van der Waals further wrote b for v, whereas for illustrating several properties $\frac{a}{b}$ was brought in connexion with T_x, and $\frac{a}{b^2}$ with p_x.

This is consequently a complete set of approximations, and with good reason Prof. Lorentz remarked to me, that in such cases we must be carefull, whether these approximations are not in contradiction, and up to what temperatures the results, deduced with the above-mentioned expression for $\frac{\partial\omega}{\partial x}$, can be used. Van der Waals himself considered therefore the deduced expression merely as a more or less rough approximation, but which is at all events better than the former expression $\frac{\partial\omega}{\partial x}=\frac{\partial}{\partial x}\left(\frac{a}{v}\right)=\frac{\partial}{\partial x}\left(\frac{a}{b}\right)$, where the term with $\frac{\partial}{\partial x}\,log\,\frac{a}{v^2}$ was omitted.

Now, I showed in my preceding communication, that at *low* temperatures, and in the case of *normal* substances, where the critical pressures rarely differ much, this omitted term has in the greater part of cases a very small value, and is of *entirely the same* order as $\frac{v-b}{v}$, which is constantly neglected.

Only at higher temperatures the term has a large value, but then the deduced expression for $\frac{\partial\omega}{\partial x}$ is not exact enough by far, for then neither p can be neglected against $\frac{a}{v^2}$, nor terms of order $\frac{v-b}{b}$ can be omitted in that case.

The matter is consequently this: at sufficiently low temperatures the former simple expression $\frac{\partial \omega}{\partial x} = \frac{\partial}{\partial x}\left(\frac{a}{b}\right)$ may be safely used, at least in the case of normal substances; but at higher temperatures equally the new expression with the term $\frac{\partial}{\partial x} \log \frac{a}{v^2}$ will be insufficient.

And we want a more accurate expression for $\frac{\partial \omega}{\partial x}$ and $\frac{\partial^2 \omega}{\partial x^2}$ the more, when we — specially with respect to the course of the plait-point-curve — also wish to know anything about the course of the spinodal curves from the lowest temperatures to the highest critical temperature.

I therefore tried to solve that problem; I was the more encouraged to do so, as soon it appeared to me, that the entirely accurate expressions are not so complicated as was expected. On the contrary, the often occurring fact presented itself here, that the exact expression is relatively more simply than the approximated one.

2. If we write the equation (2) in the form

$$\omega = \frac{a}{v} + RT \log (v-b) - p\,(v-b) - pb,$$

then we obtain:

$$\frac{\partial \omega}{\partial x} = \frac{\partial}{\partial x}\left(\frac{a}{v}\right) + \left(\frac{RT}{v-b} - p\right)\frac{\partial (v-b)}{\partial x} - p\,\frac{db}{dx}.$$

Now $\frac{RT}{v-b} - p = \frac{a}{v^2}$, consequently we find further:

$$\frac{\partial \omega}{\partial x} = \frac{1}{v}\,\frac{da}{dx} - \frac{a}{v^2}\,\frac{\partial v}{\partial x} + \frac{a}{v^2}\,\frac{\partial v}{\partial x} - \frac{a}{v^2}\,\frac{db}{dx} - p\,\frac{db}{dx},$$

or

$$\underline{\frac{\partial \omega}{\partial x} = \frac{1}{v}\,\frac{da}{dx} - \left(p + \frac{a}{v^2}\right)\frac{db}{dx},} \quad \ldots \ldots \quad (3)$$

where $\frac{\partial v}{\partial x}$ appears no more.

If we write now:

$$a = (1-x)^2\, a_1 + 2x\,(1-x)\, a_{12} + x^2\, a_2\,,$$

and if we put $a_{12} = \sqrt{a_1 a_2}$, by which the calculations and the results are simplified in some way, without affecting much the exactness of these results [1]), then we have:

---

[1]) I am convinced, that the expression $a_{12} = \sqrt{a_1 a_2}$ is exact in the case of normal substances. At all events the inaccuracy, which results from this supposition, will certainly not be greater than that of the equation of state used.

$$\underline{a=((1-x)\sqrt{a_1}+x\sqrt{a_2})^2.}$$

Further we admit for b the ordinary linear relation

$$\underline{b=(1-x)\,b_1+xb_2\,.}$$

The suppositions, on which the following calculations are based, are consequently the following.

1st. the equation of state of VAN DER WAALS, with b independent of v and T.

2nd. the ordinary suppositions about a and b.

3rd. the special supposition $a_{12}=\sqrt{a_1a_2}$.

From the expressions for a and b used results:

$$\left\{\begin{aligned}
&\frac{da}{dx}=2\Big((1-x)\sqrt{a_1}+x\sqrt{a_2}\Big)(\sqrt{a_2}-\sqrt{a_1})=2\sqrt{a}\,.\,(\sqrt{a_2}-\sqrt{a_1})\\
&\frac{d^2a}{dx^2}=2\,(\sqrt{a_2}-\sqrt{a_1})^2\\
&\frac{db}{dx}=b_2-b_1\quad;\quad\frac{d^2b}{dx^2}=0.
\end{aligned}\right.$$

If we did not put $a_{12}=\sqrt{a_1a_2}$, then we should have found $\dfrac{d^2a}{dx^2}=2(a_1+a_2-2a_{12})$, so only somewhat less simple.

3. We will now calculate $\dfrac{\partial^2\omega}{\partial x^2}$.

For (3) we can write:

$$\frac{\partial\omega}{\partial x}=\frac{2\sqrt{a}}{v}(\sqrt{a_2}-\sqrt{a_1})-\left(p+\frac{a}{v^2}\right)(b_2-b_1),$$

so that we obtain, when for shortness' sake α is written for $\sqrt{a_2}-\sqrt{a_1}$, and β for b_2-b_1:

$$\frac{\partial^2\omega}{\partial x^2}=\frac{2}{v}(\sqrt{a_2}-\sqrt{a_1})^2-\frac{2\sqrt{a}}{v^2}(\sqrt{a_2}-\sqrt{a_1})\frac{\partial v}{\partial x}-$$

$$-(b_2-b_1)\left\{\frac{2\sqrt{a}}{v^2}(\sqrt{a_2}-\sqrt{a_1})-\frac{2a}{v^3}\frac{\partial v}{\partial x}\right\}=$$

$$=\frac{2\alpha^2}{v}-\frac{2\alpha\beta\sqrt{a}}{v^2}+\left(\frac{2a\beta}{v^3}-\frac{2\alpha\sqrt{a}}{v^2}\right)\frac{\partial v}{\partial x}$$

$$=\frac{2}{v}\left\{\alpha^2-\alpha\beta\frac{\sqrt{a}}{v}+\frac{\sqrt{a}}{v}\left(\beta\frac{\sqrt{a}}{v}-\alpha\right)\frac{\partial v}{\partial x}\right\}.$$

Consequently we must calculate $\dfrac{\partial v}{\partial x}$.

From the equation of state $\left(p+\frac{a}{v^2}\right)(v-b)=RT$ we deduce:

$$\left(p+\frac{a}{v^2}\right)\left(\frac{\partial v}{\partial x}-\frac{db}{dx}\right)+(v-b)\left(\frac{1}{v^2}\frac{da}{dx}-\frac{2a}{v^3}\frac{\partial v}{\partial x}\right)=0,$$

yielding

$$\frac{\partial v}{\partial x}=\frac{\left(p+\frac{a}{v^2}\right)\frac{db}{dx}-\frac{v-b}{v^2}\frac{da}{dx}}{p+\frac{a}{v^2}-\frac{2a(v-b)}{v^3}},$$

or also

$$\frac{\partial v}{\partial x}=\frac{\frac{db}{dx}-\frac{1}{RT}\frac{(v-b)^2}{v^2}\frac{da}{dx}}{1-\frac{2a/v}{RT}\frac{(v-b)^2}{v^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Substituting this in the last equation for $\frac{\partial^2\omega}{\partial x^2}$, we obtain:

$$\frac{\partial^2\omega}{\partial x^2}=\frac{2}{v}\left[\left(\alpha^2-\alpha\beta\frac{\sqrt{a}}{v}\right)\left\{1-\frac{2a/v}{RT}\frac{(v-b)^2}{v^2}\right\}+\right.$$

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

since $\frac{da}{dx}=2\alpha\sqrt{a}$ and $\frac{db}{dx}=\beta$. Further treatment yields after important simplification:

$$\frac{\partial^2\omega}{\partial x^2}=\frac{2}{v}\frac{\left(\alpha-\beta\frac{\sqrt{a}}{v}\right)^2}{1-\frac{2a/v}{RT}\frac{(v-b)^2}{v^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Comparing this entirely exact expression with that, deduced in my former communication, where p and $\frac{v-b}{v}$ were neglected, we see that the exact expression (5) is already simpler than the approximated one, which may easily be written down by means of the expressions for $\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right)$ and $\frac{\partial^2}{\partial x^2}\log\frac{a}{v^2}$, deduced there.

4. Consequently equation (4) passes into

$$RT=\frac{2x(1-x)}{v^3}\frac{(\alpha v-\beta\sqrt{a})^2}{1-\frac{2a/v}{RT}\frac{(v-b)^2}{v^2}},$$

that is to say into

$$RT - 2\,\frac{a}{v}\,\frac{(v-b)^2}{v^2} = \frac{2x(1-x)}{v^3}\,(\alpha v - \beta\sqrt{a})^2\,.$$

or into

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

Now $\alpha v - \beta\sqrt{a} = \alpha(v-b) + \alpha b - \beta\sqrt{a}$

$$= \alpha(v-b) + \alpha(b_1 + x\beta) - \beta(\sqrt{a_1} + x\alpha)$$

$$= \alpha(v-b) + (\alpha b_1 - \beta\sqrt{a_1}) = \alpha(v-b) + (b_1\sqrt{a_2} - b_2\sqrt{a_1}).$$

Therefore we obtain (compare also VAN DER WAALS, Cont. II, p. 45):

$$\underline{RT = \frac{2}{v^3}\left[x(1-x)\left\{(b_1\sqrt{a_2} - b_2\sqrt{a_1}) + \alpha(v-b)\right\}^2 + a(v-b)^2\right]} \quad \ldots (6)$$

being, with the above mentioned suppositions, the sought, quite general expression for $T = f(v,x)$, by which for each given temperature the v,x-projection of the spinodal curve is entirely determined. We may also construct a "spinodal surface" $T = f(v,x)$, and immediately deduce from the subsequent sections $T = \text{const.}$ the forms of the spinodal curves of the transversal- and longitudinal plaits, and this in just the same v,x-representation as is used by VAN DER WAALS for the projection of the spinodal curves of the surfaces $\psi = f(T,v,x)$ for different values of T.

5. The equation (6) gives rise to some results, which may be deduced from it without further calculation.

1st. Is $v = b$, that is to say, is the limit of volume b_x reached at any value of x, then (6) reduces to the equation of the boundary-curve, lying in the v,x-plane:

$$RT = \frac{2}{b^3}\,x(1-x)(b_1\sqrt{a_2} - b_2\sqrt{a_1})^2\,, \quad \ldots \quad (6a)$$

viz. the same expression, which was formerly found for small values of v by means of the approximating method.

It is obvious at present, that *only* for $v = b$ the expression (6*a*) holds rigorously good. In every other case terms with $v-b$ must be added. But it also results from the found expression (6), that *as long as* terms with $v-b$ may be neglected, the formula (6*a*) gives approximately the projection of the spinodal curve on the T,x-plane, without it being necessary to take into account the corrective-term with $\frac{\partial^2}{\partial x^2}\log\frac{a}{b^2}$, indicated by VAN DER WAALS. In a former communication

I showed already, that this correction-term is small in the case of *normal* substances, about of order $v-b$.

As the second member of the expression (6^a) is always *positive*, even when a_{12} should be $< \sqrt{a_1 a_2}$, the *longitudinal* plait on the ψ-surface (for it is obvious, that in the neighbourhood of $v=b$ the spinodal curve belongs to the longitudinal plait, which can be regarded as a prominence of the transversal plait) will *always* close itself above a definite temperature at the side of the small volumes.

This temperature T_0 is the plaitpoint-temperature, corresponding to (6^a); it is given by (6^a), in connexion with the expression for $\frac{dT}{dx}=0$, deduced from it, yielding for the plaitpoint after elimination of T the value

$$x_c = \frac{1}{r}\left[(r+1)-\sqrt{r^2+r+1}\right],$$

where $r=\frac{b_2-b_1}{b_1}$. (compare VAN DER WAALS, Cont. II, and also my preceding communication, p. 579). Only when $b_2=b_1$ ($r=0$), x_c will be $={}^1/_2$. In each other case x_c will be removed to the side of the smallest molecular volume.

Just *at* T_0 the closing will take place at the limit of volume $v=b$ ($x=x_c$); for values of $T<T_0$ the longitudinal plait will remain *unclosed* up to the smallest volumes. For in that case (compare the representation in space) a section T=const. will cut the boundary-curve (6^a), lying in the boundary-plane $v=b$, in a straight line.

This temperature T_0 may consequently be regarded in any respect as a *third* critical temperature. For *above* that temperature *a formation of two liquid layers* will never present itself at values of v in the neighbourhood of b, that is to say at very high pressures; just in the same manner as *above* the ordinary critical temperatures of the single substances can never appear a liquid phase in presence of a gaseous one.

2nd. Is $v=\infty$, then for each value of x, T will be $=0$, that is to say, the equation (6) cannot be satisfied in that case. The plait will consequently never extend to $v=\infty$.

3rd. Is $x=0$ or 1, then (6) passes into the two boundary-curves, lying in the two limiting T,v-planes, viz.

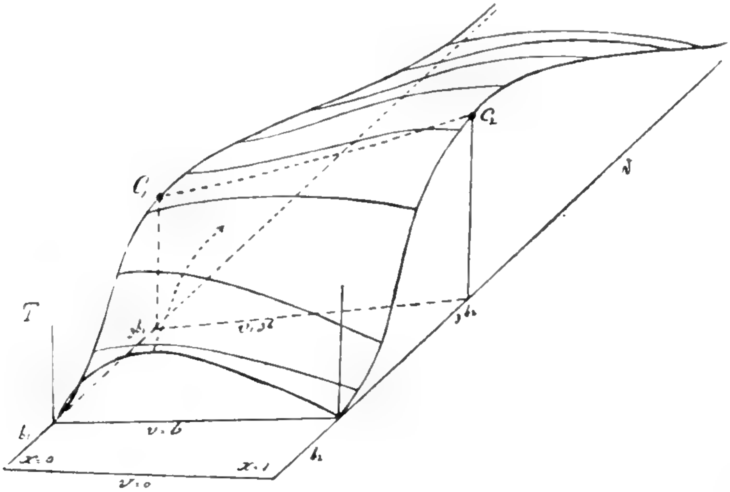
$$RT=\frac{2a_1}{v^3}(v-b_1)^2 \quad \text{and} \quad RT=\frac{2a_2}{v^3}(v-b_2)^2.$$

With $v=3\,b_1$ (resp. $3b_2$) these two curves yield duly:

$$RT_1 = \frac{8}{27}\frac{a_1}{b_1} \quad ; \quad RT_2 = \frac{8}{27}\frac{a_2}{b_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6^b)$$

which is again a good test of the exactness of our formula, deduced above.

These two critical points are at the same time plaitpoints of the (transversal) plait, for it can easily be shown, that $\left(\frac{\partial T}{\partial v}\right)_x$ and also $\left(\frac{\partial T}{\partial x}\right)_p$ will be there $= 0$.



Before deducing the equation of the plaitpoint-curve, I shall first point out, that the second member of (6) is *always positive*, as consisting of the sum of two essential positive terms, so that the T, v, x-surface possesses nowhere points beneath the v, x-plane, which of course cannot occur, because T cannot be negative. Further, that from (6^a) and (6^b) results, that as to the limiting-curve (6^a), there will be found $T = 0$ for $x = 0$ and $x = 1$, and as to the limiting-curves (6^b), T assumes again the value 0, as well for $v = b_1$ (resp. b_2), as for $v = \infty$.

Since the values of ${}^{T_2}/_{T_1}$ and ${}^{b_2}/_{b_1}$ can be very different, according to different substances, the surface (6) will also present very different forms. Generally a greater value of b corresponds with a greater value of T_c, and in that case the surface has the form, as is indicated in the figure. It is manifest already at superficial consideration, that this form will be pretty complicated.

6. We will now determine from (6) the locus of the plaitpoints.

This may be found by combination of the two conditions

$$\left(\frac{\partial\mu_1}{\partial x}\right)_{p,T}=0 \quad ; \quad \left(\frac{\partial^2\mu_1}{\partial x^2}\right)_{p,T}=0,$$

leading to

$$\frac{\partial f}{\partial x}+\frac{\partial f}{\partial v}\left(\frac{\partial v}{\partial x}\right)_{p,T}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

when f represents the second member of (6). Indeed, this second member has in all points of the spinodal curve on the ψ-surface the same value, so that we have, by passing along an element of that curve:

$$\frac{\partial f}{\partial x}dx+\frac{\partial f}{\partial v}dv=0\,.$$

But in the plaitpoint we may regard an element of the spinodal curve also as an element of the connodal curve, that is to say as the line which joins the two tangent-points of a double tangent-plane, when the tangent-points have approached each other to an infinitely small distance. And as in these two tangent-points the pressure has the same value, the latter does not vary, when at the plaitpoint we pass along the considered element of the spinodal curve. Consequently we have:

$$dv=\left(\frac{\partial v}{\partial x}\right)_{p,T}dx,$$

which yields immediately equation (7).

For shortness, we will write in the following $b_1\sqrt{a_2}-b_2\sqrt{a_1}=\boldsymbol{\pi}$, by which the second member of (6) passes into

$$f=\frac{2}{v^3}\left[x(1-x)\left\{\boldsymbol{\pi}+\alpha(v-b)\right\}^2+a(v-b)^2\right].$$

The value of $\left(\frac{\partial v}{\partial x}\right)_{p,T}$ will be found from (4), viz.

$$\left(\frac{\partial v}{\partial x}\right)_{p,T}=\frac{\beta-\frac{2\alpha\sqrt{a}}{RT}\frac{(v-b)^3}{v^2}}{1-\frac{2\,a/v}{RT}\frac{(v-b)^2}{v^2}}\,.$$

And since the denominator of this expression cannot become ∞, (7) passes into

$$\left(1-\frac{2\,a/v}{RT}\frac{(v-b)^2}{v^2}\right)\frac{\partial f}{\partial x}+\left(\beta-\frac{2\alpha\sqrt{a}}{RT}\frac{(v-b)^2}{v^2}\right)\frac{\partial f}{\partial v}=0\,. \quad . \quad (7^a)$$

Now we have:

$$\left.\begin{aligned} {}^1/_2\, v^3 \frac{\partial f}{\partial x} &= \theta^2(1-2x) - 2x(1-x)\theta\alpha\beta - 2a(v-b)\beta + 2\alpha\sqrt{a}(v-b)^2 \\ {}^1/_2\, v^3 \frac{\partial f}{\partial v} &= \qquad\qquad 2x(1-x)\theta\alpha + 2a(v-b) \qquad\qquad - \frac{3\varphi}{v} \end{aligned}\right|,$$

where θ is written for $\pi + a(v-b)$, and φ for ${}^1/_2\, v^3 f$.

The equation ($7a$) becomes consequently:

$$\left\{1 - \frac{2^a/_v}{RT}\frac{(v-b)^2}{v^2}\right\}\left\{\theta^2\,(1-2x) + 2\alpha\sqrt{a}\,(v-b)^2\right\} - \left\{\beta - \frac{2\alpha\sqrt{a}}{RT}\frac{(v-b)^2}{v^2}\right\}\frac{3\varphi}{v} +$$

$$+ 2\left\{x\,(1-x)\,\theta\alpha + a\,(v-b)\right\}\left[\left\{\beta - \frac{2\alpha\sqrt{a}}{RT}\frac{(v-b)^2}{v^2}\right\} - \beta\left\{1 - \frac{2^a/_v}{RT}\frac{(v-b)^2}{v^2}\right\}\right] = 0.$$

The expression between [ ] is obviously:

$$-\frac{2\sqrt{^a/_v}}{RT}\frac{(v-b)^2}{v^2}(\alpha v - \beta\sqrt{a}) = -\frac{2\sqrt{^a/_v}}{RT}\frac{(v-b)^2}{v^2}\,\theta,$$

as $\alpha v - \beta\sqrt{a} = \pi + a\,(v-b) = \theta$. Further we have $RT = \frac{2\varphi}{v^3}$, in consequence of (6), so that we obtain:

$$\left\{1 - \frac{a(v-b)^2}{\varphi}\right\}\left\{\theta^2\,(1-2x) + 2\alpha\sqrt{a}\,(v-b)^2\right\} - \left\{\beta - \frac{\alpha\sqrt{a}\,v(v-b)^2}{\varphi}\right\}\frac{3\varphi}{v} -$$

$$- \frac{2\theta\sqrt{a}\,(v-b)^2}{\varphi}\left\{x\,(1-x)\,\theta\alpha + a\,(v-b)\right\} = 0.$$

And since $\varphi - a\,(v-b)^2 = x\,(1-x)\,\theta^2$, we have, after multiplication with φ:

$$x(1-x)\theta^2\left[\theta^2(1-2x) + \underline{2\alpha\sqrt{a}(v-b)^2}\right] - 3\frac{x(1-x)\theta^2 + a(v-b)^2}{v}\left\{\beta\varphi - \alpha\sqrt{a}.v(v-b)^2\right\} -$$

$$- 2\theta\sqrt{a}\,(v-b)^2\left[\underline{x\,(1-x)\,\theta\alpha} + a\,(v-b)\right] = 0.$$

In this expression the underlined terms vanish. And for $\beta\varphi - \alpha\sqrt{a}\,.\,v\,(v-b)^2$ may be written:

$$\beta x\,(1-x)\,\theta^2 - \sqrt{a}\,(v-b)^2\,(\alpha v - \beta\sqrt{a}) = \beta x\,(1-x)\,\theta^2 - \sqrt{a}\,(v-b)^2\,\theta,$$

so that we obtain, after dividing by θ, and multiplying by v:

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

$$\left. - 3\sqrt{a}\,\beta x\,(1-x)\,\theta + 3a\,(v-b)^2\right] = 0,$$

or finally:

$$\Big| x(1-x)\theta^3\Big[(1-2x)v-3x(1-x)\beta\Big]+\sqrt{a}(v-b)^2\Big[3x(1-x)\theta(\theta-\beta\sqrt{a})+$$
$$+a(v-b)(v-3b)\Big| = 0\,, \quad . \quad . \quad . \quad (8)$$

where $\theta-\beta\sqrt{a}$ may be substituted by $\alpha v - 2\beta\sqrt{a}$.

This is consequently the sought equation of the v, x-projection of the locus of all the plaitpoints, which can appear on the ψ-surfaces at different values of T. Combined with (6), we find the points of the surface, represented by (6), which satisfy the plaitpoint-condition, that is to say the equation of the plaitpoint-curve as space-curve. Equation (6) may be written:

$$RT = \frac{2}{v^3}\Big[x(1-x)\,\theta^2 + a(v-b)^2\Big], \quad . \quad . \quad . \quad (6)$$

where thus $\theta = \pi + \alpha(v-b)$, and $\pi = b_1\sqrt{a_2} - b_2\sqrt{a_1}$.

For $v = b$ (8) passes into

$$(1-2x)\,b - 3x(1-x)\,\beta = 0,$$

yielding $x_c = \frac{1}{r}\Big[(r+1) - \sqrt{r^2+r+1}\Big]$, as we have deduced already above (in § 5) for that limiting-case.

To conclude, we remark, that the sections for constant volume of the surface, given by (6), *only* extend down to $T=0$ ($x=0$ and 1) for $v=b$. For all volumes $>b$, T will assume for $x=0$ and 1, as is obvious from (6), a *finite* value, viz. $\frac{2a(v-b)^2}{v^3}$. The T, x-boundary-curve suddenly ends then at the T-axis at the designed value of T (also compare the space-representation).

The proper discussion of the equations (6) and (8) must be reserved for a separate communication. It will appear then, that the different forms of the spinodal- and plaitpoint-curves, which occur specially in the case of anomalous substances, are already possible in the case of *normal* substances, provided the proportion of the two critical temperatures T_2/T_1 be sufficiently large. The spinodal curves, given by (6), will appear easily calculable, and as to the course of the plaitpoint-curve (there are two, independent of each other), some conclusions will be deduced in a simple way.

It will also appear, which indeed results already from (6), that the longitudinal- and the transversal plaits — at least with respect to the *spinodal* curves (compare also VAN DER WAALS, Cont. II, p. 175) — are no separate plaits, but *one* single plait, of which the plaitpoint is lying, according to the different circumstances, either on the side of the small volumes, or somewhere else.

Chemistry. — *"On miscibility in the solid aggregate condition and isomorphy with carbon compounds."* [First communication]. By Dr. F. M. Jaeger. (Communicated by Prof. H. W. Bakhuis Roozeboom).

(Communicated in the meeting of March 25, 1905).

Since the discovery of isomorphy by Mitscherlich the power of isomorphous compounds to form, on being mixed, a homogeneous solid phase of gradually-varying composition has been experimentally demonstrated in numerous cases.

In recent years several investigators have started theories as to the course of the melting curves likely to be exhibited by such mixing-series, and in conjunction with the theory of the equilibrium of phases and with the aid of thermodynamical developments, a fairly clear idea has been formed of the special cases which may be expected to occur with substances of the said kind.

On the other hand, it is not permissible to draw conclusions as to existing isomorphy, *solely* on account of the course of the melting curve or the solubility lines. Since the introduction in chemistry of the idea of "solid solutions", many cases have already been pointed out where amorphous or even crystallised solid solutions exist of substances which bear either *no* or an unknown crystallonomic relation to each other. We have only to think for instance of amorphous glasses and on the other hand of the cristalline mixtures of ferric-chloride and sal-ammoniac. The difficulty is felt in a particularly striking manner in the chemistry of the carbon compounds; not only do we know continuous series of crystalline mixtures between morphotropously allied carbon-containing derivatives, as in Muthmann's terephthalic-acid derivatives, but such mixing even in the crystalline condition, has also been observed in the case of organic molecules which have little or nothing in common.

Bruni and his collaborators, who have made a long series of cryoscopic determinations conclude that the most dissimilar organic substances may yield "mixed crystals" and "solid solutions" of whose crystallonomic relation not only nothing as a rule is known, but of which the crystallographer will think the chances of isomorphy but very small.

In any case the relation existing between "crystallonomic form-relation" and "miscibility" is as yet quite unknown. If substances are isomorphous, that is if crystalline phases possess regulated molecular structures, which may be assumed to be formed from each other by a slight deformation, such phases may jointly yield a homogeneous mixing-phase of variable composition and their relations based on the equilibrium of phases will take the course indicated by theory. But the reverse is by no means the case and the question as to the existence of "isomorphy" can only be satisfactorily solved by a crystallonomic investigation.

The problem has a particular interest in so far as it relates to the determination of the limits in which morphotropously-related kinds of molecules may exhibit such a miscibility. For the word "isomorphy" relates to a number of special cases in a series of much more general phenomena of crystallonomy, namely, to those which show the relation between the chemical constitution of the substances which have substitution-relations, with their innate crystalline form, which phenomena are expressed by the name of morphotropy. If the chemical relation of such substitution derivatives is confined *within* certain limits such morphotropous substances may become "isomorphotropous" and will then be able to combine with each other in a limited or may be unlimited proportion. And if the relation of such substances has become so intense that a nearly identical property must be attributed to their crystal-structures on account of *all* their physical properties, such isomorphotropous substances actually become "isomorphous" and mixing is then always possible.

From the above it follows that the idea of "isomorphy" admits of a certain gradation; only the crystallonomer can determine in each case the degree of "isomorphy" by measuring the size indicated by the parameters of the molecular structure in the cases to be compared and particularly by studying the analogy in the cohesion-phenomena of the crystal-phase. As the differences in the values of the said molecular structure-parameters become smaller and a more complete similarity in the directions of cleavage and nature of surface of the similar limiting planes is found, a more complete isomorphy exists and the probability of a complete miscibility in the crystallised condition is at the same time enhanced.

It cannot be doubted that in the cases investigated by BRUNI there may be instances of such *real* isomorphy and the following research may even prove this fact. But it must also not be lost sight of that many cases of miscible substances supposed to be instances of "isomorphy" are only cases of isomorphotropy or even only of morphotropy within relatively large limits.

All this renders it highly desirable to undertake an exhaustive investigation of organic substances as to their miscibility in the solid condition, coupled with that of their crystalline form so as to elucidate the matter. The following research is a first communication on this subject.

I. Nitro- and Nitroso-Derivatives of the Benzene-Series.

In consequence of some crystallographic facts, I intended long ago to make a special study of morphotrophic action of NO_2 and NO substitution in organic molecules. The matter became still more important to me by the observation of the transformation of *o-Nitrobenzaldehyde* into crystallised *o-Nitrobenzoic acid* under the influence of light, and by a recent treatise of Bruni and Callegari (Gazz. Chim. It. (1904) **34**. II, 246) who determined this formation of solid solutions according to cryoscopic determinations. These investigators arrive at the following conclusions:

1. As a rule aromatic *nitroso*derivatives may form solid solutions with the corresponding *nitro*derivatives.

2. In those solid solutions, also in the liquid ones which have a green colour the nitroso-compounds have the simple molecular size.

It was particularly the first conclusion, which I wanted to submit to a further investigation.

a. *Paranitrodiethylaniline and Paranitrosodiethylaniline.*

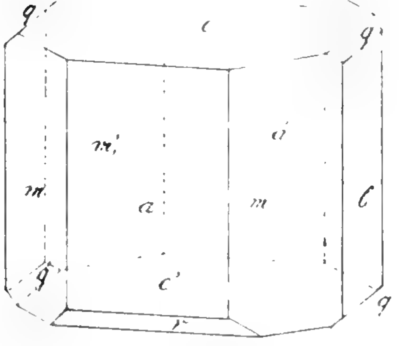
First of all I have extended the investigations *paranitrodiethylaniline* by Schrauf and myself [1]). As I could only get proper crystals of the *nitroso*-derivative from ethyl-acetate + ligroïne it was necessary to obtain the crystals of the *nitro*-derivative from the same solvent in order to get strictly comparable preparations.

1. p-Nitrodiethylaniline.

$C_6H_4.(NO_2).N(C_2H_5)_2$: *meltingpoint*: 73°,6.

Crystals from ethyl-acetate + ligroïne. (Fig. 1).

Fig. 1.



p-Nitrodiethylaniline, from ethyl-acetate.

Fig. 2.

p-Nitrodiethylaniline, from ethyl-alcohol.

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[1]) Jaeger, Z. f. Kryst. **40**. 127. (1905); cf ibid. **11**, 105, Ref.

F. M. JAEGER. "On miscibility in the solid aggregate condition and isomorphy with carbon compounds." (1st Communication).

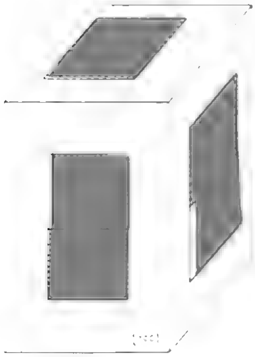

Fig. 3.

Pleochroism of p-Nitro-diaethyl-aniline.

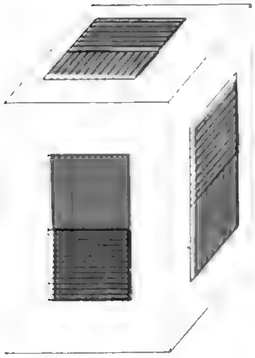

Fig. 5.

Pleochroism of p-Nitroso-diaethyl-aniline

Brownish-yellow crystals, short prismatic or somewhat extended towards the *b* axis and flattened towards {100} with a beautiful reddish-violet reflexion on {101}.

Monoclino-prismatic.

$$a : b : c = 1{,}0342 : 1 : 1{,}9788.$$
$$\beta = 80^\circ 34'.$$

The measurements are identical with those formerly given by me. The habitus of the crystals is, however, different from those previously obtained from alcohol (Fig. 2): *c* and *m* give ideal reflexes; *a* very good, but often somewhat curved; *c* alone has a violet reflexion; the reflex is coloured light-lilac. Etch-figures on {100} corresponded with the indicated symmetry.

Very completely cleavable parallel {001}; fairly so towards {010} with conchoidal fracture plane.

Optical behaviour. The optical behaviour of the compound is very interesting. (Fig. 3).

First of all the crystals are strongly pleochroic; on {001}, sulphur-yellow and blood red; the inflexion indicates the direction of the vibration of the polarised rays; on {010} yellow and orange; on {100} yellow and orange-yellow. On {001} are seen in convergent light two red absorption hyperboles like the opening arms of an axial cross.

On {100} an eccentric axial image is visible, the axial angle is very small so that there is apparently present the image of a monaxial crystal with a crossing of the axial planes for red and green light. The axes for the red lie in a plane ∥ *b*-axis, for the green in one ⊥ *c*-axis. The angle for the red rays is smaller than that of the green rays. The double refraction is positive; the first diagonal inclines to the normal *in* the plane of symmetry; on {100} there are, therefore, at the same time an inclined and a horizontal dispersion.

The angle of inclination is somewhat larger than in the case of the nitroso-derivative.

2. p-Nitrosodiethylaniline.

Some time ago [1]) I made some preliminary communications on paranitrisodiethylaniline $C_6H_4\underset{(4)}{(NO)}\underset{(1)}{N(C_2H_5)_2}$ melting point 82°,2. I have since succeeded in obtaining this compound in a form more

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[1]) F. M. JAEGER. Ueber morphotropische Beziehungen bei den in der Amino-Gruppe substituirten Nitro-Anilinen. Z. f. Kryst. **40** (1904) 112—146.

suitable for investigation, so as to be able to make a clear comparison with the corresponding *para*-nitro-derivative.

The said crystals had the appearance of small emerald green rectangular plates, which were most readily obtained from acetone. They are very poor in combination forms and only exhibit $a = \{100\}$ predominating, $m = \{110\}$ and $b = \{010\}$ whilst $a = \{100\}$ is generally present in a rudimentary condition. They were determined as monoclino-prismatic with $\beta =$ about 85°53′ and $a : b = 10166 : 1$; on $\{100\}$ an interfering image is visible with slight inclination to the normal on that plane; the axial angle is small, the dispersion an average of $\rho < v$ round the sharp bissectrix, the double refraction is positive.

More accurate investigations have, as will be shown, practically confirmed these data. I obtained the improved material from a mixture of ethyl-acetate and ligroine, in which the compound was dissolved on warming. On slow evaporation small rectangularly bounded, thicker plates or also emerald green prisms are formed, which on some planes possess a splendid violet reflexion. They exhibit a particular lustre and but rarely a curvature of $\{100\}$; therefore very accurate determinations could be executed.

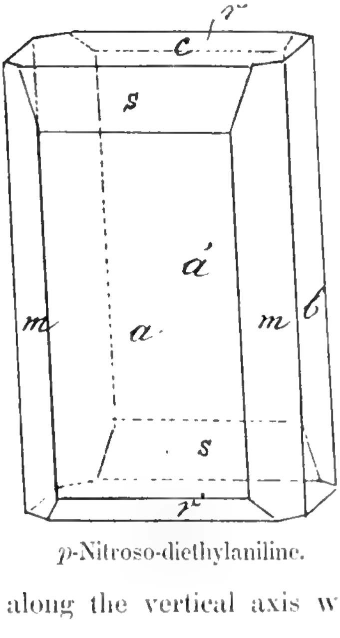
The symmetry is *monoclino-prismatic*: the axial relation:

$$a : b : c = 1{,}0178 : 1 : 1{,}9611.$$

$$\beta = 85°43'.$$

Forms observed: $a = \{100\}$, broadest developed of all and well reflecting, sometimes a little curved; $m = \{110\}$ and $b = \{010\}$, about equally developed, but b generally a little broader, although sometimes much narrower than m and much sharper reflecting with light-violet reflex; $c = \{001\}$, with ideal reflexion also with a violet reflex image; $r = \{\bar{1}02\}$, lustrous, mostly narrower, sometimes a trifle better developed and sharply reflecting; the reflexes are often violet, mostly, however, colourless or yellowish; $s = \{101\}$, broad but very dull and only approximately measurable; $t = \{\bar{1}.0.13\}$, very narrow in vicinal form has been observed in a few cases.

Fig. 4.



p-Nitroso-diethylaniline.

The habitus of the crystals is elongated along the vertical axis with flattening towards $\{100\}$.

		Measured:	*Calculated.*
$a : c$	$= (100) : (001) =$	*85° 43′	
$a : m$	$= (100) : (110) =$	*45 25½	
$c : r$	$= (001) : (\bar{1}02) =$	*45 59½	—
$r : a$	$= (\bar{1}02) : (\bar{1}00) =$	48 19	48° 17½
$a : s$	$= (100) : (101) =$	26 39	26 29
$s : c$	$= (101) : (001) =$	59 4	59 14
$c : m$	$= (001) : (110) =$	87 5	87 0
$m : b$	$= (110) : (010) =$	44 33	44 34½
$m : r$	$= (\bar{1}10) : (\bar{1}02) =$	62 11	62 9⅔
$m : s$	$= (110) : (101) =$	52 0 (circa)	51 5

The crystals cleave very completely towards {001} with a lustrous separation plane; incompletely towards {010} with a conchoidal fracture. Etch figures were not obtained.

Optical behaviour. The compound exhibits interesting optical properties.

First of all the splendid, violet reflexion of the planes {001}, {010} and {$\bar{1}$02}, which is wanting on the other planes. This reflexion is not due to a streaking of these planes. If we cleave a crystal along c or b the plane of separation also has that reflexion and a streak made with the crystals on porcelain also exhibits the same phenomenon. The light reflexes of the goniometer lamp on these planes are coloured a beautiful pale lilac; on the other planes white, sometimes yellowish.

Further, the compound exhibits on {100}, {010} and {010} the pleochroic behaviour as seen in Fig. 5; the inflexion again indicates the direction of the vibration of the two polarised rays, which arrive along the normal on the respective plane. On {100} a difference is only observable with thicker crystals, on {001} the colours are light-green and dark, somewhat bluish-green; on {010} the difference is most pronounced, namely light-green and dark violet; the latter colour is indeed, as I noticed, no surface reflexion but the colour of the phase in transmitted light. On {001} feeble absorption bundles of hyperbolic form are observable resembling an axial cross opening when the table is turned.

The optical axial plane is nearly horizontal; the acute bissectrix makes a small angle with the normal on {100}. In convergent light a very fine axial image is visible with a small axial angle and an average dispersion of rhombic character; the dispersion of the said diagonal is $\varrho < v$, the double refraction is positive.

Calling the crystallonomic axes respectively a, b, c the optical orientation of the elasticity-ellipsoid is therefore in the same order: γ, β, α in which $\alpha > \beta > \gamma$. The double refraction is feeble.

On {100} and {001} orientated extinction; on {010} the very small inclined angle of the elasticity axis with the vertical axis could not be sharply defined on account of the strong absorption; it is not distinguishable from 90°.

The specific gravity of the crystals was found to be 1.240 at 15°; the equivalent volume is, therefore, 143.53 and the topical axes become:

$$\chi : \psi : \omega = 4,2363 : 4,1623 : 8,1626.$$

The complete *isomorphy* of *p-Nitrodiethylaniline* and *p-Nitrosodiethylaniline* is therefore firmly established. The properties of both substances are given here by way of a comparison.

p-Nitrodiethylaniline:	*p-Nitrosodiethylaniline:*
Monoclino-prismatic.	Monoclino-prismatic.
$a : b : c = 1,0342 : 1 : 1,9788$.	$a : b : c = 1,0178 : 1 : 1,9611$.
$\chi : \psi : \omega = 4,4276 : 4,2807 : 8,4710$.	$\chi : \psi : \omega = 4,2363 : 4,1623 : 8,1626$.
$d = 1,225$	$d = 1,240$
$v = 158,36$	$v = 143,53$
Angular values:	Angular values:
$(110) : (100) = 45° 34'$	$(110) : (100) = 45° 25\frac{1}{2}'$
$(100) : (10\bar{2}) = 51° 13'$	$(100) : (10\bar{2}) = 48° 17\frac{1}{2}'$
$(100) : (001) = 80° 34'$	$(100) : (001) = 85° 43'$
In ethyl-acetate + ligroine the habitus is flattened towards {100} elongated towards the *c*-axis; sometimes towards the *b*-axis.	In ethyl-acetate + ligroine the habitus is flattened towards {100} and elongated towards the *c*-axis.
Very completely cleavable towards {001}, fairly so towards {010}, with a conchoidal fracture.	Very completely cleavable towards {001}, fairly so towards {010} with conchoidal fracture.
On {001} violet reflexion.	On {001}, and on {010}, {$\bar{1}$02} violet reflexion.
Optical orientation: γ, β, α.	Optical orientation: γ, β, α,
Double refraction, positive.	Double refraction, positive.
On {100} a but little-inclined axial image with small axial angle; axial plane parallel the *b*-axis for the red, parallel the *c*-axis for the green rays; dispersion: $\varrho < v$.	On {100} a but little-inclined axial image with small axial image; axial plane parallel the *b*-axis; rhombic dispersion: $\varrho < v$.
Colour: brownish-yellow.	Colour: emerald green.
Strongly pleochroic: blood red-orange-yellow.	Strongly pleochroic: violet-pale green-bluishgreen.
On *c* absorptionbundles.	On *c* absorptionbundles.

There is not the least doubt that the two substances possess a quite analogous structure; cleavability, optical orientation whilst the nature of the surface of the crystalplanes is quite in agreement.

From mixed solutions of the two components are formed small greenish-black mixed crystals with a vivid steel-blue reflexion.

As generally happens in the case of most isomorphous mixtures, the crystallisation power is considerably smaller than with each of the components separately. Under the microscope such mixed crystals consist of thin olive-green little plates, which on their predominating plane show little or no pleochroism. In convergent light a splendid interfering image may be observed: slight inclination to the normal on the horizontal plane, elliptical rings, and small axial angle, larger however than in the two components. The double refraction is positive: the dispersion has a rhombic character and shows: $\varrho < v$.

From the last motherliquors are deposited mixed crystals of a lighter shade representing silky needles as those above with less surface reflexion. Otherwise they are optical continuations of the above described mixed crystals. From mixtures of the two components in a melted condition these mixed crystals depose on the sides of the testtube in a fine steel-blue lustrous condition.

The behaviour of the two isomorphous substances in the liquid condition is elucidated by the investigation of the melting curve of binary mixtures. On account of the dark colour of the fusion, the course of the solidification curve was traced by the graphical method; the determinations were made as usual in the VAN EYK apparatus. It should be noticed that all these fusions solidify to solid phases, which also exhibit a splendid violet or blue reflexion.

The nitroderivative has a greater latent heat of fusion than the nitrosoderivative; in both cases the caloric effect was, however, very readily observable in the solidification. The lower solidifying line can by no means be determined so sharply as the upper one.

It was found that:

A mixture of 100 % of *p-Nitro* and 0 % *p-Nitroso*-derivative melted at 73°,6.

A mixture of 85,14 % *p-Nitro-* and 14,86 % *p-Nitroso*-derivative commences to solidify at 75°,2 and completely solidifies at 74°,9.

A mixture of 72,5 % of *p-Nitro-* and 27,5 % *p-Nitroso*-derivative commences to solidify at 76°,2 and completely solidifies at 75°,9.

A mixture of 54,4 % of *p-Nitro-* and 45,6 % of *p-Nitroso*-derivative commences to solidify at 77°,6 and completely solidifies at 77°,3.

A mixture of 38,64 % of *p-Nitro-* and 61,36 % *p-Nitroso*-derivative commences to solidify at 78°,2 and completely solidifies at 77°,9.

A mixture of 10,0 % *p-Nitro-* and 90,0 % of *p-Nitroso*-derivative commences to solidify at 80°,8 and completely solidifies at 80°,6.

A mixture of 0 % of *p-Nitro-* and 100 % of *p-Nitroso*-derivative melted at 82°,2.

The composition is given in molecule-percents.

In fig. 6 the course of the melting curve is represented graphically and the double line for the initial and final solidifying points is shown. It will be seen that the character of the line points to a continuous series of mixed crystals; the average temperature-interval between initial and final solidification amounts to about 0°,3.

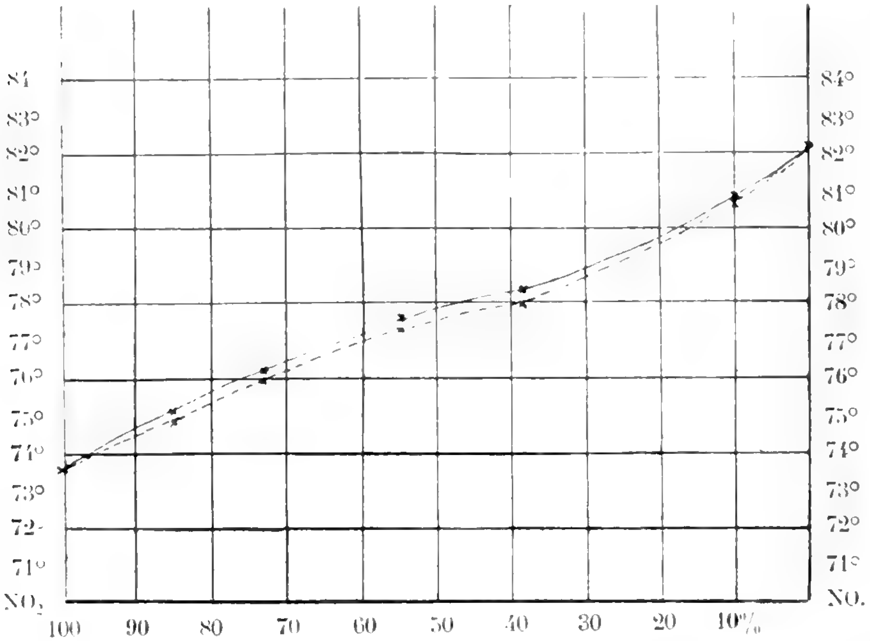


Fig. 6.

The result of the research reveals the complete isomorphy of *p-Nitro-diethylanaline* and *p-Nitroso-diethylaniline* and also their complete miscibility in the solid state.

Chemistry. — “*On Orthonitrobenzyltoluidine*”. By Dr. F. M. Jaeger.

(Communicated by Prof. A. F. Holleman).

(Communicated in the meeting of March 25, 1905).

Some time ago the *o-Nitrobenzyl* derivate of *para-toluidine*, (melting point 72° C.) was investigated by Nordenskjöld, who described it as being *tetragonal* with the parameter-relation $a : c = 1 : 0{,}6230$; the compound exhibits only one combination-form, namely {111} and is optically monaxial: positive. (Bull. Geol. Instit. Upsala, (1892), 84, also Ref. Zeits. f. Kryst. **24**, 147).

For comparison I have investigated the *o-Nitrobenzyl*-derivative of *orthotoluidine* [1]).

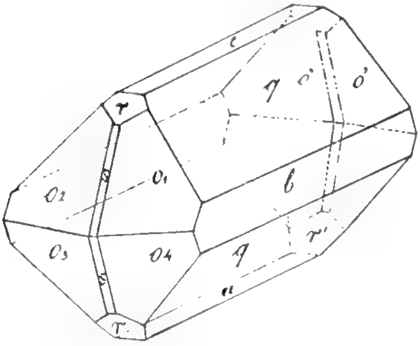
Recrystallised from acetone in which the compound (m. p. 96°) is very soluble, the substance forms very large, transparent, pale yellow or rather pale greenish-yellow crystals possessing a strong lustre and assuming a more brownish tinge on prolonged exposure to the air. Elongated, prismatic needles are also occasionally obtained.

The first-named crystals are nearly isometrically developed and possess many combination forms; they admitted very well of accurate measurements.

Rhombic-bipyramidal.

The parameters are:

$$a : b : c = 0{,}8552 : 1 : 0{,}6138.$$



o-Nitro Benzyl-*o*-Toluïdine.

Forms observed: $q = \{021\}$, strongly predominating and lustrous; $o = \{211\}$, broadly developed and yielding sharp reflexes; $r = \{101\}$, well formed and lustrous; $c = \{001\}$, narrower but well reflecting; $b = \{010\}$, dull sometimes present with only a single plane; mostly a little broader than c, but also somewhat smaller; $s = \{201\}$, narrow and unsuitable for measurement; the symbol has been deduced from the zone-relation.

The habitus is mostly thick-prismatic along the a-axis; particularly the smaller crystals possess a very regular form.

	Measured:	*Calculated:*
$c : q = (001) : (021) =$	*50° 50′	—
$c : r = (001) : (101) =$	*35 40	—
$b : q = (010) : (021) =$	39 9	39° 10′
$o : r = (211) : (101) =$	27 20	27 10
$o : o = (211) : (21\bar{1}) =$	65 8	65 18
$o : c = (211) : (001) =$	57 26	57 21
$o : o = (211) : (2\bar{1}1) =$	38 46	38 40
$q : o = (021) : (211) =$	53 16½	53 18
$q : r = (021) : (101) =$	59 1′	59 8′
$b : o = (010) : (211) =$	70 38	70 40

Completely cleavable parallel {021}, distinctly towards {211}.

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[1]) Ber. d. d. Chem. Ges. 25. 3582.

In oil of cloves as immersion liquid the situation of the elasticity directions on the planes of {010}, {021} and {001} orientated normally in regard of the *a*-axis. The optical axial plane is {100}; the first diagonal stands perpendicularly on {010}. On the planes of {021} a brightly coloured interferential image is visible in convergent polarised light; extraordinarily strong dispersion of a rhombic character with $\varrho > v$ around the first bissectrix. In oil of cloves the apparent axial angle amounts to about 49° for the red and 46° for the green rays.

The oil caused on {021} little solution-figures, which had the form of isosceles trapezia: they agree with the indicated symmetry of the crystals.

The specific gravity is *1,278*, at 15°, the equivalent-volume is *189,28*, and the topical axes are:

$$\chi : \psi : \omega = 6{,}0875 : 7{,}1175 \,;\, 4{,}3688$$

Although differing from Nordenskjöld's *para*-derivative in symmetry, the analogy of the two isomers is still distinctly recognisable in the value of the relation *b : c*.

o-Nitrobenzyl-para-Toluïdine: a : b : c = 1,000 : 1 : 0,6230.
o-Nitrobenzyl-ortho-Toluïdine: a : b : c = 0.8552 : 1 : 0,6138.

The difference in position of the methyl- and amino-group with regard to each other therefore causes chiefly only a variation of the crystal parameters in one direction.

Chemistry. — *"On position-isomeric Dichloronitrobenzenes."* By Dr. F. M. Jaeger. (Communicated by Prof. A. F. Holleman).

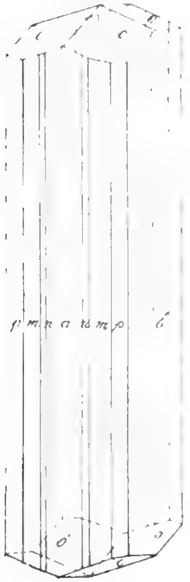
(Communicated in the meeting of March 25, 1905).

Of the six theoretically-possible dichloronitrobenzenes, which I received some time ago for investigation from Prof. Holleman, I succeeded in obtaining four in such a measurable form that their crystallographical determination could be satisfactorily undertaken.

Notwithstanding the great power of crystallisation of most of them, the preparation of properly developed crystals is a troublesome and very tedious matter. This is partly due to the very great solubility in most of the organic solvents, which in connection with the low melting points of these compounds often causes a not inconsiderable supersaturation. During the spontaneous crystallisation, which then takes place, no well-formed individuals, but crystal-aggregates are formed, which are difficult of investigation. In addition, the peculiar softness of the crystals causes most of them to exhibit curved planes and considerable geometrical deviations. Again, owing to the heat of the source of light during the measurement the crystals soon become a dull surface, so that the inaccuracy of the measurements is still further increased by the less sharp limitation of the signal reflexes.

Of the substances examined the *ortho*-dichloroderivatives are both rhombic, the *meta*-derivatives probably all monoclinic and the *para*-dichloroderivative triclinic; only the geometrically well-defined substances of this series are described here in detail. In crystalline form they show comparatively little resemblance to each other, chiefly in consequence of the considerable deformation of the molecule owing to the mutual attraction of the Cl-atoms and of the (NO_2)-group.

Fig. 1.



1-2-Dichloro-3-Nitro-Benzene.

a. 1-2-*Dichloro-3-Nitro-Benzene.*

$C_6H_3 . \underset{(1)}{Cl} . \underset{(2)}{Cl} . \underset{(3)}{(NO_2)}$; melting point: 61° à 62° C.

This compound crystallises from a mixture of ethyl-acetate and ether and also from glacial acetic acid, on very slow evaporation of the solvent, in colourless silky needles, which are limited by small, lustrous pyramidal planes (Fig. 1).

Rhombic-bipyramidal.

$$a : b : c = 0,6472 : 1 : 0,2780.$$

Forms observed: $a = \{100\}$ and $b = \{010\}$ equally strongly developed and both very lustrous; $p = \{230\}$, $m = \{110\}$, $n = \{430\}$; the latter form is the smallest of the three and reflects less sharply than p and m; a sometimes shows a delicate streak parallel with $o : a'$; $o = \{133\}$ lustrous, yielding good reflexes.

The vertical zone is, geometrically very well constructed. The angular values observed in different crystals differ but inconsiderably from the average values.

	Measured:	*Calculated:*
$a : p = (100) : (230) =$	*44° 9′	—
$o : o = (133) : (1\bar{3}3) =$	*30 51½	—
$p : m = (230) : (110) =$	11 21	11°14′
$m : n = (110) : (430) =$	7 7½	7 1
$n : b = (430) : (010) =$	27 23	27 35½
$a : o = (100) : (133) =$	82 16	82 7
$b : o = (010) : (103) =$	74 36	74 34
$o : o = (133) : (\bar{1}33) =$	15 32	15 46

Readily cleavable along *o*. On *m* and *p* right-angled little etch-figures are visible in cassia-oil, which correspond with the indicated symmetry. In the vertical zone the direction of the optical elasticity axis is orientated on all the planes. An axial image was not observed.

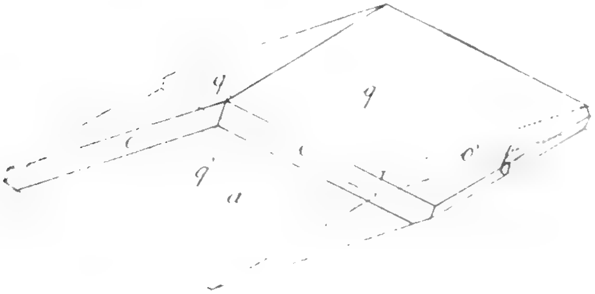
The specific gravity of the needles as determined by means of a solution of mercuric-potassium-iodide was 1,721 at 14°. The equivalent-volume is therefore 111.56 and the topical axes become;

$$\chi : \psi : \omega = 5{,}5190 : 8{,}5272 : 2{,}3706..$$

b. 1-3-*Dichloro*-2-*Nitro-Benzene.*

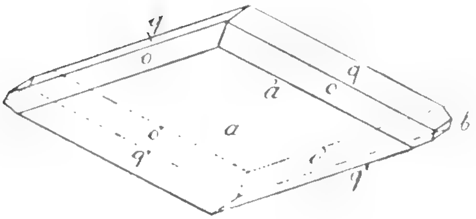
$C_6 H_3 . \underset{1}{Cl} . \underset{3}{Cl} . \underset{2}{(NO_2)}$; melting point: 71° C.

Fig. 2a



1-3-Dichloro-2-Nitro-Benzene.

Fig. 2b.



1-3-Dichloro-2-Nitro-Benzene.

The compound crystallises from carbon disulphide in large, colourless, thin plates of parallelogram shape or also in smaller thick crystals as shown in figs. 2*a* and 2*b*. The crystals are often opaque and difficult to measure: sometimes, however, they are more lustrous and very clear.

Monoclino-prismatic.

$a : b : c = 0{,}6696 : 1 : 0{,}4149.$

$\beta = 87° \, 51^2/_3{}'.$

Forms observed: $a = \{100\}$ generally strongly predominating and always sharply reflecting; $q = \{011\}$, lustrous and either quite as narrow as *o* or else the broadest developed of all, so that the crystals appear short-prismatic towards the clino-axis; $o = \{111\}$, generally small, mostly streaked parallel with $a : o$ and reflecting rather dullisly: $b = \{010\}$, very small and often only present in a rudimentary form.

	Measured:	*Calculated*:
$a : o = (100) : (111) =$	* 58°44′	—
$q : q = (011) : (0\bar{1}1) =$	* 45 2$^1/_2$	—
$a : q = (100) : (011) =$	* 88 1$^1/_2$	—
$o : q = 111 : (01\bar{1}) =$	127 55	128°25′
$o : q = 111 : (011) =$	29 17	29 17$^1/_2$
$a : b = (100) : (010) =$	89 57	90 0
$o : o = (111) : (1\bar{1}1) =$	38 38 (about)	38 16

A distinct cleavability was not observed.

The crystals deposited from acetone, which were very large but dull, show a predominance of *a* over *b*; they are much elongated along the vertical axis and further possess a form which is probably {233} with (233) : (100) = 67° 33′, calculated 67° 24′. On *a* there is diagonal extinction: the optical axial plane is {010}. One optical axis descends almost perpendicularly on *a*.

The specific gravity is 1,603, at 17°, the equivalent volume 119,77.

Topical axes : $\chi : \psi : \omega = 5{,}0596 : 7{,}5561 : 3{,}1350$.

Although the parameter-relation $a : b$ and the angle β in this isomer are comparable with those of the 1-2-3-derivative:

1-3-*Dichloro*-2-*Nitro-Benzene*: $a : b = 0{,}6696 : 1$; $\beta = 87°\ 52'$
1-2-*Dichloro*-3-*Nitro-Benzene*: $a : b = 0{,}6472 : 1$; $\beta = 90°$.

their crystalline forms are still rather different; the relation $\frac{b}{c}$ of the latter substance is about $1\frac{1}{2}$ that of the first derivative.

e. 1-3-*Dichloro*-5-*Nitro-Benzene.*

$C_6H_3 . \underset{1}{Cl} . \underset{3}{Cl} . \underset{5}{(NO_2)}$; melting point: 65° C.

In alcohol or glacial acetic acid, in which solvents the compound exhibits a remarkably great crystallisation power, there are generally formed very long, flat columns of considerable thickness, or also right-angled or obtusely truncated pale-sherry coloured small thin plates. Owing to the great softness of the substance and its great plasticity, the crystals are in most cases so ill-formed and distorted that measurements become impossible. With very slow evaporation we sometimes get better formed crystals although they are very poor in planes. They have a peculiar odour resembling nitrobenzene.

Monoclino-prismatic.

$a : b = 0{,}5940 : 1$; $\beta = 58°\ 43'$.

Forms observed: $a = \{100\}$, broad and very lustrous; $b = \{010\}$, narrower and less lustrous; it is often absent altogether; $m = \{110\}$, narrow and $c = \{001\}$, small but very reflecting; the habitus is elongated along the *c*-axis and then flattened {100}.

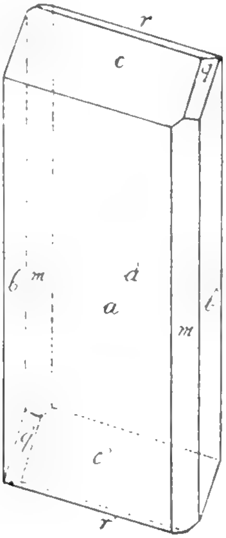
	Measured:	*Calculated*:
$b : m = (010) : (110) =$	* 63 5	
$a : c = (100) : (001) =$	* 58 43	—
$a : m = (100) : (110) =$	26 58	26°55′
$m : m = (110) : (\bar{1}10) =$	126 15	126 10
$m : c = (110) : (001) =$	—	62 25
$b : c = (010) : (001) =$	89 57	90 0

The crystals are completely cleavable along {010}, readily so along {001}.

On {100} extinction occurs on orientation; on {010} under 28° with regard to the vertical side. The optical axial plane is {010}; at the border of the vision-sphere an optical axis is visible on {100}; the axial angle is small. The direction of the vertical axis is here the axis of the greatest elasticity.

On {100} etch excrescences were observable with a circumference of isosceles trapezia, whose angular points appear to be connected by straight lines with a point situated in the centre; this point lies nearer to the smallest than to the largest of the two parallel sides of the trapezium. They agree with the indicated symmetry.

Fig. 3.



1-4-Dichloro-2-Nitro-Benzene.

The specific gravity is 1,692, at 14° C.; the equivalent volume is, therefore, 113,4.

d. 1-4-*Dichloro*-2-*Nitro-Benzene.*

$C_6H_3.\underset{(4)}{Cl}.\underset{(1)}{Cl}.\underset{(2)}{(NO_2)}$: Melting point: 54°,5 C.

In most solvents this substance shows a very great crystallisation power, but measurable crystals are but rarely obtainable, as most of the individuals exhibit important geometrical deviations on account of the great softness of the material and often possess curved and very dull planes.

Some time ago the crystal form was incompletely determined by Bodewig; he investigated crystals deposited from carbon disulphide but did not succeed in obtaining combinations admitting of a complete determination of the crystal parameters (Zeits. f. Kryst. **1**. 589; Ann. Ch. Phys. (**4**). **15**. 257).

From acetone I always obtained the largest crystals, sometimes some centimetres in length; they are quite of the prismatic type of the crystals investigated by Bodewig and possess in addition a lateral prism; they exhibit, however, such considerable deviations and are generally so opaque that an accurate measurement is out of the question.

I succeeded best by crystallisation from ethyl-acetate mixed with a little carbon-tetrachloride; the pale sherry coloured crystals flattened towards {100} so obtained, are very well formed and admit of accurate measurement.

Triclino-pinacoidal.

$$a : b : c = 0{,}8072 : 1 : 0.8239$$

$A = 79^\circ 33'$ $\alpha = 92^\circ 48'$

$B = 114^\circ 51\tfrac{1}{2}'$ $\beta = 112^\circ 51'$

$C = 58^\circ 35'$ $\gamma = 60\ 5'$

Forms observed: $a = \{100\}$, predominant, well-reflecting, better than $b = \{010\}$, which form is also narrower; $c = \{001\}$, very lustrous and well developed; $m = \{110\}$, narrow but well-reflecting; $q = \{011\}$, narrow very lustrous; $r = \{\bar{1}01\}$, somewhat broader and yielding good reflexes.

The crystals are flattened along a and elongated in the direction of the c-axis.

		Measured:	*Calculated:*
$a : c$	$= (100) : (001) =$	$*\ 65^\circ\ 8\tfrac{1}{2}'$	
$a : b$	$= (100) : (010) =$	$*121\ 25$	—
$b : c$	$= (010) : (001) =$	$*100\ 27$	—
$a : r$	$= (\bar{1}00) : (\bar{1}01) =$	$*\ 50\ 12\tfrac{1}{2}$	—
$c : q$	$= (001) : (011) =$	$*\ 45\ 39$	—
$q : b$	$= (011) : (010) =$	$54\ 44$	$54^\circ 48'$
$c : r$	$= (001) : (\bar{1}01) =$	$64\ 40\tfrac{1}{2}$	$64\ 40\tfrac{1}{2}$
$m : b$	$= (110) : (010) =$	$75\ 23$	$75\ 19$
$m : a$	$= (110) : (100) =$	$46\ \ 2$	$46\ \ 6$
$r : q$	$= (\bar{1}01) : (011) =$	$51\ 50$	$51\ 35$
$m : r$	$= (\bar{1}\bar{1}0) : (\bar{1}01) =$	$65\ 36$	$65\ 22$
$m : q$	$= (110) : (011) =$	$62\ 54$	$63\ \ 3$

The crystals are very completely cleavable towards $\{001\}$; th plane of cleavage is very lustrous.

On $\{100\}$ obtuse-angular extinction; its amount is small, only about 7° 40′ in regard to the vertical side; in convergent light a dark hyperbole is noticed on this plane.

The specific gravity of the crystals is 1,696 at 12° C.; the equivalent volume is, therefore, 113,20.

The topical axes are $\chi : \psi : \omega = 4{,}8484 : 6{,}0065 : 5{,}1422$.

Physics. — H. Kamerlingh Onnes and W. Heuse. "*On the measurement of very low temperatures. V. The expansion coefficient of Jena and Thüringer glass between* $+16°$ *and* $-182°$ C."

Communication N°. 85 from the Physical Laboratory at Leiden.

(Communicated in the Meeting of June 27, 1903)

§ 1. At Leiden the hydrogen thermometer (cf. Comm. N°. 27 May '96) is taken as the standard for very low temperatures. To reach the degree of accuracy otherwise obtainable with this, it is necessary to know the expansion coefficient of Jena glass 16^{III} to about $1 \%_0$. Hence we have determined the two coefficients in the quadratic formula assumed for the linear expansion of glass below 0° C. At the same time we have, in precisely the same circumstances made a similar determination for the Thüringer glass, from which the piezometers mentioned in Comm. N°. 50 (June 99), N°. 69 (April '01), and N°. 70 (May '01) were made, in order to be able to calculate and apply the correction for expansion to the results attained with these piezometers.

Some time previously we made measurements on expansion coefficients, among others on platinum. The value for this metal was required for the reduction, from the measurements mentioned in Comm. N°. 77 (Febr. '02), of the galvanic resistance at low temperatures. But the results which we have lately obtained for the two above mentioned kinds of glass appear to us to be the first that are worth to be published; the final reduction of the measurements named above was postponed till the required accuracy was reached. However the measurements on platinum must be repeated.

Although the field of measurements at low temperatures is hardly touched, still we consider that in this field preliminary and approximate values are worth little. In the majority of cases approximate values of this kind can be obtained by extrapolation, and thus only those determinations which are accurate enough to allow a judgment on the question whether such an extrapolation is allowed or not, are really of use in advancing our knowledge. We have hence arranged our observations on the expansion coefficient so as to reach an accuracy of $\frac{1}{200}$.

For general the investigation of expansion at low temperatures it will be required to determine on the one hand the linear coefficient of solids and on the other the absolute coefficients for those substances, which remain liquid to very low temperatures, e. g. pentane, in such an hydrostatic manner as Dulong and Petit's (improved by Regnault). The determination of the relative expansion of the liquid chosen can then serve as a control and as the starting point for further measurements. The present investigation forms the first part of this general program and gives the linear expansion of glass with an accuracy which suffices for our present purpose. From the description of our measurements it will be seen that with practically the same apparatus and in nearly the same way it will be possible to determine the absolute expansion of pentane.

§ 2. We have determined the two coefficients a and b in the formula for the linear expansion $L = L_0 (1 + at + bt^2)$, for the two varieties of glass from three observations for each. These were made at ordinary temperature, at about $-90°$, C. and at about $-180°$ C., by measuring directly and at the same time the lengths of the rods of the two substances.

The rods were drawn out at each end to a fine point which could be accurately observed with a microscope. At the bottom and top, the two rods project out of a vertically placed cylindrical vessel. The bath is closed at the lower end and is filled with a liquefied gas giving the required temperature. Care is taken that the points shall be kept as nearly as possible at the temperature of the surrounding air, and also that the air between the points and the objective of the microscope shall be at the same temperature. The lengths are then read directly against a scale by a cathetometer arranged as a vertical comparator.

Although this arrangement gives a convenient method for the determination of length it necessitates a considerable difference in temperature between the middle and the ends of the rods. To correct for this, use is made of the method employed in Comm. N° 83 (Febr. '03) for the determination of the corrections along a piezometer or thermometer stem. This depends upon the use of a uniform platinum wire wound uniformly round the rod. Its use depends upon the assumption, that the change of resistance of a wire wound in this manner is nearly proportional to the mean change of temperature of the rod. This will be further considered in § 4.

After this general view we may consider certain details.

1st. *The glass rods* were about 1 m. long and had diameters of 5 mm. [1]). Round these 0.1 mm. thick platinum wires were wound spirally and soldered to brass rings *A*, *B*, *C*, *D* (Pl. I fig. 1.) which were tightened by screws.

Between *B* and *C*, the part which was immersed in liquified gases, there were 140 turns with a pitch of about 0.5 cm. Between *A* and *B* or *C* and *D* where the temperature changes rapidly there were 25 and 40 turns respectively with a pitch of 0.25 cm. Care is taken

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[1]) A platinum tube provided with glass ends similar to those described above was used for the determinations on platinum.

that the pitch remains constant in each section *A* to *B*, *B* to *C*, or *C* to *D*. At *A*, *B*, *C*, and *D* platinum wires *a*, *b*, *c*, *d*, *e*, *f*, *g*, and *h* about 15 cm. long and 0.5 mm. thick are soldered in pairs. At the other ends they are connected to copper wires. In order to prevent faults in insulation the spirally wound wires lay in shellac they were also covered with a layer of tissue paper for purposes of protection. The portions *A* to *B* and *C* to *D* were enveloped in successive layers of fishglue and writing paper to about a thickness of 0.25 cm., in order that the distribution of temperature should be as even as possible along the rod. This protection was found to be proof against the action of either liquid nitrous oxide or oxygen. To allow of contraction on cooling the paper layers were only pasted together at both ends.

2nd. *The cylindrical vacuum jacket.* The bath for the liquid gases has the form of a tubular vacuum glass. Usually vacuum glasses are made so that there is but one edge connecting the cooled and uncooled walls. When it is necessary to remove liquid at the bottom of a vacuum glass the lower surfaces are connected by a spiral tube. However we required something quite different i.e. a double-walled *tube* open at both ends and capable of holding a rubber stopper in one. If such a vacuum tube were made by blowing simply together inner and outer walls it would certainly crack when cooled, owing to the different expansion of the outer and inner walls. Also it did not appear to be possible to make the outer wall sufficiently elastic by blowing several spherical portions in it (see fig. 1).

Fig. 1.

Hence the outer wall was divided by a thin brass case V_1, Pl. I, which allows a compression or expansion of 2 mm. This copper box was inserted by platinising and coppering the two glass surfaces and then soldering them to the copper box. The vacuum tube thus produced was silvered and evacuated in the usual manner. In the first arrangement the top was left clear in order to allow of the observation of the surface of the liquid. In later arrangements we preferred a float. Such tubes with compound elastic walls appeared to be suitable for our purpose and will probably also be found to be useful for the solution of various other problems. An example of how easily tensions arise which cause such glass apparatus to crack, was found when the rubber stopper at the bottom was pushed in too far. On admitting the liquid oxygen the rubber became hard before it had reached the temperature of the liquid, which temperature the glass immediately above had reached

H. KAMERLINGH ONNES and W. HEUSE. On the measurement of very low temperatures V. The expansion coefficient of Jena and Thüringer glass between + 16° and − 182° C.

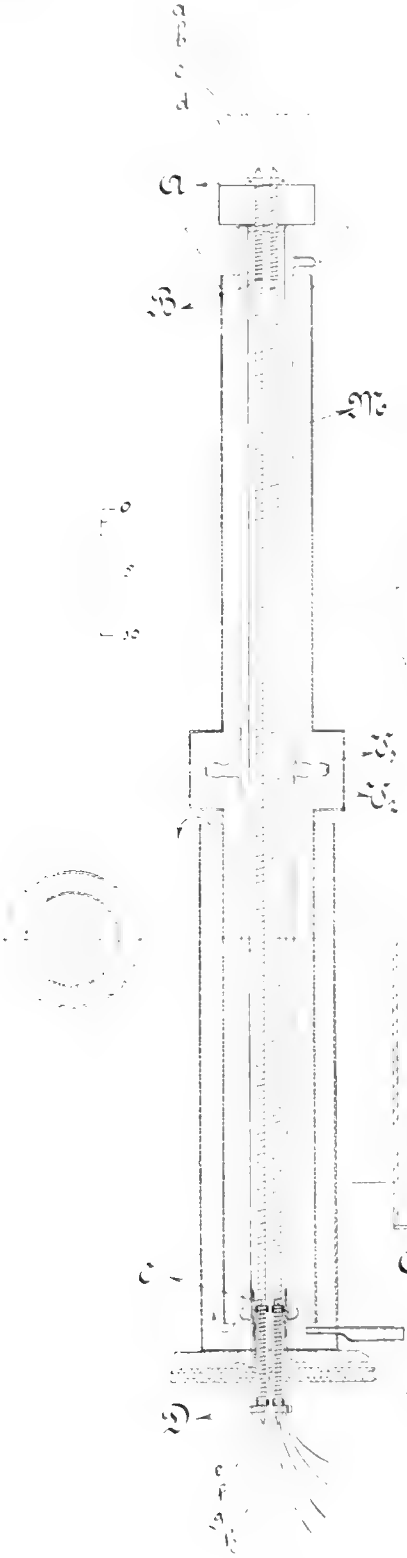
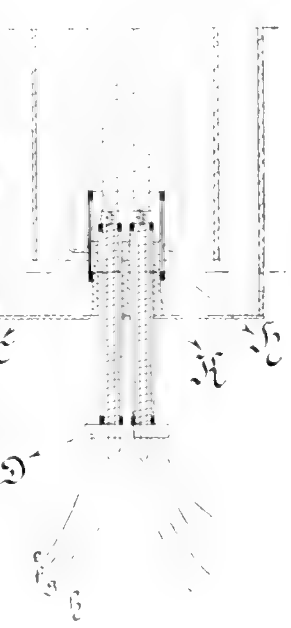


Fig. 2.



already, and the lower rim cracked off. Later we made the connection tube and the stopper more elastic (cf. *II* Pl. I fig. 2) by inserting between them a collar formed of several layers of paper glued together at the borders. In this way a closure was obtained which was perfectly tight, a quite necessary item, for otherwise the escaping liquid streams past the reading points as a cold vapour, which disturbs the uniform distribution of temperature supposed to exist in the ends of the rods and obtained by continually blowing air on to the points which is necessary also for keeping them dry. At the top, the rods are supported sideways so that no strain is caused in them. They are protected from the cold vapours which arise from the bath. From the front and side elevation of the upper end, Fig. 1, the arrangement of paper used for this protection can be clearly understood, and the course of the vapour can be followed as it streams over the wall of the bath through channels of cardboard. This arrangement has moreover the advantage, that the outer surface of the vacuum vessel is also cooled. This is of great importance in the beginning. The cold gas and cooled air are so conveyed away by various paper screens, that they do not come into the neighbourhood of the cathetometer or the standard scale, and also that air at the ordinary temperature remains between these and the points. At the commencement the liquefied gas is introduced in drops through an opening in the cork at the upper end, and afterwards carefully in small quantities. When the bath is once full, fresh liquid is continually added in small quantities to keep the level at the same height. The liquids used were nitrous oxide and oxygen obtained in the manner described in Comm. No. 14 (Dec. '94) and No. 51 (Sept. '99). In both cases considerable purity was aimed at, in consequence the temperature of the bath did not change during the measurements. There is no doubt that the temperatures at the top and the bottom of the bath were not the same but this introduced no difficulty since in the calculation only the mean temperature as determined by the platinum resistance was required.

3rd. *The comparator* (*cathetometer and scale*). We used the instruments which are described in Comm. No. 60 (Sept. '00). The scale was very carefully enveloped in wool and paper to protect it from changes of temperature. Its temperature was read by two thermometers divided into $^1/_{20}$ and symmetrically placed above and below, while the room temperature was maintained as constant as possible. The telescopes were provided with the microscope objectives which had been used for the measurements on the viscosity of liquid methyl chloride (Comm. No. 2, Febr. '91) and which can be used at a distance of 10 cms. In this case one revolution of the head (divided into 100 parts) of the micrometer screw (cf. Comm. No. 60 § 15) was equivalent to 60 to 70 μ. The levels on the telescopes were carefully calibrated; at the distance used, one division on the levels corresponded to from 4 to 6 μ and the uncertainty in reading was less than 0.2 division or about 1 μ. After each setting, 30 seconds was allowed to elapse before reading and former measurements have shown that this is sufficient for the attainment of equilibrium.

The field of view of the microscopes was also investigated by measuring at various points a $^1/_5$ mm. scale, but no irregularity could be found.

4th. *Measurement of resistance.* The doubled conducting wires a, b, c etc. at the ends of each measuring wire AB, etc. (cf. Pl. I) were lead to eight cups of mercury for each rod, which cups could be connected in pairs to the wires from the WHEATSTONE bridge. By measuring

$$w_1 = a + AB + b$$
$$w_2 = c + AB + d$$
$$w_3 = a + c$$
$$w_4 = b + d$$

the resistance of the wire AB

$$w_t = \frac{w_1 + w_2 - w_3 - w_4}{2}$$

can be determined[1]). The galvanometer with reading scale (see Comm. N° 25, April '96) had a resistance of 6 ω and a sensitiveness of 2.5×10^{-7}. Thermoelectric forces in the circuit of copper leads, platinum leads and platinum resistances are unavoidable, they were, however, only small and could be eliminated.

§ 3. *Survey of a determination.* A complete determination comprises focussing the microscopes, referring to the standard scale, and reading the thermometers, as well as the various determinations of resistance between A and B, B and C, C and D.

In the following table all the readings for the determination of length of the Jena rod in liquid oxygen are given. Column A contains the readings of the micrometer heads, B the corresponding positions of the levels, C the nearest division on the standard scale, D and E the micrometer and level readings for this and F the temperatures.

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[1]) In our case the influence of the shunt between A and B, C and D was so small that it could be neglected and then $w_3 + w_4$ could be determined at once.

TABLE I. JENA GLASS.

25/5 '03	*A*	*B*	*C*	*D*	*E*	*F*
$1^h30'$						
Point below	27.82	6.1				16.44
Millimeter			116 117	34.23 20.07	5.2 5.1	
Point above	19.44	6.1				16.70
Millimeter			1127 1128	33.33 17.14	5.8 5.8	
Point below	27.83	6.0				16.54
„ above	19.47	6.0				16.80
$1^h45'$						

The readings on the micrometer head are now reduced to a standard position of the level and the temperature readings are corrected. This gives the following.

TABLE II. JENA GLASS

25/5 '03	*A*	*B*	*C*	*D*
1^h30				
Point below	27.81			16.37
Millimeter		116 117	34.30 20.15	
Point above	19.43			16.63
Millimeter		1127 1128	33.35 17.16	
Point below	27.83			16.47
„ above	19.47			16.73
1^h45				

Point below	116.458
„ above	1127.859

time $1^h37'.5$ Length 1011.401

Nothing new was in the method used for the determination of resistance. It is hence only necessary to give the final results, as the means of the various measurements reduced to the same time.

To calculate the temperature we have used the following preliminary formula, obtained in the measurements described in Comm. N°. 77

TABLE III. JENA GLASS.

	t	0°
w'_{AB}	4.82	6.29
w'_{BC}	8.77	33.95
w'_{CD}	4.37	10.17

TABLE IV. JENA GLASS.

A Date	*B* Mean time.	*C* Temp. scale.	*D* L_T	*E* $L_{(16°)}$	*F* 	 W'_t	*G* W'_0	*H* ϑ	*I*
20 V.	4^h10	15.58	1012.594	1012.587	top	6.66	6.29		
		.63	.595	.588	middle	36.04	33.95	16.03	
		.69	.593	.587	bottom	10.66	10.17		
22 V.	3^h15	17.74	1011.834	1011.865	top	5.10	6.29		$\gamma_s =$ 5.61
		17.82	.836	.868	middle	22.45	33.95	- 87.87	
		18.00	.844	.880	bottom	6.98	10.17		$\gamma_i =$ 78.1
22 V.	5^h20	18.32	1011.827	1011.868	top	5.01	6.29		$\gamma_s =$ 9.86
		18.41	.815	.858	middle	22.13	33.95	- 87.87	
					bottom	6.91	10.17		$\gamma_i =$ 82.0
23 V.	1^h15	16.68	1012.567	1012.579	top	6.68	6.29		
		16.68	.573	.585	middle	36.09	33.95	16.41	
					bottom	10.72	10.17		
25 V.	12^h10	16.08	1011.408	1011.409	top	4.82	6.29		$\gamma_s =$ 2.18
		.13	.411	.413	middle	8.77	33.95	-182.9	
		.17	.406	.409	bottom	4.37	10.17		$\gamma_i =$ 51.0
25 V.	1^h15	16.38	1011.407	1011.414	top	4.68	6.29		$\gamma_s =$ 48.3
		.55	.401	.411	middle	8.77	33.95	-182.9	
					bottom	4.34	10.17		$\gamma_i =$ 52.8
26 V.	3^h10	17.30	1012.565	1012.588	top	6.70	6.29		
		.49	.567	.594	middle	36.12	33.95	16.64	
					bottom	10.66	10.17		

with platinum wire of the same kind as that used in the present instance

$$w_t = w_0 \,(1 + 0.003864\, t - 0.0_5 103\, t^2)$$

thus $$t_{BC} = -\,182^{\circ}.99.$$

The calculation of the temperatures of the projecting portions from the values w_{AB} and w_{CD} will be described in § 4.

In the following table the final results [1] for all the determinations are given, the standard scale at 16° C. being taken as the reference length. Column E thus contains the values for the rod lengths reduced to this reference. We have used as the expansion coefficient of brass between 16° and 17° the value 17.8×10^{-6}. Column I refers to the ends, and its contents will be considered in § 4.

TABLE V. THÜRINGER GLASS.

A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*
20 V.	2^h45	15.42	1013.107	1013.091	top 6.47	6.12		
		.44	.108	.098	middle 36.53	34.53	15.08	
					bottom 10.21	9.68		
22 V.	12^h30	17.08	1012.244	1012.263	top 4 59	6.12		λ= 26.6
		.33	.238	.262	middle 22.55	34.53	-87.71	
		.37	.239	.263	bottom 6.51	9.68		λ= 85.4
		.35	.240	.264				
23 V.	11^h40	16.68	1013.086	1013.098	top 6.52	6.12		
		.68	.088	.100	middle 36.70	34.53	16.36	
					bottom 10.23	9.68		
25 V.	3^h20	17.04	1011.744	1011.763	top 3.81	6.12		λ= 1.0
		.12	.748	.768	middle 8.95	34.53	-182.79	
		.19	.740	.761	bottom 5.29	9.68		λ= 25.9
		.25	.738	.760				
26 V.	11^h50	16.56	1013.095	1013.105	top 6.46	6.12		
		.67	.098	.110	middle 36 60	34.53	15.61	
					bottom 10.18	9.68		

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[1] The numerical values are slightly different from the values given in the original Dutch paper according to a new and more exact calculation. The final results for the dilatation given in the original are quoted § 6 footnote.

§ 4. *Discussion of the measurements.* In § 2 we have already remarked that the mean temperature of the platinum wire, wound round the portion BC of the rods, which is at the temperature of the bath, may, with sufficient accuracy, be put as equal to the mean temperature of that portion of the rod itself. Throughout this length, the differences of temperature or the length over which they are found, are on the whole small, so that only the mean temperature comes into account. Further consideration is however necessary in respect to the relation of the temperatures of the ends AB and CD and the resistances determined.

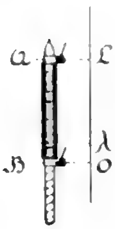

Fig. 2.

Let us suppose that the level of the liquid reaches to a position λ, fig. 2, and hence that the upper portion of AB is outside the liquid. We may suppose that, for the length λ, the rod has the temperature of the bath. The resistance of the wire between B and λ is then $w_t = w_0 \, (1 + pt + qt^2)$ where t is the temperature of the bath.

Also we may suppose that at A, which was damp but just free from ice, the temperature was about 0° C. Further let us suppose that between λ and L the temperature gradient is linear, in other words that the external conduction may be neglected in comparison with the internal conduction of the glass. There is every reason to assume that this was true to the first approximation, since the glass rods were well enclosed in paper the conductivity of which is about $^1/_{100}$ of that of glass. Then, neglecting the conduction of the platinum wire, itself the resistance of an element of the wire between λ and L is $w dx$, where $w = w_0 \, (1 + pt_x + qt_x^2)$ and the whole resistance $\int\limits_{x=\lambda}^{x=L} w dx$.

Further for x between 0 and λ, $t_x = t_1$, between λ and L, $t_x = t - \frac{t}{L-\lambda}(x-\lambda)$ and for $x = L$, $t_x = 0$, so that

$$W_{AB} = W_{(AB)_0} \frac{\lambda}{L} (1 + pt + qt^2) +$$

$$+ \int\limits_{x=\lambda}^{x=L} W_{(AB)_0} \frac{1}{L} \left[1 + p \left(t - \frac{t}{L-\lambda} (x - \lambda) \right) - q \left(t - \frac{t}{L-\lambda} (x - \lambda) \right)^2 \right] dx.$$

From this λ, the only unknown, can be obtained. One of the most unfavourable cases, that for the upper end of the Jena glass rod in N_2O, shows when calculated that the linear form for the resistance can be employed in our measurements without difficulty, in place of the quadratic form. We found $\lambda = 8.4$ cm. with the quadratic and $\lambda = 9.0$ cm. with the linear formula. The uncertainty thus introduced into the determination of length, is less than 1μ.

In order to determine the influence of various suppositions with regard to the distribution of temperature in the rod, we have calculated the change in length which would be produced, if the temperature was $-87°$ C. from 0 to λ and 0° from λ to L, in place of the distribution assumed above. The change was hardly 0.1μ and thus lies within the degree of accuracy. However an important control indispensable for more accurate determinations would be obtained by measurements on a rod with similar ends AB and CD, but where BC was only a few centimeters long [1]).

To apply generally the method of this section for the determination of mean temperature it may be necessary to subdivide the portion of at variable temperature AB into more parts while for each of these separate portions the resistance would have to be found. In our case this would have been an unnecessary complication.

§ 5. *Influence of errors.* These can be fully considered by the aid of $a = \frac{L_t - L_{t_1}}{L_t} \; \frac{1}{t - t_1}$.

The accuracy of the cathetometer reading can be put at 2μ (the whole contraction being 1200μ). This gives $d\bar{a} = 2 \times 10^{-8}$. For the mean temperature of the portion BC the error is certainly less than 0.5 deg. C, whence $da = 1.5 \times 10^{-8}$, and for that of the ends we found 1μ. Hence a greater uncertainty than $da = 4 \times 10^{-8}$ is not to be expected. Although the division of this error between a and b cannot well be made, it is certain that an error in the temperature determination has by far the greatest influence on b.

§ 6. *Final results.* For the observed lengths L_{tNO_2} at the temperature t_{NO_2} in nitrous oxide, L_{tO_2} in oxygen, and L_{16^0} at ordinary temperature we have the three equations

$$L_{tNO_2} = (L_{BC_0} + \lambda_i + \lambda_s)\,(1 + at_{NO_2} + bt^2{}_{NO_2}) +$$
$$+ L_{4_0} + L_{5_0} + \left(L_{s_0} - \lambda_s + L_{i_0} - \lambda_i\right)\left(1 + \frac{1}{2}\, at_{NO_2} + \frac{1}{3}\, bt^2{}_{NO_2}\right)$$

and two analogous ones for L_{tO_2} and L_{16^0}, with $L_{BC_0} = 840$ mM., $L_{i_0} = 97$, $L_{s_0} = 59$ for Jenaglass, and $L_{BC_0} = 834$, $L_{i_0} = 96$, $L_{s_0} = 60$, for Thüringerglass. For L_{BC_0} (the length of the part BC in the figure at 0° C.), L_{i_0}, L_{s_0} (that of the parts CD and AB in the figure) are assumed approximate values; the exact values L_{4_0} and L_{5_0} to be

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[1]) For Jenaglass in oxygen we found a negative value of λ, we made therefore the calculation on another supposition viz. that from A in the direction of B the rod has the temperature 0° over a length of λ' cm. (cf. Table IV).

ascribed accordingly to the lengths at 0° C. of the points projecting beyond A and D follow from the equations. These equations give $L_{4_0} + L_{5_0} = 16.587$ and $L_{4_0} + L_{5_0} = 23.095$ for Jena and Thüringer glass respectively, and further:

$$L = L_0 \ (1 + at + bt^2)$$

$$V = V_0 \ (1 + k_1 t + k_2 t^2)$$

Jena glass 16^{III} $\left\{ \begin{array}{l} a = 7.74 . 10^{-6}, b = 0.00882 . 10^{-6} \\ k_1 = 23.21 . 10^{-6}, k_2 = 0.0265 . 10^{-6} \end{array} \right.$

Thüringer glass (n°. 50) $\left\{ \begin{array}{l} a = 9.15 \ 10^{-6}, b = 0.0119 \ 10^{-6} \\ k_1 = 27.45 \ 10^{-6}, k_2 = 0.0357 \ 10^{-6} \end{array} \right.$

The value found for Jenaglass 16^{III} differs much from that obtained by WIEBE and BÖTTCHER [2]) and from those obtained afterwards by THIESEN and SCHEEL [3]) for temperatures between 0° and 100°.

Physics. — "*The motion of electrons in metallic bodies*, III." By

Prof. H. A. LORENTZ.

(Communicated in the meeting of March 25, 1905).

§ 16. We may now proceed to examine the consequences to which we are led if we assume *two* kinds of free electrons, positive and negative ones. We shall distinguish the quantities relating to these by the indices 1 and 2; e.g. N_1 and N_2 will be the numbers of electrons per unit of volume, m_1 and m_2 their masses, $\frac{3}{2h_1}$ and $\frac{3}{2h_2}$ the mean squares of their velocities. For simplicity's sake, all electrons of the same sign will be supposed to be equal, even if contained in different metals. As to the charges, these will be taken to have the same absolute value for *all* particles, so that

$$e_2 = -e_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

Our new assumption makes only a slight difference in the formula for the electric conductivity; we have only to apply to both kinds of electrons the considerations by which we have formerly found the equation (21). Let a homogeneous metallic bar, having the same temperature throughout, be acted on in the direction of its length by an electric force E; then, just as in § 8, we have for each kind of electrons

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[1]) In the original was given

Jena 16^{III} $a = 7.78$ $b = 0.0090$
Thüringer n° 50 $a = 9.10$ $b = 0.0120$.

[2]) WIEBE und BÖTTCHER. Z. f. Inst. k. 10, pg. 234. 1890.

[3]) THIESEN und SCHEEL, Wiss. Abt. der Ph. techn. Reichsanstalt. Bd. II S. 129. 1895.

$$v = \frac{4\pi l A e}{3hm} E.$$

The electric current per unit of area of the normal section, is the sum of the currents due to the positive and the negative particles. We may therefore represent it by

$$\left(\frac{4\pi l_1 A_1 e_1^2}{3h_1 m_1} + \frac{4\pi l_2 A_2 e_2^2}{3h_2 m_2} \right) E$$

and we may write for the coefficient of conductivity

$$\sigma = \sigma_1 + \sigma_2, \quad \ldots \ldots \ldots \quad (49)$$

if

$$\sigma_1 = \frac{4\pi\, l_1\, A_1\, e_1^2}{3h_1\, m_1} \quad , \quad \sigma_2 = \frac{4\pi\, l_2\, A_2\, e_2^2}{3h_2\, m_2}$$

or (cf. § 8)

$$\sigma_1 = \sqrt{\frac{2}{3\pi}} \cdot \frac{l_1 N_1 e_1^2 u_1}{\alpha T} \quad , \quad \sigma_2 = \sqrt{\frac{2}{3\pi}} \cdot \frac{l_2 N_2 e_2^2 u_2}{\alpha T} \quad . . (50)$$

These latter quantities may be called the *partial conductivities* due to the two kinds of electrons.

§ 17. In all the other problems that have been treated in the preceding parts of this paper, we now encounter a serious difficulty. If either the nature of the metal or the temperature changes from one section of the circuit to the next, we can still easily conceive a state of things in which there is nowhere a continual increase of positive or negative electric charge; this requires only that the *total* electric current be 0 for every section of an open circuit and that it have the same intensity for every section of a closed one. But, unless we introduce rather artificial hypotheses, it will in general be found impossible to make each partial current, i. e. the current due to each kind of electrons considered by itself, have the same property. The consequence will be that the number of positive as well as that of negative electrons will increase in some places and diminish in others, the change being the same for the two kinds, so that we may speak of an accumulation of "neutral electricity" in some points and of a diminution of the quantity of neutral electricity in others. Now, supposing all observable properties to remain stationary, as indeed they may, we must of necessity suppose that a volume-element of the metal contains at each instant the same number of really free electrons. This may be brought about in two ways. We may in the first place imagine that all electrons above the normal number that are introduced into the element are immediately caught by the metallic atoms and fixed to them, and that, on the other hand, in those places from which electrons are carried away by the two currents, the loss is supplied by a new production of free electrons. This hypothesis would imply a state of the circuit that is not, strictly speaking, stationary and which I shall call "quasi-stationary". Moreover, we should be obliged to suppose that the production of free electrons or the accumulation of these particles in the metallic atoms could go on for a considerable length of time without making itself anyways felt.

In the second place we may conceive each element of volume to contain not only free positive and negative electrons, but, in addition to these, a certain number of particles, consisting of a positive and a negative electron combined. Then, the number of free electrons might be kept constant by a decomposition or a building up of such particles and we could arrive at a really stationary state by imagining a diffusion of this "compound electricity" between different parts of the circuit.

§ 18. The mathematical treatment of our problems is much simplified by the introduction of two auxiliary quantities.

In general, in a non-homogeneous part of the circuit, the acceleration X will be composed of the part X_m, represented by (30), and the part $\frac{e}{m}E$, corresponding to the electric force E. The formula (21) for the flow of a swarm of electrons may therefore be replaced by

$$\mathbf{r}=\frac{2}{3}\pi l\left[\frac{1}{h^2}\left(-\frac{2hA}{m}\frac{dV}{dx}+\frac{2heA}{m}E-\frac{dA}{dx}\right)+2\frac{A}{h^3}\frac{dh}{dx}\right]. \quad . \quad (51)$$

This will be 0, if the electric force E has a certain particular value, which I shall denote by E and which is given by

$$\mathrm{E}=\frac{1}{e}\frac{dV}{dx}+\frac{m}{2he}\frac{d\log A}{dx}+\frac{m}{e}\frac{d}{dx}\left(\frac{1}{h}\right). \quad . \quad . \quad . \quad . \quad (52)$$

For any other value of the electric force the flow of electrons will be

$$\mathbf{r}=\frac{4}{3}\pi l\frac{eA}{hm}(E-\mathrm{E}).$$

and if, in order to obtain the corresponding electric current, we multiply this expression by e, we shall find the product of $E-\mathrm{E}$ by the coefficient of conductivity, in so far as it depends on the kind of electrons considered.

Substituting in (52) the value (14) and applying the result to the positive and the negative electrons separately, we find

$$\left.\begin{aligned} E_1 &= \frac{1}{e_1}\frac{dV_1}{dx} + \frac{2}{3}\frac{\alpha T}{e_1}\frac{d\log A_1}{dx} + \frac{4}{3}\frac{\alpha}{e_1}\frac{dT}{dx} \\ E_2 &= \frac{1}{e_2}\frac{dV_2}{dx} + \frac{2}{3}\frac{\alpha T}{e_2}\frac{d\log A_2}{dx} + \frac{4}{3}\frac{\alpha}{e_2}\frac{dT}{dx} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (53)$$

If the area of a normal section is again denoted by Σ, the intensities of the partial currents are given by

$$i_1 = \sigma_1 (E - E_1)\,\Sigma, \qquad i_2 = \sigma_2 (E - E_2)\,\Sigma \quad . \quad . \quad . \quad . \quad (54)$$

and that of the total current, on account of (49), by

$$i = i_1 + i_2 = (\sigma E - \sigma_1 E_1 - \sigma_2 E_2)\,\Sigma \quad . \quad . \quad . \quad . \quad . \quad (55)$$

Putting

$$j_1 = \frac{\sigma_1}{\sigma}\, i \quad , \quad j_2 = \frac{\sigma_2}{\sigma}\, i,$$

we may also write

$$i_1 = j_1 + \frac{\sigma_1\sigma_2}{\sigma}(E_2 - E_1)\,\Sigma, \qquad i_2 = j_2 + \frac{\sigma_1\sigma_2}{\sigma}(E_1 - E_2)\,\Sigma.$$

It appears from these formulae that, whenever E_1 differs from E_2, the partial currents i_1 and i_2 will *not* be proportional to the conductivities σ_1 and σ_2.

§ 19. The above results lead immediately to an equation determining the electromotive force F in an open circuit composed of different metals, between which there is a gradual transition (§ 6) and which is kept in all its parts at the same temperature. Let P and Q be the ends of the circuit and let us reckon x along the circuit in the direction from P towards Q.

The condition for a stationary or a quasi-stationary state is got by putting $i = 0$ in (55). Representing the potential by φ, so that

$$E = -\frac{d\varphi}{dx},$$

we get

$$\frac{d\varphi}{dx} = -\frac{\sigma_1}{\sigma} E_1 - \frac{\sigma_2}{\sigma} E_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

and finally, taking into account the values (53), in which we now have $\frac{dT}{dx} = 0$, and integrating from P to Q,

$$\varphi_Q - \varphi_P = -\frac{1}{e_1}\int_P^Q \frac{\sigma_1}{\sigma}\frac{dV_1}{dx}\,dx - \frac{1}{e_2}\int_P^Q \frac{\sigma_2}{\sigma}\frac{dV_2}{dx}\,dx -$$

$$-\frac{2}{3}\frac{\alpha T}{e_1}\int_P^Q \frac{\sigma_1}{\sigma}\frac{d\log A_1}{dx}dx - \frac{2}{3}\frac{\alpha T}{e_2}\int_P^Q \frac{\sigma_2}{\sigma}\frac{d\log A_2}{dx}dx \quad . \quad . \quad . \quad (57)$$

At the same time the intensities of the partial currents are given by

$$i_1 = \frac{\sigma_1\sigma_2}{\sigma}(E_2 - E_1)\,\Sigma \quad , \quad i_2 = \frac{\sigma_1\sigma_2}{\sigma}(E_1 - E_2)\,\Sigma .$$

These values, which are equal with opposite signs, will in general vary along the circuit, so that, even in this simple case, we cannot avoid the complications I have pointed out in § 17. Nor can the difficulty be easily overcome. Indeed, we can hardly admit that the state of two pieces of different metal, in contact with each other and kept at a uniform temperature is not truly stationary. If, in order to escape this hypothesis, we have recourse to the considerations I presented at the end of § 17, we must suppose the neutral electricity to be continually built up in some parts of the system and to be decomposed in other parts. The first phenomenon will be accompanied by a production and the second by a consumption of heat. That these effects should take place in a system whose state is stationary and in which there are no differences of temperature, is however in contradiction with the second law of thermodynamics.

The only way out of the difficulty, if we do not wish to confine ourselves to *one* kind of free electrons, seems to be the assumption that there is no accumulation of neutral electricity at all, i. e. that i_1 and i_2 are simultaneously 0. This would require that $\mathbf{E}_1 = \mathbf{E}_2$, or in virtue of (53)

$$\frac{1}{e_1}\frac{dV_1}{dx} + \frac{2}{3}\frac{\alpha T}{e_1}\frac{d\log A_1}{dx} = \frac{1}{e_2}\frac{dV_2}{dx} + \frac{2}{3}\frac{\alpha T}{e_2}\frac{d\log A_2}{dx} \quad . \quad . \quad (58)$$

Since $e_2 = -e_1$, we might further conclude that

$$\frac{2}{3}\alpha T\frac{d\log(A_1 A_2)}{dx} + \frac{d(V_1 + V_2)}{dx} = 0,$$

which means that

$$\log(A_1 A_2) + \frac{3}{2\alpha T}(V_1 + V_2) = \psi(T)$$

ought to have the same value in all parts of the circuit. We should therefore have to regard this expression as a function of the temperature, independent of the nature of the metal [1]).

If we suppose the contact of two metals to have no influence on the number of free electrons in their interior, we must understand by A_1 and A_2 in the above equation quantities characteristic for each

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[1]) Cf. DRUDE, Annalen der Physik, 1 (1900), p. 591.

metal and having, for a given temperature, determinate values, whether the body be or not in contact with another metal.

By the assumption $E_1 = E_2$, (56) simplifies into

$$\frac{d\varphi}{dx} = -E_1 = -E_2$$

and (57) becomes

$$\varphi_Q - \varphi_P = \frac{1}{e_1}(V_{1P} - V_{1Q}) + \frac{2}{3}\frac{aT}{e_1} \log\left(\frac{A_{1P}}{A_{1Q}}\right) =$$

$$= \frac{1}{e_2}(V_{2P} - V_{2Q}) + \frac{2}{3}\frac{aT}{e_2} \log\left(\frac{A_{2P}}{A_{2Q}}\right), \quad . \quad . \quad (59)$$

a formula which is easily seen to imply the law of the tension-series.

§ 20. The question now arises, whether, with a view to simplifying the theory of the thermo-electric current, we shall be allowed to consider E_1 and E_2 as equal, not only in the junctions, but also in the homogeneous parts of the circuit, in which the differences of temperature come into play. This seems very improbable. Indeed, supposing for the sake of simplicity V_1 and V_2 to be, for a given metal, independent of T, so that in a homogeneous conductor $\frac{dV_1}{dx} = 0$ and $\frac{dV_2}{dx} = 0$, we find from (53), putting $E_1 = E_2$,

$$\frac{2}{3}\frac{aT}{e_1}\frac{d \log A_1}{dx} + \frac{4}{3}\frac{a}{e_1}\frac{dT}{dx} = \frac{2}{3}\frac{aT}{e_2}\frac{d \log A_2}{dx} + \frac{4}{3}\frac{a}{e_2}\frac{dT}{dx},$$

or, since $e_2 = -e_1$,

$$T\frac{d \log (A_1 A_2)}{dx} = -4\frac{dT}{dx},$$

which can hardly be true. It would imply that the product $A_1 A_2$ is inversely proportional to the fourth power of the absolute temperature and this would require in its turn, as may be seen by means of (13) and (14), that the product $N_1 N_2$ should be inversely proportional to T itself.

We are therefore forced to admit inequality of E_1 and E_2. Now, it may be shown that, whatever be the difficulties which then arise in other questions, the theory of the *electromotive force* remains nearly as simple as it was before. For an open circuit we have again to put $i = 0$; hence, the formula (56) will still hold, as may be inferred from (55), if we replace E by $-\frac{d\varphi}{dx}$. The equation for the electromotive force becomes therefore

$$F = \varphi_Q - \varphi_P = -\int_P^Q \frac{1}{\sigma} (\sigma_1 \mathrm{E}_1 + \sigma_2 \mathrm{E}_2)\, dx \quad . \quad . \quad . \quad (60)$$

In the case of a closed circuit, which we get by making the points P and Q coincide, we shall integrate (55) along the circuit after having multiplied that equation by $\frac{dx}{\sigma \Sigma}$ and replaced E by $-\frac{d\varphi}{dx}$. The intensity i being everywhere the same, the result takes the form

$$i \int \frac{dx}{\sigma \Sigma} = F. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

This is the mathematical expression of OHM's law.

§ 21. It must further be noticed that the equation (60) agrees with the law of the thermo-electric series. This may be shown as follows. If we suppose the temperature to be the same throughout a junction, we may easily infer from what has been said in § 19 that the part of the integral corresponding to such a part of the circuit can be represented as the difference of two quantities, which are both functions of the temperature, but of which one depends solely on the nature of the first metal and the other on that of the second. Considering next a homogeneous part of the circuit between two junctions, we may remark that in this E_1 and E_2 have the form $f(T)\frac{dT}{dx}$ and that the rations $\frac{\sigma_1}{\sigma}$ and $\frac{\sigma_2}{\sigma}$ are functions of the temperature. We may therefore write for the corresponding part of (60)

$$\int_{T'}^{T''} \chi(T)\, dT.$$

This integral, which is to be taken between the temperatures T' and T'' of the junctions, may be considered as the difference of the values, for $T = T'$ and $T = T''$, of a certain quantity depending on the nature of the metal.

Combining these results, we see that the electromotive force in a given circuit is entirely determined by the temperatures of the junctions, and that, if there are two of these between the metals I and II, the electromotive force $F_{I,II}$ we have examined in § 10 *c* may still be represented by an equation of the form

$$F_{I,II} = \zeta_I(T') - \zeta_I(T'') - \zeta_{II}(T') + \zeta_{II}(T''),$$

the function $\zeta_I(T)$ relating to the first, and the function $\zeta_{II}(T)$ to the second metal. The law of the thermo-electric series may immediately be inferred from this formula. However, in order to obtain this result, it has been necessary to adopt the hypothesis expressed by (58).

I shall terminate this discussion by indicating the way in which our formulae have to be modified, if, in the direction of the circuit, the electrons are acted on not only by the electric force caused by the differences of potential, but also by some other force proportional to their charge and whose line-integral along the circuit is not 0. Let us denote this force, per unit charge, by E_e and let us write for its line-integral

$$\int E_e\, dx = F_e.$$

This latter quantity might be called the "external electromotive force" acting on the circuit. Now, in the formulae (54), we must replace E by $E + E_e$. Consequently, (55) becomes

$$i = \{\sigma (E + E_e) - \sigma_1 \mathrm{E}_1 - \sigma_2 \mathrm{E}_2\},$$

and treating this equation in the same way as we have done (55), we find instead of (61)

$$i \int \frac{dx}{\sigma \Sigma} = F + F_e .$$

§ 22. I shall not enter on a discussion of the conduction of heat, the PELTIER-effect and the THOMSON-effect.

In the theory which admits two kinds of free electrons, all questions relating to these phenomena become so complicated that I believe we had better in the first place examine more closely the HALL-effect and allied phenomena. Perhaps it will be found advisable, after all, to confine ourselves to one kind of free electrons, a course in favour of which we may also adduce the results that have been found concerning the masses of the electrons. These tend to show that the positive charges are always fixed to the ponderable atoms, the negative ones only being free in the spaces between the molecules. If however a study of the HALL-effect should prove the necessity of operating with both positive and negative free electrons, we shall be obliged to face all the difficulties attending this assumption.

Geology. — *"Contributions to the knowledge of the sedimentary boulders in the Netherlands. I. The Hondsrug in the province of Groningen. 2. Upper Silurian boulders. Second communication: Boulders of the age of the Eastern Baltic zones H and I."* By Dr. H. G. JONKER. (Communicated by Prof. K. MARTIN).

H.

Besides the Borealis-limestone, described in my preceding communication (33) and on which I am going to touch later on, boulders with *Pentamerus*-remains near Groningen are rare. I can mention but three pieces here, in two of which the species is not to be made out, while in the third, found in the "Noorderbegraafplaats" in Groningen, *Pentamerus estonus* EICHW. occurs. Nor is this determination beyond doubt and especially the possibility of its being *Pentamerus oblongus* Sow. can in my opinion not be excluded, as indeed in outward appearance the latter corresponds almost perfectly with the former (12, p. 81 and 3, T. XVIII, f. 4^a). As however, the latter form in Gothland has no doubt to be looked upon partly as the real *P. estonus* EICHW. (27, p. 98), nothing can be said for certain about its origin, as the rock, a weathered, yellow limestone does not give sufficient indications for it. I mention this boulder however for completeness' sake.

With regard to the Borealis-limestone I wish to add, that after all I did find an almost complete specimen of *Pentamerus borealis* EICHW., in the Groningen museum, evidently from a Groningen boulder. The correspondence with the specimens from Weissenfeld, mentioned before, is however not very great, the top of the ventral valve in our specimen being much more curved and thus agreeing more with EICHWALD's description.

A close investigation removing the existing confusion with regard to the Upper Silurian Pentamerus-species is really most desirable.

31. Clathrodictyon-limestone.

White limestone, sometimes having a more or less light-yellowish-gray tinge. At the surface and in cavities the colour is rather yellow. It is always crystalline and the very irregular fractured surfaces show a peculiar fatty silk-gloss, which is most characteristic of them. If the colour becomes a little darker, as is sometimes the case, the gloss remains preserved. The rock is a real Stromatopora-limestone, which may be distinctly perceived in some pieces, as they consist of slightly curved, concentric layers the surface of which is covered with small knobby mamelons (25, Pl. XVII, f. 14), which make it more than probable that we have to do here with

Clathrodictyon variolare Rosen sp.

Its structure, however, is not easily traced on account of the crystalline character of the stone.

This species of boulder further contains real fossils only in the form of peculiar conical cavities, mostly slightly bent towards the point. On the inside they are invariably set with annular edges, which on an average are lying a little more than 1 mm. from each other in specimens of an average size. The cavity is often completely filled up with crystalline calcite bright as water. Its rather thick wall presents on the outside small irregularly running lines of growth. **Friedrich Schmidt**, Akademiker in St. Petersburg, whom I sent a piece of this limestone, was kind enough to inform me that these cavities originate from *Cornulites* sp. (1, T. 26, f. 5—8), a fossil of the I-zone in Oesel, frequently occurring near St. Johannis.

These boulders are by no means rare near Groningen as appears from the following list:

"Noorderbegraafplaats",	Groningen	6
"Boteringesingel",	,,	7
"Nieuwe Kijk in 't Jatstraat",	,,	1
"Nieuwe Veelading",	,,	3
"Schietbaan",	,,	1
Behind the "Sterrebosch",	,,	1
	,,	1
Café "the Passage", Helpman		1
Villa "Edzes" near Haren		1
The "Huis de Wolf" near Haren		1
"Klein-Zwitserland" near Harendermolen		1

About the occurrence of the mentioned species of Stromatopora **Nicholson** records it from Borkholm and Worms in the Borkholm stratum in Esthonia, but he has especially found them frequently in the Estonus-zone there, chiefly near Kattentack. (25, p. 151). He does not record it from Gothland, though this fact is not sufficient altogether to exclude its occurrence there. Moreover **Lindström** mentions three other species of this genus (16, p. 22). Among my material for comparison is a specimen from Klein-Ruhde, to the west of Kattentack in the H-zone in Esthonia. This rock is somewhat darker, more grayish; but yet examples are to be found among our pieces which perfectly resemble it, so that the correspondence may really be called striking. The described *Cornulites* do not occur in it which it is true cannot surprise us in a piece of so small dimensions (7 × 6 × 2 c.M.).

Finally I wish to state that in a boulder of stromatopora-limestone in Gothland, I found analogous *Cornulites*-cavities, which petrographically does not altogether agree with our pieces. The place where it is found is immediately to the north of Högklint, on the field (not in the beach). But this fossil is of little importance for the further determination of the age of the rock, as most likely various species will be implied in the name of *Cornulites serpularius* SCHLOTH. which is usually given.

Taking everything into consideration, it seems possible (perhaps even probable) to me that this Clathrodictyon-limestone comes from the H-zone in Esthonia or from its western continuation.

In connection with this must be said that among the very numerous stromatoporae of the Hondsrug (of which specific determinations are hardly ever possible) two occur which from their characteristic astrorhizae may be called:

Stromatopora discoidea LONSD. sp. . . . . 25, Pl. XXIV, f. 2.

Both pieces, found in the "Noorderbegraafplaats" and in the "Violenstraat" in Groningen, consist of fine-grained crystalline (stromatopora-) limestone; the former is all over white and therefore closely resembles Clathrodictyon-limestone, the latter is rather grayish and also partially weathered, which fact decreases the correspondence.

This species, very common in Wenlock limestone from England, also occurs in the neighbourhood of Wisby in Gothland. NICHOLSON calls those Gothland specimens however usually highly mineralised (25, p. 191), which with my material from Gothland corresponds but to this extent that this fossil occurs only as a not always very thick crystalline crust in marl or marly limestone. LINDSTRÖM records it only from *h* (16, p. 22), his youngest zone of the Upper Silurian of Gothland (*f*, DAMES). Contrary to this I allege to have found a specimen (it is true somewhat differing in a smaller number of astrorhizae) in the calcareous marl immediately to the north of Högklint, occurring there as firm rock; this fossil comes from a stratum about 1 M. above the beach. This petrographical and stratigraphical occurrence is, it seems to me, hardly to be referred to the age *h*; the other specimen in the Groningen museum supports my observation only to the length of containing marly remains still distinctly to be seen. The place where it was found is, however, not further indicated.

Our Groningen fossils have upon the whole but little in common with these Gothland pieces; meanwhile this fossil also occurs in Esthonia near Klein-Ruhde in the Estonus-zone. That is why these two pieces have been mentioned here though no further data can be brought forward to prove their origin from these Eastern Baltic regions through want of material for comparison.

I.

Boulders which correspond in age with the Lower Oesel zone in the Eastern Balticum, are not rare near Groningen. BONNEMA already pointed it out some years ago (31); this short essay, however, has more of a palaeontological character, so that I wish to complement these communications and enter into further particulars.

32. Baltica-limestone.

In an unweathered state rather hard, tough, fine-grained-crystalline limestones of a bright-gray or light-brownish-gray colour. Some pieces are almost impalpable; some parts are coloured bluish-gray on the inside, so that the rock may originally have had that colour. Through weathering the bright-gray tinge passes into light-yellowish-gray; the uneven fractured surfaces then are very often covered with sallow-yellowish and brown spots. Crystalline calcite rarely occurs. The limestone is rather pure, but a little marly and hardly ever slightly dolomitic. Real dolomites are not among them. Stratification is imperceptible. The dimensions of the pieces found amount to 25 cm.

Fossils are not present in great numbers, chiefly Ostracoda, among which Leperditia-shells are the most important. Whilst bright-brown in the unweathered rock, the valves which sometimes occur frequently in a single piece, have become nearly white by weathering. As is often the case with the younger Leperditia-limestones, which are to be described later on, this limestone is not unfrequently connected with Stromatopora-limestone; the fossils to be mentioned below, however, never occur in it. Besides these large Ostracoda-remains, small Beyrichia- and Primitia-valves are also frequently found but they become only distinctly visible through weathering. The fossil fauna consists of the following species.

Leperditia baltica His. sp.	
Strophomena rhomboidalis Wilck. sp.	
Strophomena sp.	
Atrypa reticularis L.	
Meristella sp.	
Encrinurus punctatus Wahlb.	
Zaphrenthis conulus Lindstr.	**28, p. 32, T. VI, f. 65—68.**
Orthoceras sp.	
Murchisonia sp.	
Tentaculites sp.	
Primitia seminulum Jones.	**14, p. 413, Pl. XIV, f. 14.**
Primitia mundula Jones	**23 T. XXX, f. 5—7; 18, p. 375, Pl. XVI.**
Beyrichia Jonesii Boll.	**17, p. 13, T. II, f. 10—11.**
Beyrichia spinigera Boll.	**23, p. 501, T. XXXI, f. 19—20.**

The first mentioned Leperditia-species is present in all pieces; all other fossils, however, occur either few and far between or in a single piece, excepting the small ostracoda. I have however not taken much pains to increase the number of species of them (for the greater part already mentioned by Bonnema), because their stratigraphical value is still but trifling nowadays. Then to determine age and origin, we can restrict ourselves to the communication where and in which strata occurs the type-fossil of this group, *Leperditia baltica* His. sp. (after which in accordance with the names of Phaseolus-limestone and Grandis-limestone, generally in use, I have called these limestones).

First of all, however, the number of the pieces found here and the special places where they were found, be given here:

"Noorderbegraafplaats",	Groningen	7
"Boteringesingel",	,,	4
"Noorderbinnensingel",	,,	5
"Violenstraat",	,,	1
"Nieuwe Boteringestraat",	,,	1
"Nieuwe Kijk-in 't Jatstraat"	,,	2
"Nieuwe Veelading",	,,	1
	,,	1
"Old Collection"		3
Helpman		2
"Hilghestede", Helpman		1
Between Helpman and Haren		2
Harendermolen		1

So in all 31 pieces. The number found is presumably much larger, because I have only mentioned here the boulders which beyond any doubt belong to this group; among the numerous limestones with Leperditia-remains which cannot be specifically determined there will no doubt be a number of this age.

Leperditia baltica His. sp.

Literature:	1869.	Kolmodin, 2, p. 13, f. 2—3.
	1873.	Schmidt, 4, p. 15—17, f. 19—21.
	1876.	Roemer, 5, T. 19, f. 7.
	1878.	Martin, 6, p. 45.
	1880.	Kolmodin, 8, p. 134.
	1883.	Schmidt, 10, p. 11—13, T. I, f. 1—3.
	1884.	Kiesow, 11, p. 275, T. IV, f. 4.
	1885.	Remelé, 13, p. 26, no. 226.
	1888.	Lindström, 16, p. 5, no. 25.
	1890.	Kiesow, 19, p. 89—91, T. XXIII, f. 14—16.
	1890.	Schmidt, 20, p. 255.
	1890.	Dames, 21, p. 1125.
	1891.	Krause, 22, p. 5, 7.
	1891.	Krause, 23, p. 488, T. XXIX, f. 1—3.
	1891.	Schmidt, 24, p. 123.
	1895.	Stolley, 27, p. 109.
	1898.	Bonnema, 29, p. 452.
	1900.	Chmielewski, 30, p. 17—20, 33; T. I, f. 17—20.
	1900.	Bonnema, 31, p. 138—140.

From the literature about this fossil, cited above, which as regards the later years is rather complete, it appears that for a long time a certain confusion and uncertainty about the limits of the species have existed, which have been removed but a few years ago. Besides the real *L. baltica* His., characterized by the comb-shaped striae on the inverted plate of the left valve (*L. pectinata* Schmidt) — which characteristic may be distinctly perceived in twenty of the boulders from here —, Schmidt had also described another species: *L. Eichwaldi* Schm. Bonnema has proved that both species have to be united (31); at nearly the same time this has also been observed by Chmielewski. The latter, however, distinguishes besides the typical form two other varieties:

L. baltica, var. *Eichwaldi* Schmidt
,, ,, ,, *formosa* Chmiel.

These two varieties are present among our boulders, var. *Eichwaldi* not unfrequently, var. *formosa* less often. But the characteristics of these varieties are by no means conspicuous, so that there are specimens which partake of the nature both of these varieties and the real species, as CHMIELEWSKI himself too has perceived. In accordance with this is the fact that these varieties are practically of no stratigraphical importance; it is on these grounds I have thought it allowable to combine all these forms in one species under the name of *Leperditia baltica* HIS. sp.

It has been frequently found in boulders. KIESOW describes it from "weisslich-grauen Mergelkalk" of Langenau, from "ziemlich verwitterter und in Folge dessen gelblich gefärbter Kalk mit zahlreichen Schalen der *Leperditia baltica* HIS. (F. SCHMIDT); daneben finden sich *Encrinurus punctatus, Atrypa reticularis,* und einige schlecht erhaltene *Beyrichien,* u. s. w." from Zoppot-Olivaer Walde, also in West-Prussia. The first stone corresponds perfectly with limestone from Langers in the N.E. of Gothland, the second shows much correspondence with the occurrence of Oesterby near Slite. Therefore he refers these pieces to Gothland. (Of the co-occurrence of *L. baltica* HIS. sp. and *L. Hisingeri* SCHM., which question I treated of in my previous communication (33, p. 560), he is afterwards not quite sure — 19, p. 90). In his excellent, already frequently cited treatise CHMIELEWSKI briefly describes six boulders in which he has found *L. baltica* in Kurland, Kowno, East and West-Prussia. Most corresponding with our boulders seems to be his: "hellbräunlich-grauer, deutlich krystallinischer, wenig thoniger, fester, unebenbrüchiger Kalkstein mit *Encrinurus punctatus* (30, p. 33)," from Kowno. He does not give a decided opinion about the origin.

Farther to the west this species is still recorded from Brandenburg by REMELÉ and KRAUSE, mostly together with fossils, which also occur in our boulders and from limestones which, so far as can be gathered from the short descriptions, correspond in some respects with ours. STOLLEY describes also various of those limestones from Sleswick-Holstein among which "ein gelber Kalk enhält neben *L. baltica* HIS., *Atrypa reticularis* L. und *Encrinurus punctatus* WAHLENBERG" is again conspicuous. From Groningen our species was already recorded in 1878 by MARTIN, from Kloosterholt afterwards also by BONNEMA (29, p. 452).

From these statements about the erratic occurrence of this species, it appears sufficiently, that it has spread from Kurland and Kowno to the Netherlands though nowhere, it is true, large numbers of such boulders have been met with. In the Scandinavian-baltic area it is found in different places in solid rock:

1st. In Malmö near Christiania which is not very important to us;

2nd. In Gothland, where Schmidt describes its occurrence as follows:

"Das grosse Centralmergelgebiet von Follingbo bis Slite und Färö, das bald aus reinen Mergeln, bald aus Mergeln mit Kalken wechselnd besteht, wird neben andern Fossilien besonders durch die ursprüngliche *Leperditia baltica* His. mit kammförmiger Zeichnung auf dem Umschlag der linken Schale characterisirt, die einerseits auch bis zu den Mergeln von Westergarn vordringt und andererseits sich vielfach auch in den oberen Kalken der Wisby-Region findet, so bei Heideby und Martebo. Auf Färö bei Lansa kommt sie zusammen mit *Zaphrentis conulus* Lindstr., *Strophomena imbrex* Vern. u. a. im Kalk vor, wechselnd mit *Megalomus*-banken." (20, p. 255). These places belong to Schmidt's middle zone; besides Kolmodin records it from Oestergarn and Hammarudd near Kräklingbo (8, p. 134), where no doubt younger strata are found. In these two places I have been seeking for a long time, but failed to find it. According to Lindström: b—c.

3rd. In Oesel this species is a type-fossil of the Lower Oesel-zone I. For a long time it was only known from dolomite from Kiddemetz (var. *Eichwaldi*) but has later also been found in limestones in the peninsula of Taggamois on the N. W. coast, thus verifying Schmidt's prediction. Only there this zone consists of crystalline limestone; everywhere else of dolomite or marl (9, p. 46—49).

With regard to the origin of these boulders whose age has now been determined, the following remarks may be stated. First of all the fact that Skåne cannot be thought of, as *Leperditia baltica* does not occur there. In general the marly character of the rock found in Gothland, argues against the possibility of its originating there; no doubt we have only to think of the north eastern part of the island. Though indeed our boulders do not make the least impression of originating in marly strata, it does not say so very much, because in Gothland the limestome with *L. baltica* cannot everywhere be decidedly looked upon as being limestone from marl. The question then about their origin is not to be solved without extensive material for comparison, which I do not possess; only a single piece of limestone from Slite does not correspond with our boulders. This limestone from Slite is differently coloured and also much more crystalline and betrays by marl-remains and a small concretion of little pyrite-crystals its origin from marl. Now as regards Oesel, from this region, too, I have but a single piece with *L. baltica* for comparison. It is from Kiro, immediately to the south of Taggamois, and corresponds much more with our boulders. It is however but a badly preserved, weathered piece, so that it is not very important.

Taking all this into consideration the origin of our boulders is probably to be found between Oesel and Gothland, where there is every reason to assume that along the line Fårö—Taggamois limestones of the age of the I-zone have been developed.

More or less closely allied to this Baltica-limestone are different boulders which for their fossil contents may best be referred to the Lower Oesel zone:

a. Yellowish-gray limestones with:

Proetus concinnus Dalm., var. *Osiliensis* Schm.	26, T. IV, f. 1—9.
Calymmene tuberculata Brünn.	26, T. I, f. 1—7.
Cyphaspis elegantula Lov. sp.	7, T. XVII, f. 7.
Encrinurus punctatus Wahlb.	
Strophomena rhomboidalis Wilck. sp.	
Orthis sp.	

They closely resemble some pieces of Baltica-limestone and most likely neither differ very much from the latter in age. Without tracing their occurrence in particulars here the following list shows sufficiently why they are mentioned here:

	Gotland (16)	Oesel (26)
P. concinnus Dalm., (var. *Osiliensis* Schm.)	(*c*—*e*)	*I*
C. tuberculata Brünn.	*c*—*f*	*I*
C. elegantula Lov. sp.	*c*	*I*

Eight pieces of this limestone are from the following places:

"Boteringesingel",	Groningen	2
"Noorderbinnensingel",	,,	2
"Nieuwe Veelading",	,,	1
	,,	1
"Hilghestede",	Helpman	1
	,,	1

Again the tract between Gothland and Oesel must be looked upon as the place of origin by reason of perfectly similar considerations as mentioned in dealing with the Baltica-limestone.

b. Perhaps two limestone-rocks also belong to this with

Bumastes barriensis Murch.

found in the "Nieuwe Veelading" and the "Schietbaan" in Groningen, while HOLM records this fossil from the Eastern-balticum from *I* (15, p. 37), LINDSTRÖM from *b—h* in Gothland (16, p. 4, N°. 64).

c. Thirdly various limestones with

Encrinurus punctatus WAHLB.

may be mentioned here. These "Encrinurus-limestones" are not further to be determined in age on account of the want of other adequate fossils. Some corals, *Favosites* and *Halysites*, together with which they sometimes occur, can be of no use for that purpose.

d. Among the great number of corals from the Groningen Hondsrug there are no doubt many of the age of the Lower Oesel zone e.g. *Thecia Swinderenana* GOLDF and others. However I do not intend to occupy myself with this question, but later on I shall deal with these together with the other corals, whose age is hardly ever to be determined between narrow limits, under the heading "Coral-limestone."

e. Finally I wish just to make mention of a single piece of dark-greenish-gray calcareous marl, which contains numerous pygidia and head-shields of a *Calymmene*-species. This boulder found in the "Boteringesingel" in Groningen suggests the marly stratum of St. Johannis of the *I*-zone in Oesel, but also corresponds fully with marls from different places in Gothland. About the origin, then, nothing can be said. Probably we have to do here with REMELÉ's "Grünlichgrauer Calymenekalk". (13, p. 27).

Here ends the enumeration of the boulders of the age *I*. Be it only added that this zone may possibly be well represented among the very manifold dolomites of Groningen. These, however, but seldom contain fossils and on account of this admit of no distinctly separated groups. At the end of the description of the Upper-Silurian boulders, I hope to be able to communicate some particulars about this.

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Anatomy. — "*Note on the Ganglion vomeronasale.*" By E. de Vries. (Communicated by Prof. T. Place.)

The description and drawings given in this note derive from a wellpreserved human embryo. This embryo was fixed in a ten percent solution of formaldehyde. After fixation the greatest diameter was 55 mm. Precise information as to the probable age of this embryo was not to be obtained, but the dimension of the embryo in connexion with the fact, that the corpus callosum was not yet formed, makes it probable that the age of the embryo may be estimated between $2^1/_2$ and 3 months.

After the embryo being hardened in alcohol the head was cut off along the base of the crane and imbedded in paraffin; a complete series of frontal sections of 10 μ was made. A slight deviation from the frontal plane existed, so that the top of the right hemisphere first appeared in these sections. The greatest part was stained in haematoxylin and eosine in the usual manner, the rest of the sections with haematoxylin only, in slightly different ways.

A description is given of the right hemisphere, — which in the microscopical sections corresponds with the left one —, concerning only that part which has a closer relation to the rhinencephalon. This description is illustrated by four drawings of successive sections and by two semi-diagrammatic figures.

These figures (Fig. V, VI) are a projection of the olfactory lobe on a sagittal plane and constructed from the series of sections. Because the plane upon which the projection is performed is sagittal, only these curvatures of the olfactory lobe are seen, which have a component in that direction. The lines in these drawings denoted from I to IV indicate the place of the four sections marked with a corresponding roman number.

The olfactory lobe, as seen in this stage of development, forms a hollow outgrowth from the base of the hemisphere vesicle. On the external surface of the lateral wall of the hemisphere, the lobe is limited by a shallow sulcus, the fissura rhinica. This sulcus runs in a fronto-occipital direction (fig. I, II, III F. rh.). On the external surface of the mesial wall of the hemisphere vesicle the olfactory lobe is bordered by a very broad sulcus which in the beginning runs also in a fronto-occipital direction but bends afterwards more vertically. This sulcus is the fissura prima of His and only to be seen in the first two figures (fig. I, II F. pr.).

Bordered by these two grooves the olfactory lobe shows a double curvature from lateral to mesial and slightly from behind forwards. The anterior cornu of the lateral ventricle forms a prolongation in the olfactory lobe reaching into the top of the bulb. This cavity shows the same curvatures as the lobe, which can partly be seen from the diagrammatic figure V. In its general feature and apart from its curvatures this cavity of the olfactory lobe has the shape of a funnel, the mouth turned to the lateral ventricle the tube to the top of the olfactory bulb.

A close relation between the form of the external and internal surfaces of the hemisphere vesicle does not exist. The internal surface of the lateral wall is thickened by the appearance of the corpus striatum. This thickening of the wall begins wellmarked at some distance (2 mm) from the top of the hemisphere vesicle; a prolongation of this thickening, described by His as the "Crus epirhinicum", which, along the top of the hemisphere unites the striatum with the rhinencephalon does not seem to exist. The ventral edge of the striatum is also clearly marked by a prominent crest, the crista ventralis corporis striati ; (fig. I, Cr. v. str.) which is bordered by a deep sulcus (fig. I, S. v. str.). This sulcus on the internal surface of the vesicle does not agree in all respects with the fissura rhinica on the external surface.

The ventral edge of the striatum first proceeds in a fronto-occipital direction and then turns more ventrally over the posterior wall of the funnellike outgrowth of the rhinencephalon. By its typical configuration it is easy to follow this ventral edge of the striatum till it goes over in an analogous formation belonging to the rhinencephalon.

This formation of the rhinencephalon appears as a thickening of the internal surface of the mesial wall of the hemisphere vesicle. It begins pretty well marked a little more distant from the top of the hemisphere than the striatum. Dorsally and ventrally this thickening is limited by a deep groove, the sulcus rhinencephali dorsalis and ventralis (fig. I and II, S. rh. d. and S. rh. v.). The ventral edge of this thickened part of the mesial wall forms a prominence, which goes over in a crest, the crista ventralis rhinencephali.

This crest first runs in fronto-occipital direction and then turns more ventrally over the posterior wall of the funnellike outgrowth of the rhinencephalon where it goes over continuously in the same formation proceeding from the stratium. This is clearly seen in figure II (Cr. v.) where the ventral crista is seen on the posterior wall of the depression of the rhinencephalon cut in a very oblique direction.

The line described by this ventral border of the corpus striatum and thickened part of the rhinencephalon has, looked at as a whole, the form of a horseshoe with its top directed to the occipital pole of the brain and meantime turned ventrally, while its opening is turned to the frontal pole of the hemisphere vesicle. The connection of rhinencephalon and striatum, which lies initially in the base of the brain comes with the outgrowth of the rhinencephalon partly on the posterior wall which borders the cavity, that proceeds in the olfactory lobe. This connection between striatum and rhinencephalon is therefore a primary one.

The olfactory bulb in this stage of development of the rhinencephalon is limited by a circular groove, the sulcus circularis bulbi (Fig. I, II, S. c. b.), which deeply cuts in on the frontal pole of the bulb, becomes more flat on both sides and is seen as a round shallow groove at the posterior pole of the bulb (Fig. V S. c. b.). The top of the bulb is turned to the mesial side and in a slightly forward direction, while the form of the bulb can be seen in the diagrammatic drawing figure V.

The nerves which belong to the formation of the rhinencephalon are of two different kinds, and leave the brain at two different places. The first kind of nerves proceed from the top of the olfactory bulb. They are easily recognised by the fact, that their nuclei are small and not very numerous, so that the fundamental substance in which they are imbedded is distinctly seen.

These nerves split up into very small tracts in the neighbourhood of the mucous membrane of the nose, where they seem to end. These nerves, which contain the olfactory nervefibres do not have any connection with the ganglion olfactorium. They all pass along this ganglion.

The second place from where the nervefibres proceed is given by the mesial part of the sulcus circularis bulbi. These nervefibres can be differentiated from the olfactoryfibres by the fact, that their nuclei are a little larger, and more numerous than the nuclei of the olfactory nervefibres; the fundamental substance in which these nuclei are imbedded deeply stains with eosine. Where these fibres leave the brain, the superficial layer of the hemisphere vesicle becomes richer in elongated nuclei (A vn. fig. I, II, III, IV and VI). They form four bundles (Rd. N. vn. fig. III, IV and VI), which all converge into the ganglion olfactorium (G. vn. fig. III, IV, VI). The nerves leaving this ganglion are arranged in five bundles (Fig. VI Nn. vn) which all went to the mesial side along the cartilagineous septum nasi (Fig. I Sp. m. n.). Unfortunately the course of these nerves could be no further traced out, the head being cut off too close along the base of the brain. In a second human embryo however, of the same age, which was not so well preserved, it was possible to find back the same relations and to see, that all these nervefibres run exclusively to the organon vomeronasale (RUYSCH, JACOBSON). In the whole course of these nerves ganglioncells are seen. The so called ganglion olfactorium has therefore no connection with the olfactory nervefibres but is the sensorial ganglion belonging to the organon vomeronasale.

In figure VI is given a semidiagrammatic drawing constructed from the sections where the whole apparatus belonging to the organon vomeronasale is projected upon a sagittal plane. The ganglion vomeronasale (G. vn.) is seen in the niveau of the top of the olfactory bulb from which proceed to the periphery the nervi vomeronasales (Nn. Vn.) and to the centrum the so called internal olfactory roots (Rd. N. vn.). which enter the brain in a large triangleshaped zone, the area vomeronasalis (A. vn.)

In the guinea pig these relations are slightly different. From the organon vomeronasale proceed two nervestrands, which at a short distance and still in the submucosa of the nose have each a ganglion. This paired ganglion vomeronasale has two roots which very soon unite and intermingle with the nervi olfactorii, with which they perforate the lamina cribrosa. Arrived at the base of the brain they enter the olfactory bulb over a large area, reaching from the sulcus circularis bulbi at the mesial side to some distance from the same sulcus at the lateral side of the olfactory bulb.

Probably the same relations occur through the whole series of vertebrate animals. Though the existence of an organon vomeronasale can be doubted in anamnia, it seems very probable, that the nerve described by LOCY (Anat. Anz. 1905, Heft 2 and 3) in Selachii is identical with the nerve of the organon vomeronasale as described here.

From the preceding description it is obvious, that we have to consider the organon vomeronasale as a special senseorgan of which the function is unknown, while the duality seen in the central tracts belonging to the rhinencephalon finds its source in the anatomical independence between the system of the olfactory nerves and the system of nerves belonging to the organon vomeronasale.

My thanks to Prof. J. W. LANGELAAN under whose direction these researches were made.

Anatomy. — *"Note on the Innervation of the Trunkmyotome".*

By J. W. VAN BISSELICK. (From the Anatomical Institute at Leiden). (Communicated by Prof. T. PLACE).

These researches form a sequel to professor LANGELAAN's first communication "On the Form of the Trunkmyotome" [1]), and were performed under his direction in the anatomical institute at Leiden.

The aim of this research was to know if one single spinal nerve innervates only one single myotome.

The method followed, existed in dissecting a spinal nerve and to see if the different territories to which the nervestrands can be followed, belonged to one and the same myotome. To this purpose an Acanthias or a Mustelus was cut through along the mid-sagittal plane and treated with a one tenth percent solution of osmic acid. The nerves stained black and were easy to follow with the naked eye or with a magnifier.

As a first result it was found, that all nerves passed through the connective tissue laying between the myotomes; therefore a minute dissection of this tissue was necessary.

The myotome itself is covered by a very thin layer of a fibrous tissue which constitutes a perimysium. This perimysium extends between the muscular fibres of the myotome forming an endomysium. It affords a continuous investment for every muscular fibre and forms in this way a frame for the muscular tissue. Where this muscular tissue is broken off the framework is continuous and enables us to recognize parts of the myotome belonging together. The myotomes covered by their perimysium are separated by a coarser and denser fibrous tissue. This intermyotomal tissue forms lamellae which have only a very loose connection with the perimysium, so that it is possible to dissect these lamellae as discrete formations. These intermyotomal septa pass over in the fibrous tissue of the skin and form a continuous formation with the latter. Where the myotome

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[1]) Proc. K. Akad. W. Amsterdam 28 May 1904.

has a simple form, this line of insertion coincides with the border of the myotome; where the myotome is elongated in a peak, this line of insertion crosses this peak.

Figure I reproduces the external surface of the myotome extended in a plane. The black line indicates the transition of the intermyotomal septum in the skin; where the myotome is elongated in a peak, it has distended the septum, because the line of transition is fixed upon the skin. The peak is covered by this distended part of the septum, and as far as the peak is adjacent to the skin, this part of the corium is doubled by this triangular sheath. Whereas on the line of transition the passage of the intermyotomal septum into the corium is a direct one, this is not the case with this adjacent part of the septum, which is only loosely connected with the corium by means of some fibres of connective tissue. This makes it possible to dissect these triangular slips from the corium.

In the same way as the myotomes, the triangular slips of the intermyotomal tissue overlap. In concordance with the direction of the peaks it is seen, that slips belonging to peaks directed towards the caudal end of the body cover each other, so, that the more caudal slip covers the more cranial one. If the peak is directed cranially the mode of overlapping is reversed, the more cranial slip being uppermost. Figure II reproduces the intermyotomal tissue as far as this formation is adjacent to the skin.

On the mesial side the intermyotomal septum goes over in the connective tissue which covers the axial skeleton and beyond this forms a lamella between the left and right half of the dorsal musculature. Ventrally the same formation goes over in the fascia transversa covering the abdominal cavity.

Figure III gives the line of passage of the intermyotomal septum. As can be seen there are two places where the muscular tissue is broken off, the myotome becoming thinner from outside to inside. The lamellae, where the muscular tissue is interrupted, cover each other and in this way two strong continuous septa are formed. The distance over which the muscular tissue is discontinuous in the neighbourhood of the sagittal plane amounts to four myotomes in the first septum and to three in the second. In agreement with this, the lamellae are built up resp. by four and by three sheaths of intermyotomal tissue. The dotted fields in figure III belong therefore together, forming one myotome, as can easily be verified by dissecting the myotome.

Each spinal nerve springs from the cord with two roots, which separately leave the spinal canal through two foramina (*AR* and

PR fig. IV). When they have quitted the canal each root separates into two filaments, one of these filaments is ascending (Asc. f.) and one is descending (Desc. f. fig. VI). Both ascending root filaments unite to form a nerve, the internal branch of the posterior division (fig. VI), the filaments of which pass over in the intermyotomal septum at the places indicated by 3 *D*—5 *D* fig. IV, and leave the septum to go over in the skin at the places indicated in the same way in fig. V. Before these filaments go over into the corium they each give off a small twig innervating the distended part of the intermyotomal septum, which is adjacent to the skin.

Before the two ascending rootfilaments join, they each give off a small branch, which also unite to form a small nerve, the first external branch of the posterior divisions (fig. VI) entering the septum at 2*D* fig. IV and leaving the septum to pass over in the skin at the corresponding place of fig. V.

Both descending rootfilaments before joining each give off a small branch, which form together a small nerve, the second external branch of the posterior division (fig. VI), which enters and leaves the intermyotomal septum at the places indicated by 1*D* in fig. IV and V.

The nerves described, all together, innervate the dorsal part of the myotome and the intermyotomal septum, and form the posterior primary division of the spinal nerve.

The descending rootfilaments also unite to form a nerve which pretty soon divides into two branches, one of these innervating the lateral part of the myotome and the intermyotomal septum; the other is, the continuation of the maintrunk, crosses the lateral part of the myotome and innervates the ventral part of the myotome and the intermyotomal septum. The branch innervating the lateral part of the myotome divides into two branches, an external and internal branch of the lateral division (fig. VI). The external branch splits up into two filaments one of which is recurrent (recurrent br. fig, VI) and innervates the top of the lateral part of the myotome. The external branch enters the septum at *L* 1. 2. fig. IV and leaves the septum at 1*L*, 2 *L* fig. V. The internal branch gives off several branches passing over in the skin at 3 *L*—6 *L* fig. V.

The branch innervating the ventral part of the myotome and the intermyotomal septum shows the same arrangement as the branch for the lateral part of the myotome. It divides into two branches one being the external branch of the anterior division, the other the internal branch (fig. VI). The external branch passes over in the septum at V 1. 2. fig. IV, splits up into two smaller branches of which one is recurrent (recurrent br. fig. VI) and leaves the septum to go over into the skin at 1 *V* and 2 *V*. fig. V.

The internal branch can be followed up to the vena lateralis (*VL* fig. IV) and then goes over in a loose plexus. On its way to the vena lateralis the internal branch gives off several filaments, which reach the skin through the intermyotomal septum 3 *V*—6 *V* fig. IV and V. Before passing over into the skin these filaments form a loose plexus covering the most ventral part of the myotome.

The roots and mainbranches of the spinal nerve have a submyotomal position and are not bound in their course by the form of the myotome; these branches on the contrary, which go over into the septum to reach the skin, are in their course fixed by the form of the myotome. The final course of the branches in the corium was not traced out with enough accuracy to give results here.

The descriptions given in this note only apply to that region of the trunk which is situated between the thoracic and first dorsal fin.

Conclusions:

I. One single spinal nerve only innervates one single myotome and the intermyotomal tissue through which the nerves pass.

II. The roots and mainbranches of the spinal nerve have a submyotomal position; the branches never perforate a myotome, but run always in the intermyotomal septum to the skin. In general they are to be found between the perimysium and the intermyotomal septum.

III. The spinal nerve shows a primary division into three parts, a posterior, lateral and anterior division in agreement with the differentiation of the myotome in a dorsal, lateral and ventral part.

IV. All larger branches are mixed nerves containing elements of the anterior and posterior roots.

Mathematics. — *"On linear systems of algebraic plane curves".*

By Prof. JAN DE VRIES.

§ 1. The points of contact of the tangents out of a point O to the curves c^n of a pencil lie on a curve t^{2n-1} which I shall call the *tangential curve* of O. It is a special case of a curve indicated by CREMONA[1]). By EMIL WEYR[2]), GUCCIA[3]) and W. BOUWMAN[4]) it has been applied when proving the properties of pencils and nets.

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[1]) CREMONA—CURTZE, Einleitung in eine geometrische Theorie der ebenen Curven (1865) p. 119.

[2]) Sitzungsberichte der Akademie in Wien, LXI, 82.

[3]) Rendiconti del Circolo matematico di Palermo (1895), IX, 1.

[4]) Nieuw Archief voor Wiskunde (1900), IV, 258.

If a linear system $(c^n)_k$ of ∞^k curves c^n is given, we can consider the locus of the points P_{k+1}, where a curve of that system has a $(k+1)$-pointed contact with a right line, passing through the fixed point O.

To determine the order $\varphi(k)$ of the locus (P^{k+1}) I consider the curves $(c^n)_k$ having in the points P of the right line l a k-pointed contact with the corresponding right line OP. Each ray OP cuts the curve individualized by P moreover in $(n-k)$ points Q. Each point of intersection of l with the locus of the points Q being evidently a point P_{k+1}, the locus (Q) is a curve of order $\varphi(k)$.

The curves of $(c^n)_k$ passing through O form a system $(c^n)_{k-1}$. The order of the locus of the points P_k where a c^n of this latter system has a k-pointed contact with OP is evidently indicated by $\varphi(k-1)$. So on l lie $\varphi(k-1)$ points P for which one of the corresponding points Q coincides with O; in other words the locus (Q) passes $\varphi(k-1)$ times through O, so it is of order $\varphi(k-1)+(n-k)$.

To determine $\varphi(k)$ we have now the recurrent relation

$$\varphi(k)=\varphi(k-1)+(n-k).$$

From this we deduce

$$\varphi(k)=\varphi(1)+\tfrac{1}{2}(k-1)(2n-k-2).$$

Here $\varphi(1)$ represents the order of the tangential curve, thus $(2n-1)$. So we find

$$\varphi(k)=\tfrac{1}{2}(k+1)(2n-k).$$

The locus of the points where a curve c^n, belonging to a k-fold infinite linear system has a $(k+1)$-pointed contact with a right line passing through a fixed point O is a curve of order $\frac{1}{2}(k+1)(2n-k)$, on which O is a $\frac{1}{2}k(k+1)$-fold point.

For $(c^n)_k$ determines on a right line r through O an involution of order n and rank k. The number of $(k+1)$-fold elements of this involution amounts to $(k+1)(n-k)$; that is at the same time the number of points P_{k+1}, lying on r. Consequently O is an $\frac{1}{2}k(k+1)$-fold point on (P_{k+1}).

§ 2. Each ray r through a fixed point O is touched by $2(n-1)$ curves c^n of a pencil (c^n); the points of contact T are the double points of the involution determined by (c^n) on r. The curves c^n indicated by these points T intersect r moreover in $2(n-1)(n-2)$ points S. When r rotates round O the points S will describe a curve which I shall call the *satellite curve* of O.

This curve passes $(n+1)(n-2)$ times through O; for if r coincides with one of the tangents out of O to c^n passing through

O one of the points S lies in O. *So the curve* (S) *is of order* $(n+1)(n-2)+2(n-1)(n-2)=(n-2)(3n-1)$.

If B is a base-point of (c^n), then only $2(n-2)$ points T (the double points of an f^{n-1}) lie on OB outside O and B. So OB touches in B the tangential curve of O whilst it is $(n-2)$-fold tangent of (S).

Each of the $2(n-2)$ curves c^n touching OB projects a point S in B. So each base-point is a $2(n-2)$-fold point of the satellite curve.

The common points of the tangential curve t^{2n-1} and the satellite curve $s^{(3n-1)(n-2)}$ form four groups.

First there are $(n+1)(n-2)$ united in O.

Secondly $2(n-2)$ lie in each base-point B.

Thirdly the two curves touch each other at each inflectional point sending its tangent through O.

Fourthly they cut each other in the points of contact of each double tangent passing through O.

Now the inflectional tangents of a pencil envelop a curve of class $3n(n-2)$. [1])

So the number of points of contact of inflectional tangents through O amounts to

$$(n-2)(3n-1)(2n-1)-(n-2)(n+1)-2(n-2)n^2-6n(n-2)=$$
$$=4n(n-2)(n-3).$$

The double tangents of the curves c^n *belonging to a pencil envelop a curve of class* $2n(n-2)(n-3)$.

§ 3. Following EMIL WEYR [2]) we consider the curve c^{n+1} generated by the pencil (c^n) with the pencil projectively conjugate to it of the tangents in a base-point B. As each c^n cuts its tangent moreover in $(n-2)$ points, B is a threefold point of the c^{n+1}. From this ensues easily that through B can be drawn $(n+4)(n-3)$ tangents to c^{n+1}. As many double tangents of the pencil (c^n) have one of their points of contact in B.

We shall now consider the satellite curve of B. On each ray r through B lie $2(n-2)$ points of contact T, so $2(n-2)(n-3)$ points S. If r coincides with one of the double tangents just mentioned, one of the points S lies in B. So B is an $(n+4)(n-3)$-fold point on (S) and the order of (S) proves to be equal to $(n+4)(n-3)+2(n-2)(n-3)=3n(n-3)$.

The tangential curve of B has in B a threefold point; for a ray

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[1]) For this is the number of tangents of t^{2n-1} which besides the n^2 tangents of OB can be drawn through O.

[2]) Sitzungsberichte der Akademie in Wien LXI, 82.

through B bears but $(2n-4)$ points T, whilst the curve t is of order $(2n-1)$.

Of the common points of t^{2n-1} and $s^{3n(n-3)}$ there are $3(n+4)(n-3)$ lying in B, $2(n-3)$ in each of the remaining (n^2-1) base-points and two in each of the inflectional points sending their tangent through B.

The number of those inflectional tangents is $3n(n-2)-9$, as each of the three inflectional tangents, having their inflectional point in B, must be counted three times. This is evident when we consider a curve of (c^3), where a base-point can lie only on inflectional tangents for which it is inflectional point itself. This number amounts to *three*, whilst the class of the envelope of the inflectional tangents is *nine*.

So we find for the number of the points of contact, not lying in B, of double tangents out of B

$$3n(n-3)(2n-1)-3(n+4)(n-3)-2(n-3)(n^2-1)-6(n-3)(n+1)=$$
$$=4(n-3)(n-4)(n+1).$$

So B lies on $2(n-4)(n-3)(n+1)$ double tangents. This number is $2(n-3)(n+4)$ less than the number of double tangents out of an arbitrary point. The $(n-3)(n+4)$ double tangents having one of its points of contact in B must thus be counted twice.

The envelope of the double tangents has in each base-point an $(n+4)(n-3)$-fold point.

§ 4. The locus of the points of contact D of the double tangents of (c^n) evidently passes $(n+4)(n-3)$-times through each base-point (§ 3). An arbitrary c^n having on its double tangents $n(n-2)(n^2-9)$ points of contact D, the curve D and c^n intersect each other in $n^2(n+4)(n-3)+n(n-2)(n^2-9)$ points. Consequently the locus of the points of contact D is a curve of order $(n-3)(2n^2+5n-6)$.[1]

We shall now consider the locus of the points W in which a c^n is intersected by its double tangents.

As each base-point B lies on $2(n-4)(n-3)(n+1)$ double tangents (§ 3) the curve W passes with as many branches through B. So it has with an arbitrary c^n in common $2n^2(n-4)(n-3)(n+1)+$ $+\frac{1}{2}n(n-2)(n^2-9)(n-4)$ points. From this ensues that the curve (W) is of order $\frac{1}{2}(n-4)(n-3)(5n^2+5n-6)$.

The curves (D) and (W) have outside the base-points a number of points in common equal to

$$\tfrac{1}{2}(n-4)(n-3)^2(5n^2+5n-6)(2n^2+5n-6)-$$
$$-2n^2(n-4)(n-3)^2(n+1)(n+4).$$

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[1] See P. H. Schoute, Wiskundige opgaven, II, 307.

From this ensues:

In a pencil (c^n)

$$\tfrac{1}{2}(n-4)(n-3)^2(10n^4+35n^3-21n^2-80n+20)$$

curves have an inflectional point of which the tangent touches the curve in one other point more.

§ 5. The locus of the inflectional points I of (c^n) has a threefold point in each base-point and a node in each of the $3(n-1)^2$ nodes of the pencil, out of which we immediately find that the curve (I) is of order $6(n-1)$ and of class $6(n-2)(4n-3)$[2].

Let us now deduce the order of the locus of the points V determined by a c^n on its inflectional tangents.

As a base-point B lies on $3(n-3)(n+1)$ inflectional tangents the curve (V) passes with as many branches through B. So with an arbitrary c^n it has $3n^2(n-3)(n+1)+3n(n-2)(n-3)$ points in common.

Consequently (V) is a curve of order $3(n-3)(n^2+2n-2)$. Now the curves (I) and (V) have besides the base-points a number of points in common represented by

$$18(n-1)(n-3)(n^2+2n-2)-9n^2(n-3)(n+1).$$

These points can only have risen from the coincidence of inflectional points with one of the points they have in common with the c^n under consideration, thus from *tangents with fourpointed contact.* Such an *undulation point,* being equivalent to two inflectional points, is point of contact for (I) and (V) from which ensues:

A pencil (c^n) *contains* $\frac{9}{2}(n-3)(n^3+n^2-8n+4)$ *curves with an undulation point.*

§ 6. Let a threefold infinite linear system of curves c^n be given.

The c^n osculating a right line l in the point P cuts the ray OP drawn through the arbitrary point O moreover in $(n-1)$ points Q.

The curves of $(c^n)_3$ passing through O form a net $(c^n)_2$ determining on l the groups of an involution I_2^n. The latter having $3(n-2)$ threefold elements, the locus (Q) passes $3(n-2)$-times through O, so it is of order $(4n-7)$.

Each of its points of intersection K with l is evidently a node on a curve of $(c^n)_3$, with l and OK for tangents.

Each right line is nodal tangent for $(4n-7)$ *curves of the system.*

From this ensues that the locus of the nodes K sending one of

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[2] See Bobek, Casopis (Prague), XI, 283.

their tangents through the point M chosen arbitrarily is a curve of order $(4n-5)$; for M is a node of a c^n, so it lies on two branches of (K).

Each point K of the arbitrary right line l is a node of a curve belonging to $(c^n)_3$. The points of intersection M and M' of the tangents in K with the right line m chosen arbitrarily are pairs of a symmetric correspondence with characteristic number $(4n-5)$. To the coincidences belongs the point of intersection M_0 of l and m, and twice even, because the c^n, having in that point a node, furnishes two points M_0' coinciding with M_0. The remaining coincidences originate from tangents in cusps. From this ensues:

The locus of the cusps of a threefold infinite linear system of curves of order n is a curve of order $4(2n-3)$.

Mathematics. — *"Some characteristic numbers of an algebraic surface."* By Prof. JAN DE VRIES.

In the following paper we shall show how by easy reasoning we can find an amount of the characteristic numbers of a general surface of order n [1]). To this end we shall make use of scrolls formed by principal tangents or double tangents.

§ 1. First I consider the scroll **A** of the principal tangents a of which the points of contact A lie in a given plane α. The curve α^n along which α cuts the surface Φ^n is evidently nodal curve of **A**. The tangents in the $3n(n-2)$ inflectional points of α^n being principal tangents of Φ^n, the scroll **A** has $3n(n-2)$ right lines and the curve α^n to be counted twice in common with Φ^n, so it is a scroll of order $n(3n-4)$.

The two principal tangents a and a' in a point of α^n have each three points in common with Φ^n; consequently α^n belongs six times to the section of **A** and Φ^n. These surfaces have moreover a twisted curve of order $n^2(3n-4)-6n$ in common containing the $3n(n-2)(n-3)$ points where Φ^n is cut by the principal tangents a situated in α. In each of the remaining $n(11n-24)$ points of intersection of this curve with α the surface Φ^n has *four* coinciding points of intersection in common with a. From this ensues:

The locus of the points in which Φ^n possesses a fourpointed tangent (flecnodal line) *is a twisted curve of order* $n(11n-24)$.

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[1]) We find the indicated numbers in SALMON-FIEDLER, "Analytische Geometrie des Raumes", dritte Auflage, II, p. 622—644, and in SCHUBERT, "Kalkül der abzählenden Geometrie", p. 236.

§ 2. I now determine the order of the scroll **B** formed by the principal tangents cutting Φ^n in points B of the plane β.

Out of each point B of the section β^n start $(n-3)(n^2+2)$ principal tangents; this number indicates at the same time the number of sheets of **B** which cut each other along β^n. The inflectional tangents lying in β^n evidently belong $(n-3)$-times to the indicated scroll. So its order is equal to

$$n(n-3)(n^2+2)+3n(n-2)(n-3)=n(n-1)(n-3)(n+4).$$

According to § 1 $n(3n^2-4n-6)$ principal tangents have their point of contact A on α^n and one of their points of intersection B on β^n. So this number indicates the order of the curve along which Φ^n is osculated by **B**. Beside this curve of contact and the manyfold curve β^n the surfaces Φ^n and **B** have still in common the locus of the points B' which determine the principal tangents AB moreover on Φ^n. This curve (B') is of order $n^2(n-1)(n-3)(n+4)-$ $-3n(3n^2-4n-6)-n(n-3)(n^2+2)=n(n-2)(n-4)(n^2+5n+3)$.

§ 3. To find how often the point A coincides with one of the $(n-4)$ points B', I shall project the pairs of points (A, B') out of a right line l. The planes through l are arranged in this way in a correspondence with the characteristic numbers $n(3n^2-4n-6)(n-4)$ and $n(n-2)(n-4)(n^2+5n+3)$. Each right line a resting on l evidently contains $(n-4)$ pairs (A, B'), so it furnishes an $(n-4)$-fold coincidence. The remaining coincidences originate from coincidences $A\equiv B'$. Now $n(3n^2-4n-6)(n-4)+n(n-2)(n-4)(n^2+5n+3)-$ $-n(n-1)(n-3)(n+4)(n-4)=n(n-4)(6n^2+2n-24)$. So this is the number of fourpointed tangents which cut Φ^n in a point B of β^n.

The points of intersection of Φ^n *with its fourpointed tangents form a curve of order* $2n(n-4)(3n^2+n-12)$.

If f is the order of the scroll of the fourpointed tangents then it is evident that we have the relation

$$nf=4n(11n-24)+2n(n-4)(3n^2+n-12)=2n^2(n-3)(3n-2).$$

The fourpointed tangents form a scroll of order $2n(n-3)(3n-2)$.

If we make the point of contact F of a fourpointed tangent to correspond to the $(n-4)$ points G which that tangent has still in common with Φ^n, a system of pairs of points (F, G) is formed, of which the number of coincidences can be determined again with the aid of the correspondence in which they arrange the planes through an axis l. By the way indicated above we find for this number:

$$n(11n-24)(n-4)+2n(n-4)(3n^2+n-12)-2n(n-3)(3n-2)(n-4)=$$
$$n(n-4)(35n-60).$$

The surface Φ^n *possesses* $5n(n-4)(7n-12)$ *fivepointed tangents.*

§ 4. Returning to the scroll **B** (§ 2) I consider the points of intersection of the twisted curve (B') with the plane β. Each point of intersection of β^n with an inflectional tangent lying in β can be regarded as the point B, each one of the remaining $(n-4)$ as a point B'. Hence the curve (B') meets $3n(n-2)(n-3)(n-4)$-times β^n on the inflectional tangents of β^n. In each of the remaining points of intersection of (B') with β we find that Φ^n is touched by a right line having elsewhere three coinciding points in common with Φ^n. Such a right line is called by me a tangent $t_{2,3}$, A being its *point of osculation*, B its *point of contact.*

The points of contact of the tangents $t_{2,3}$ *form a curve of order* $n(n-2)(n-4)(n^2+2n+12)$.

§ 5. In each point C of the curve γ^n according to which Φ^n is cut by the plane γ I shall regard the $(n-3)(n+2)$ tangents c which touch Φ^n moreover in a point C''. On the scroll **C** of the double tangents c the curve γ^n is a manyfold curve in which $(n-3)(n+2)$ sheets meet. Each double tangent situated in γ representing two right lines of **C** the order of this scroll is equal to

$n(n-3)(n+2)+n(n-2)(n-3)(n+3)$ or $n(n-3)(n^2+2n-4)$.

The surfaces Φ^n and **C** touch each other along the locus (C'') of the two points of contact. Of this curve the plane γ contains the points of contact of the right lines c lying in γ besides the points $C \equiv C''$, where a right line c is a fourpointed tangent. So the order of (C'') is $n(n-2)(n^2-9)+n(11n-24)$ or $n(n^3-2n^2+2n-6)$.

Besides the curve (C'') to be counted twice and the curve γ^n to be counted $2(n-3)(n+2)$-times **C** and Φ^n have moreover in common the locus of the points S determined by the double tangents c on Φ^n. The curve (S) is of order $n^2(n-3)(n^2+2n-4) - 2n(n^3-2n^2+2n-6) - 2n(n-3)(n+2)$ or $n(n-4)(n^3+n^2-4n-6)$.

To the points of (S) lying in γ belong the points of intersection of γ^n with its double tangents c. As each of the two points of contact of c can be regarded as point C these points of intersection S must be counted twice. The remaining $n(n-4)(n^3+n^2-4n-6) - n(n-2)(n^2-9)(n-4)$ points S lying in γ are apparently points of osculation of the tangents $t_{2,3}$. So from this ensues:

The points of osculation of the principal tangents touching Φ^n *moreover elsewhere form a curve of order* $n(n-4)(3n^2+5n-24)$.

The curves (A) and (B) formed by the points of osculation and the points of contact of the tangents $t_{2,3}$ have the points of contact of the fivepointed tangents in common. Taking this into account we find (by again projecting out of an axis l) for the order of the scroll of the right lines $t_{2,3}$ the expression $n(n-2)(n-4)(n^2+2n+12)+$ $+n(n-4)(3n^2+5n-24)-5n(n-4)(7n-12)$.

The principal tangents of Φ^n *which moreover touch the surface form a scroll of order* $n(n-3)(n-4)(n^2+6n-4)$.

§ 6. The double tangents c cutting Φ^n in points D of the plane δ form a scroll **D**, on which the section δ^n of Φ^n with δ is a manyfold curve bearing $\frac{1}{2}(n-3)(n-4)(n^2+n+12)$ [1]) sheets. As moreover every double tangent of δ^n belongs to $(n-4)$ different points D the order of **D** is equal to

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

According to § 5 $n(n-4)(n^3+n^2-4n-6)$ double tangents c have one of their points of contact C in a given plane γ and at the same time one of their points of contact D in the plane δ. So this number indicates the order of the curve along which **D** and Φ^n touch each other. If we take the manyfold curve δ^n into consideration, it is evident that the points D' which the right lines of **D** have in common with Φ^n besides the points of contact C and the points of intersection D lying in δ, form a twisted curve (D') the order of which in equal to

$$n^2(n-1)(n+2)(n-3)(n-4)-2n(n-4)(n^3+n^2-4n-6)-$$
$$\tfrac{1}{2}n(n-3)(n-4)(n^2+n+2)=\tfrac{1}{2}n(n-2)(n-4)(n-5)(2n^2+5n+3).$$

This curve evidently cuts δ $(n-4)(n-5)$-times on each double tangent of δ^n. In each of its remaining points of intersection with δ the surface Φ^n is touched by a right line, which is tangent to the surface in two more points. From this ensues:

The points of contact C *of the threefold tangents of* Φ^n *form a curve* (C) *of order* $\frac{1}{2}n(n-2)(n-4)(n-5)(n^2+5n+12)$.

§ 7. On each right line c of the scroll **D** lie $(n-5)$ points D' which can be arranged in $\frac{1}{2}(n-5)(n-6)$ pairs D', D''. If these pairs of points are projected out of an axis l by pairs of planes λ', λ'', these form a symmetric system, the characteristic number of which is $\frac{1}{2}n(n-2)$ $(n-4)(n-5)(2n^2+5n+3)(n-6)$. Each right line c cutting l determines a plane λ evidently representing $(n-5)(n-6)$ coincidences $\lambda' \equiv \lambda''$. The remaining coincidences of the system (λ) originate from coincidences $D' \equiv D''$, thus from threefold tangents d. As however

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[1]) In Cremona—Curtze, *Theorie der Oberflächen*, page 66 we find the expression $\frac{1}{2}(n-3)(n-4)(n^2+n-2)$ by mistake for the number of double tangents cutting Φ^n in one of its points.

each of the three points of contact of a right line d can be formed when D' coincides with D'' the number of threefold tangents cutting Φ^n on the curve δ^n is but the third part of the number of the indicated coincidences of (λ), thus equal to

$$\tfrac{1}{3}\, n\,(n-4)\,(n-5)\,(n-6)\,\{(n-2)\,(2n^2+5n+3) - (n-1)\,(n+2)\,(n-3)\} = \tfrac{1}{3}\, n\,(n-4)\,(n-5)\,(n-6)\,(n^3+3n^2-2n-12).$$

This is at the same time the order of the curve (D) formed by the points D which the threefold tangents d have still in common with Φ^n.

Now we can also find the order x of the scroll (d). This scroll being touched by Φ^n in the points of (C) and being cut in the points (D) we have namely

$$nx = n\,(n-2)\,(n-4)\,(n-5)\,(n^2+5n+12) + \tfrac{1}{3}\, n\,(n-4)\,(n-5)\,(n-6)\,(n^3+3n^2-2n-12).$$

Out of this we find

The threefold tangents of Φ^n *form a scroll the order of which is* $\frac{1}{3}\, n\,(n-3)\,(n-4)\,(n-5)\,(n^2+3n-2)$ [1]).

§ 8. To find the degree of the spinodal curve I consider the pairs of principal tangents a, a' of which the common point of contact A lies in the plane α. If two rays s and s' of a pencil (S, σ) are conjugate to each other, when they rest on two right lines a and a', then in (S, σ) a symmetric correspondence with characteristic number $n\,(3n-4)$ is formed. The coincidences can be brought to three groups.

First a and a' can cut the same ray s; their plane of connection is then tangential plane, their point of intersection A lies on the polar surface of S. Such a ray s coincides with two of the rays s' conjugate to it. So the first group contains $n\,(n-1)$ double coincidences.

Secondly s can cut the curve α^n; then too it coincides with two rays s'. So the second group consists of n double coincidences.

Finally a single coincidence is formed when a coincides with a'. The number of these coincidences evidently amounts to $2n\,(3n-4) - 2n\,(n-1) - 2n = 4n\,(n-2)$. From this ensues:

The parabolic points form a twisted curve (spinodal line) *of order* $4n\,(n-2)$.

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[1]) In SALMON-FIEDLER we find on page 638 by mistake $n^2+3\,n+2$ instead of $n^2+3\,n-2$.

On page 643 we find the derivation of the number of fourfold tangents and of the numbers of tangents $t_{1,2}$, $t_{3,2,2}$ and $t_{3,3}$.

Mathematics. "*The equation of order nine representing the locus of the principal axes of a pencil of quadratic surfaces.* By Mr. K. Bes. (Communicated by Prof. J. Cardinaal).

1. In These Proceedings of Jan. 28th 1905 appears a communication by Prof. Cardinaal: "On the equations by which the locus of the principal axes of a pencil of quadratic surfaces is determined."

2. Prof. Cardinaal deduces three non-homogeneous equations of order two between two variable parameters λ and k, and tries to arrive at the equation of the demanded surface by elimination of these parameters. The result obtained by him (8) seems to be an equation of order 12. This is incongruent with the result arrived at geometrically, which made an equation of order nine to be expected. This incongruency is attributed to factors, which the equation arrived at may contain, but these factors are not indicated.

3. The method of elimination described in my paper "Théorie générale de l'élimination" (Verhandelingen, Vol. VI, n°. 7) gives the means to set aside this incongruency and to determine in reality the equation sought for by Prof. Cardinaal.

To this end we can start from his equations (5) after having made them homogeneous with respect to the variable parameters, which may be done by assuming the equation (1) of the pencil of surfaces in the form:

$$\mu A + \lambda B = 0 .$$

If now we develop the equations (5), they assume the following form:

$$\left.\begin{array}{l}
(a_{11}A_1+a_{12}A_2+a_{13}A_3)\mu^2+(a_{11}B_1+a_{12}B_2+a_{13}B_3+b_{11}A_1+b_{12}A_2+b_{13}A_3)\lambda\mu+ \\
\quad +(b_{11}B_1+b_{12}B_2+b_{13}B_3)\lambda^2+A_1\mu k+A_1\lambda k=0 , \\
(a_{12}A_1+a_{22}A_2+a_{23}A_3)\mu^2+(a_{12}B_1+a_{22}B_2+a_{23}B_3+b_{12}A_1+b_{22}A_2+b_{23}A_3)\lambda\mu+ \\
\quad +b_{12}B_1+b_{22}B_2+b_{23}B_3)\lambda^2+A_2\mu k+B_2\lambda k=0 , \\
(a_{13}A_1+a_{23}A_2+a_{33}A_3)\mu^2+(a_{13}B_1+a_{23}B_3+a_{33}B_3+b_{11}A_1+b_{23}A_2+b_{33}A_3)\lambda\mu+ \\
\quad +(b_{13}B_1+b_{23}B_2+b_{33}B_3)\lambda^2+A_3\mu k+B_3\lambda k=0 .
\end{array}\right\} \quad (a)$$

The coefficients of these equations are linear functions of the variable coordinates x, y and z. To simplify we can introduce the following notations:

$$\begin{aligned}
P_1 &= a_{11}A_1 + a_{12}A_2 + a_{13}A_3 . \\
P_2 &= a_{12}A_1 + a_{22}A_2 + a_{23}A_3 . \\
P_3 &= a_{13}A_1 + a_{23}A_2 + a_{33}A_3 . \\
Q_1 &= a_{11}B_1 + a_{12}B_2 + a_{13}B_3 + b_{11}A_1 + b_{12}A_2 + b_{13}A_3 . \\
Q_2 &= a_{12}B_1 + a_{22}B_2 + a_{23}B_3 + b_{12}A_1 + b_{22}A_2 + b_{23}A_3 . \\
Q_3 &= a_{13}B_1 + a_{23}B_2 + a_{33}B_3 + b_{13}A_1 + b_{23}A_2 + b_{33}A_3 . \\
R_1 &= b_{11}B_1 + b_{12}B_2 + b_{13}B_3 . \\
R_2 &= b_{12}B_1 + b_{22}B_2 + b_{23}B_3 . \\
R_3 &= b_{13}B_1 + b_{23}B_2 + b_{33}B_3 ,
\end{aligned}$$

by which the equations (a) pass into the following:

$$\left.\begin{aligned} P_1\mu^2 + Q_1\lambda\mu + R_1\lambda^2 + A_1\mu k + B_1\lambda k = 0\,, \\ P_2\mu^2 + Q_2\lambda\mu + R_2\lambda^2 + A_2\mu k + B_2\lambda k = 0\,, \\ P_3\mu^2 + Q_3\lambda\mu + R_3\lambda^2 + A_3\mu k + B_3\lambda k = 0\,, \end{aligned}\right\} \quad . \quad . \quad . \quad (b).$$

4. Which condition now must exist between the coefficients of these equations if they are to allow of a mutual system of roots? The answer is that no condition is demanded for this. These equations are namely satisfied independent of the value of the coefficients by the system of roots:

$$\lambda = 0\,, \quad \mu = 0\,, \quad k \text{ arbitrary.}$$

The result arrived at by applying the method indicated in § 118 of my paper. "Théorie générale de l'élimination" agrees with this. According to this method we should have to find for the resultant the quotient of two determinants successively of order 15 and of order 3. In the case under consideration where we have

$$a_6 = 0\,, \quad b_6 = 0 \text{ and } c_6 = 0\,,$$

we always obtain, in whatener way we choose the determinants, as quotient a quantity which is identically zero.

So the above-mentioned equation (8) can be nothing else but an identity.

5. This result having been fixed it is no longer difficult to answer the question how to obtain the equation of the demanded locus. To this end we must express the condition that the equations (b) are satisfied by a second system of roots.

The condition in demand is, that all determinants are equal to zero contained in the assemblant (85) appearing in § 118 of the already mentioned paper. Applied to the equations (b) it gives but one equation, namely

$$\begin{vmatrix} P_1 & & & P_2 & & & P_3 & & \\ Q_1 & P_1 & & Q_2 & P_2 & & Q_3 & P_3 & \\ R_1 & & P_1 & R_2 & & P_2 & R_3 & & P_3 \\ A_1 & Q_1 & & A_2 & Q_2 & & A_3 & Q_3 & \\ B_1 & R_1 & Q_1 & B_2 & R_2 & Q_2 & B_3 & R_3 & Q_3 \\ & & R_1 & & & R_2 & & & R_3 \\ & A_1 & & & A_2 & & & A_3 & \\ & B_1 & A_1 & & B_2 & A_2 & & B_3 & A_3 \\ & & B_1 & & & B_2 & & & B_3 \end{vmatrix} = 0\,,$$

this being the equation of the demanded locus. It is of order nine agreeing to the geometrical researches of Prof. CARDINAAL.

Physics. — "*A formula for the osmotic pressure in concentrated solutions whose vapour follows the gas-laws*". By Dr. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS).

§ 1. The formula for the osmotic pressure may be derived in two different ways: by a thermodynamic and by a kinetic method. When putting these two in opposition I mean by no means an absolute contrast, on the contrary I believe — an opinion which I hope soon to treat more fully elsewhere — that without an equation of state based on kinetic considerations thermodynamics has nothing to start from and that therefore we can only oppose "purely kinetic" and "thermodynamic-kinetic" considerations.

Not numerous are those who have tried to find formulae for the osmotic pressure of more concentrated solutions by a thermodynamic method. Only HONDIUS BOLDINGH [1]) and after him VAN LAAR [2]) have pointed out that it appears from the theory of the thermodynamic potential that the concentration of the solution should not be taken into account in the form x, but as log $(1-x)$ and that for further approximation a correction term of the form ax^2 must be applied, and lately the latter has again come forward to advocate with great zeal the validity of this result.

More numerous are the attempts to determine the osmotic pressure in concentrated solutions by direct, molecular-theoretic methods; I may mention those of BREDIG [3]), NOYES [4]), BARMWATER [5]), WIND [6]).

This fact is surprising because VAN 'T HOFF himself, though he has a definite conception of the nature of the osmotic pressure, has never dared to base his equations on it, but has clearly indicated as basis of his theory of the osmotic pressure the thermodynamic considerations, by means of which he derives the osmotic pressure from the gas-laws. And; it is the more surprising because all these attempts wish to follow the train of thought which led VAN DER WAALS to his equation of state, though VAN DER WAALS himself has clearly shown, that in his opinion the osmotic pressure must not be sought in this way, but by the thermodynamic method, in connection with the equation of state given by him. That notwithstanding this so often the other way has been followed, seems noteworthy to

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[1]) Diss. Amsterdam 1893.

[2]) Zsch. phys. Ch. **15**, 466 (1894).

[3]) Zsch. phys. Ch. **4**, 444.

[4]) Zsch. phys. Ch. **5**, 53.

[5]) Zsch. phys. Ch. **28**, 115.

[6]) Arch. Néerl. (2) **6**, 714.

me on account of the predilection which it shows for purely kinetic considerations. The reasons why I do not share this predilection in this case, will appear from another communication, occurring in these Proceedings; here I shall confine myself to the thermodynamic method, and specially to the form given by VAN DER WAALS.

§ 2. In § 18 of his Théorie Moléculaire VAN DER WAALS treats the case, that of a binary mixture the first component can expand through a given space, whereas the other is confined to a part of that space. He demonstrates that for equilibrium a difference in pressure between the parts of the space is required which for dilute solutions has the value indicated by the law of VAN 'T HOFF. In this a thesis is used, which is very plausible (and which moreover may be proved in the same way as the condition for equilibrium in the general case) that namely equilibrium is established when the thermodynamic potential of the first component is the same in the two parts of the space. I shall here apply this condition to a binary mixture of arbitrary components and arbitrary concentration, the vapour of which follows the gas-laws, and which is in equilibrium with one of the components in pure condition under the pressure of its own vapour through a semipermeable wall. How such an equilibrium might be reached in reality in a special case, and whether this would be possible, need not be discussed.

§ 3. We assume that there are $(1-x)$ molecules passing through the membrane and x non passing molecules, then the thermodynamic potential of the first substance in the mixture is

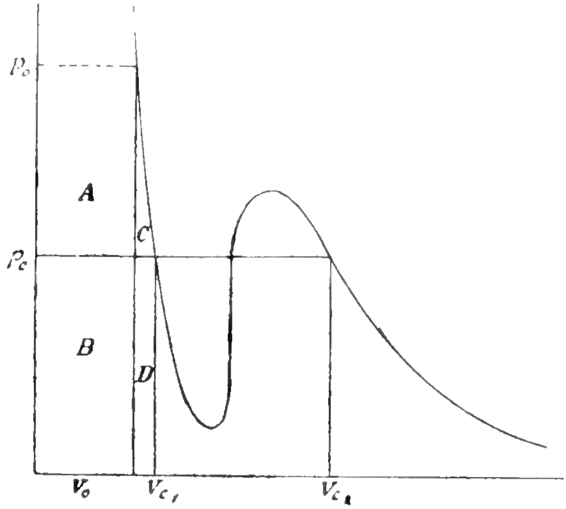
$$M_1 \mu_1 = \psi - v \left(\frac{\partial \psi}{\partial v}\right)_x - x \left(\frac{\partial \psi}{\partial x}\right)_v =$$

$$= \int_v^{\gamma} p dv + p v + MRT\, l\,(1-x) - x \int_v^{\gamma} \left(\frac{\partial p}{\partial x}\right)_{vT} dv + F(T)$$

in which the integrations must be extended from a volume γ so large that all the laws of ideal gases apply there, to the volume in question, $F(T)$ being a function of the temperature, which occurs here only as an additive constant. In order to be able to carry out the integrations, we require — as mentioned above — an equation of state $p = f(v, T)$.

For this purpose I shall adopt VAN DER WAALS' equation with constant b; though in this way we certainly do not get strictly accurate results, yet we shall be able to decide about the quantities which must occur in the formula.

§ 4. If in fig. 1 the isotherm of the mixture is indicated and the horizontal line is drawn according to the well-known law of MAXWELL 1)), then the pressure indicated by that line is what VAN DER WAALS calls the pressure of coincidence of the mixture and denotes by the symbol p_c. The volumes at the end of that line we call v_{c_1} and v_{c_2}, and p_o and v_o represent pressure and volume of the mixture in equilibrium in the above mentioned way.



Now the integral $\int_{v_0}^{V} pdv$ may be split into three parts:

$$\int_{v_o}^{v_{c_1}} pdv + \int_{v_{c_1}}^{v_{c_2}} pdv + \int_{v_{c_2}}^{V} pdv$$

For the middle quantity we may write:

$$\int_{v_{c_1}}^{v_{c_2}} pdv = p_c (v_{c_2} - v_{c_1})$$

As according to our suppositions the vapour follows the gaslaws, we have:

$$p_c \, v_{c_2} = MRT.$$

For the same reason we may replace p in the third integral by

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1) Through a mistake in the plate this line is drawn much too high here. Also the form of the isotherm is imperfectly represented. But the figure is merely given as a schematic representation.

MRT/v. Carrying out the integration we get $MRT \log \gamma/v_{c_2}$, for which we may also write $MRT \log p_c/p_\gamma$. We get then:

$$\int_{v_o}^{\gamma} p dv + p_o v_o = \int_{v_o}^{v_{c_1}} p dv + p_o v_o - p_c v_{c_1} + MRT + MRT\, l\, p_c/p_\gamma.$$

§ 5. Let us consider the first three terms. The first is represented in the figure by the area $C + D$, the second by $A + B$, the third by $B + D$. The three terms together are therefore $A + C$. If now as we assumed, the vapour is very dilute, and therefore the temperature far from the critical, hence also the isotherm very steep when cutting the line of coexistence liquid-vapour (or strictly speaking: at the pressure p_c, which however is very near the line of coexistence on the liquid side), then we may neglect C by the side of A, and we are the more justified in this as the pressure p_o is higher, so the mixture in question more concentrated. For $C = \int_{v_o}^{v_{c_1}} p dv - D$. If we introduce

$$p = \frac{MRT}{v - b_x} - \frac{a_x}{v^2}$$

and integrate, we get:

$$\frac{C}{A} = \frac{MRT\, l (v_{c_1} - b) + \frac{a}{v_{c_1}} - MRT\, l (v_o - b) - \frac{a}{v_o} - \left(\frac{MRT}{v_{c_1} - b} - \frac{a}{v_{c_1}^2}\right)(v_{c_1} - v_o)}{\left(\frac{MRT}{v_o - b} - \frac{a}{v_o^2}\right) v_o - \left(\frac{MRT}{v_{c_1} - b} - \frac{a}{v_{c_1}^2}\right) v_o}$$

If we arrive at very high pressures, $v_o - b$ approaches zero and numerator and denominator become both infinite, but the denominator of a higher order than the numerator. It is already apparent from the form of the isotherm which becomes steeper and steeper, that when neglecting C by the side of A we make proportionally a smaller mistake the higher p_o is. And that the neglect is allowed for small osmotic pressures is selfevident. We may therefore put for the three terms discussed in this §:

$$A = (p_o - p_c)\, v_o.$$

§ 6. It remains to calculate the term $\int_{v}^{\gamma} \left(\frac{\partial p}{\partial x}\right)_{vT} dv$. This integral too we separate into three parts $\int\limits_{v_o}^{v_{c_1}} + \int\limits_{v_{c_1}}^{v_{c_2}} + \int\limits_{v_{c_2}}^{\gamma}$. The last integral is now zero according to the law of AVOGRADO. The middle one we find from the equation already used above:

$$\int\limits_{v_{c_1}}^{v_{c_2}} pdv = p_c\,(v_{c_2} - v_{c_1})$$

by differentiating, taking into consideration that the limits of the integral are functions of x. We get:

$$\int\limits_{v_{c_1}}^{v_{c_2}} \left(\frac{\partial p}{\partial x}\right)_{v,T} dv + \left[p\,\frac{\partial v_c}{\partial x}\right]_1^2 = \frac{\partial p_c}{\partial x}\,(v_{c_2} - v_{c_1}) + p_c\,\frac{\partial v_{c_2}}{\partial x} - p_c\,\frac{\partial v_{c_1}}{\partial x}.$$

Now at the limits of the integral p is p_c; we retain therefore on the left and the right only the first members.

Finally the first part $\int\limits_{v_o}^{v_{c_1}} \left(\frac{\partial p}{\partial x}\right) dv$. As we were allowed to neglect $\int\limits_{v_o}^{v_{c_1}} pdv$, we might be inclined to think that this term too might be omitted. But as follows form the equation of state:

$$\frac{\partial p}{\partial x} = \frac{MRT}{(v-b)^2}\,\frac{db}{dx} - \frac{da/ax}{v^2},$$

this integral appears to be of higher order than the other for small values of $v - b$. We therefore retain it. Carrying out the integration we get:

$$-\left[\frac{MRT}{v-b}\,\frac{db}{dx} - \frac{da/dx}{v}\right]_{v_o}^{v_{c_1}}.$$

Here we may substitute $p + a/v^2$, for $MRT/v - b$, so that our expression for the thermodynamic potential becomes:

$$M_1\mu_1 = MRT\,l\,(1-x) + p_o v_o - p_c v_o + MRT + MRT\,l\,p_c/p_\gamma - x\,\frac{\partial p_c}{\partial x}\,(v_{c_2} - v_{c_1}) +$$

$$+ x\,\frac{db}{dx}\,(p_c - p_o) + x\,\frac{db}{dx}\left\{\frac{a}{v_{c_1}^2} - \frac{a}{v_o^2}\right\} - x\,\frac{da}{dx}\left\{\frac{1}{v_{c_1}} - \frac{1}{v_o}\right\} + F(T).$$

§ 7. This value must now be equated to the thermodynamic potential of the same substance in pure condition. As we suppose it to be under the pressure of its own vapour, the quantity to be calculated is the same as the thermodynamic potential of its saturated vapour, i. e.

$$\int_{v_{coex.}}^{\gamma} p dv + p_{coex.}\, v_{coex.} + F(T)$$

where we denote by the index *coex.* that the quantity must be taken on the line of coexistence. Now is on account of the assumed validity of the gaslaws

$$\int_{v_{coex.}}^{\gamma} p dv + p_{coex.}\, v_{coex.} = MRT\, l\, p_{coex.}/p_{\gamma} + MRT$$

If we equate the expression obtained here with that of the preceding §, then $F(T)$, MRT and $MRT\, log p_{\gamma}$ neutralise each other on both sides. What is left we may write in this way:

$$(p_o - p_c)\left(v_o - x\frac{db}{dx}\right) = - MRT\, log\frac{p_c(1-x)}{p_{coex.}} + x\frac{\partial p_c}{\partial x}(v_{c_2} - v_{c_1}) +$$

$$+ x\frac{da}{dx}\left(\frac{1}{v_{c_1}} - \frac{1}{v_o}\right) + xa\frac{db}{dx}\left\{\frac{1}{{v_{c_1}}^2} - \frac{1}{{v_o}^2}\right\}$$

Now v_{c_1} and v_o can never differ much. If the osmotic pressure of an aqueous solution amounts e.g. to 1000 Atm., these volumes differ only a few percents. In the two last terms, which themselves can only be correction terms, we may therefore put $v_{c_1} = v_o$ in any case, so that those terms vanish. Further we may neglect v_{c_1} by the side of v_{c_2} and write $MRT log p_c$ for v_{c_2}. Our equation becomes then:

$$p_o - p_c = - \frac{MRT}{v_o - x\frac{db}{dx}}\left\{log\frac{p_c(1-x)}{p_{coex.}} - x\frac{dlog p_c}{dx}\right\}$$

The remaining v_o may, of course, not be replaced by v_{c_1}, first because this expression occurs here in the principal term and then because the substitution of v_{c_1} for v_o would of course be more felt in a term of the order $1/v-b$ than in $1/v$. But in any case, when we have really to do with osmotic pressures, the pressure will never be so large that we could not compute v_o with the aid of the coefficient of compressibility of the saturated liquid without any difficulty.

§ 8. The quantity $p_o - p_c$, which we have found, is not identical with the osmotic pressure; the latter is rather $p_o - p_{coex.}$, but the transition of one quantity to the other is without any difficulty. If we neglect in our formula the terms, which are multiplied by x by the side of those in which this is not the case, if we put $p_0 = p_{coex.}$ and if we take $v_{coex.}$ instead of v_0, which is permissible for very dilute solutions we get:

$$P = p_0 - p_{coex.} = - \frac{MRT}{v_{coex.}} \, log \left(1 - x \right)$$

which gives the well-known formula of VAN 'T HOFF when the *log* is developed and the higher powers omitted.

I wish to point out, that also a more accurate treatment yields the logarithmic form which BOLDINGH and VAN LAAR have advocated — and there could not be any doubt but it must be so — but that it also shows that VAN LAAR's statement[1]) was too absolute when he asserted that a correction term need never be applied in the numerator $v_{coex.}$ (or v_0) in connection with the size of the molecules.

In the second place I draw attention to the fact that we find the osmotic pressure exclusively expressed in what VAN DER WAALS has called thermic quantities (in opposition to caloric quantities). It appears to be unnecessary to take into consideration the heat of dilution or other quantities of heat, which VAN 'T HOFF[2]) seems to deem necessary for concentrated solutions and which EWAN[3]) has taken into consideration. Even if we had avoided all the introduced neglections, so when we had not assumed, that the vapour follows the gaslaws, nor that $v_0 = v_{c_1}$ may be put in some terms, nor that the area C' may be neglected compared to A, nor (the most important) that b is constant, we should evidently not have had to deal with any quantity of heat. This seems important to me, as both theoretically and experimentally the caloric quantities are much less accessible than the thermic ones.

Physics. — "*Kinetic derivation of* VAN 'T HOFF's *law for the osmotic pressure in a dilute solution.*" By Dr. PH. KOHNSTAMM. (Communicated by Prof. VAN DER WAALS).

§ 1. When we leave out of account the more intricate theories as that of POYNTING[4]), who tries to explain the osmotic pressure from an association of solvent and dissolved substance, and that of

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[1]) l. c.

[2]) K. Svenska Vet. Ak. Hand. **21.** Quoted by EWAN Zsch. phys. Ch. **14** 409 en 410.

[3]) Zsch. phys. Ch. **14,** 409 en **31,** 22.

[4]) Phil. Mag. **42,** 289.

BACKLUND [1]), who seems [2]) to require even ether waves to explain it, chiefly two theories have been developed about the nature of the osmotic pressure: the static and the kinetic theory. The first theory finds warm advocates in PUPIN [3]) and BARMWATER [4]); it seems however doubtful to me whether they have closely realised the consequences of their assertions. At least the latter brings forward as an objection to the kinetic nature of the osmotic pressure: "Ein molekulares Bombardement in einer Flüssigkeit ist mir immer etwas sonderbar vorgekommen"; notwithstanding he considers the equation of state of VAN DER WAALS by no means as a "sonderbar" instance of false ingenuity, but as an example to be followed. However this may be, he who does not want to break with all our conceptions about heterogeneous equilibrium, will not be able to explain such an equilibrium in another way than statistically i. e. as a stationary condition of a great number of moving particles. This does, of course, not detract from the fact that the question may be put what forces are required to bring about that state of equilibrium. This implies that the adherents of the static theory need not be altogether mistaken when they assert that the cause of the osmotic pressure is to be found in forces of attraction. On this point I shall add a few remarks at the end of this communication.

§ 2. Of much more importance than this static theory of the osmotic pressure is the kinetic theory. The great majority of its advocates (I shall speak presently about the few exceptions) take as their basis the equality, which has been proved experimentally and by means of thermodynamics, of the osmotic pressure and the gas pressure (the pressure which the molecules of the dissolved substance in the same space would exercise, when they were there alone and in rarefied gas state) and derives from this that they have both the same cause in this sense that the dissolved substance is present in the two cases in the same state and so acts in the same way: this is then expressed in about this way that the solvent converts the dissolved substance into the rarefied gas state. This conception seems doubly remarkable to me: first because it seems to be pretty well generally prevailing [5]), secondly because it alone seems to me to be able to

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[1]) Lunds Univ. Aarsskrit **40**.

[2]) I know his paper only from an abstract in the Beibl. **29**, 375.

[3]) Diss. Berlijn 1889.

[4]) Diss. Kopenhagen 1898 and Zsch. phys. Ch. **28**, 115.

[5]) It is naturally difficult to give a proof of this opinion, therefore I shall only adduce the following citations as a confirmation.

"If we look a little more closely into the matter, we find that in the case of dilute solutions, at least, there is far more likelihood of the dissolved substance explain, why the theory of the osmotic pressure has become so quickly popular, whereas GIBBS' method for the solution of the same problems was scarcely noticed. In fact the view mentioned possesses all qualities required for great popularity: it seems to give a very simple, clearly illustrating explanation for the striking law discovered by VAN 'T HOFF; it is allied to the universally known gaslaws; it seems to make us acquainted in the osmotic pressure with a quantity, which is as characteristic for the dissolved state as the well-known external pressure for a gas. On the other hand it does not seem to carry weight that this "explanation" is, properly speaking, no more than an explanation of words, which leaves undecided exactly that which had to be explained, viz. how it is, that the solvent acts on the dissolved substance in this way. It is, however, worse that this explanation clashes with everything we know of liquids and gases, and therefore is to be rejected. We need only think of the well-known experiment with a bell jar, closed at the bottom by a membrane, filled with a solution of cane sugar and placed in a vessel with pure water, which forces its way in till equilibrium has been established. If now the pressure P, exerted on the membrane, was a consequence of the fact, that the dissolved substance in the bell jar was in a state which more or less resembles the gasstate, then those molecules of the dissolved substance would have to exert the same pressure also on the glass wall of the bell jar, in other words, the water molecules would exert the same pressure

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being in a condition comparable with that of a gas." (WALKER, Introduction to Physical Chemistry, 148).

"Ich glaube dargethan zu haben — *im Gegensatz zu der zur Zeit allgemeinen Auffassung* — dass es nicht notwendig ist eine freie Bewegung der gelösten Moleküle wie für die Gase anzunehmen. Wenn ein fester Körper in einer Flüssigkeit gelöst, oder eine Flüssigkeit mit einer anderen gemengt wird, so wird eine neue Flüssigkeit erhalten, von deren Molekülen es nicht gestattet ist, andere Beweglichkeit anzunehmen, als diejenige, die Flüssigkeiten charakterisiert." (BARMWATER l. c. pag. 143). "Aus den klassischen Arbeiten von VAN 'T HOFF und ARRHENIUS geht nun hervor, dass die Körper bei Gegenwart von Lösungsmittel thatsächlich mehr oder minder dem Gaszustand näher gerückt werden," and a little before: "Andererseits konnte ich mir .... nicht verhehlen, dass gerade diese Gegenwart und Einwirkung des Lösungsmittels doch die notwendige Vorbedingung für den Eintritt des gasähnlichen Zustandes sei: .... daher ist aber ein gasähnlicher (also kinetischer) Zustand nur unter dieser Einwirkung vorhanden und hört sofort auf, sobald diese Einwirkung beseitigt ist. *Es sei betont, dass diese Auffassung durchaus nichts Neues bietet, dass sie vielmehr wohl einem Jeden eigen ist, der den Begriff des osmotischen Druckes kennen gelernt hat.*" BREDIG. l.c. p. 445 and 444). The italics are mine, the spacing the cited authors'.

Finally cf. VAN LAAR's address in the "Bataafsch Genootschap", p. 2 and 3 and the example cited there.

on that wall from the inside and from the outside (of 1 atm.). This now is a perfectly unacceptable result, as immediately appears from what follows. Let us imagine the same solution as in the bell jar inclosed in a cylinder with a piston under the pressure of its saturated vapour $p - \angle p$, where $\angle p$ is the decrease of vapourpressure. The cane sugar molecules contribute nothing to that pressure or hardly anything [1]), as appears from the fact that they cannot pass into the vapour (at least not in a measurable degree); all the pressure is furnished by the water molecules. Now we compress the liquid, till it has got a pressure $P + p$, it is now in perfectly the same condition as the liquid in the bell jar, when we except the immediate neighbourhood of the membrane. On the supposition made just now the water molecules would exert a pressure p against the piston, the sugar molecules a pressure P, i. e. the pressure of the latter would have increased by an amount about 1000 times that of the former, whereas their initial pressure was at least a hundred thousand times smaller. And the result would be that the, let us say 2, sugar molecules, which are found to every 1000 water molecules would exert a pressure twice as great as the 1000 particles together. It is beyond doubt that the pressure $P + p$ on the piston or the glass wall of the bell jar is exclusively exerted by the watermolecules, and if he meant this, LOTHAR MEYER was certainly right when he asserted [2]), that the osmotic pressure was a result of the collisions of the solvent.

Also in this respect the theory of the gaslike character of the dissolved substance falls short, as it leaves perfectly unexplained why in an isolated solution, e.g. a cane sugar solution, which in a glass vessel stands under atmospheric pressure, nothing is perceived of the gaslike character of the dissolved substance. For that in this case solvent and dissolved substance are less closely in contact than in the osmotic experiment, cannot seriously be asserted.

§ 3. If therefore we must not seek the explanation of the laws of the osmotic pressure in a particular condition of matter, characteristic of dilute solutions, then the remarkable fact formulated by VAN 'T HOFF calls the more peremptorarily for an explanation.

Nobody less than LORENTZ and BOLTZMANN have made attemps to do this [3]), but even their endeavours do not seem to me to have solved the problem entirely. In saying this I agree with Prof. LORENTZ's own opinion, at the beginning of his paper he terms it a "freilich nur zum Teil gelungene Untersuchung". As to the reasons of this partial failure, however, I shall most likely differ in opinion with Prof. LORENTZ.

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[1]) Perhaps the pressure of these molecules would even prove to be negative.

[2]) Zsch. Phys. Ch. **5**, 23.

For what is the case? The behaviour of liquids is entirely dominated by the occurrence of the quantities a and b in the equation of state. Only matter in dilute solution seems to emancipate itself from it, according to the law of VAN 'T HOFF, where neither the a nor the b occurs. This fact calls for an explanation. Now it is not difficult to understand, why the a can disappear here; the membrane is bounded on one side by the solution, on the other side by the pure solvent. If we now think it thin compared to the extent of the sphere of action, then it is clear that at the membrane the force $\frac{a_x}{v_0^2}$ which works towards the solution, is in first approximation neutralized by the force $\frac{a}{v_q^2}$ towards the other side. It is more difficult to see why also the b vanishes, i. e. why the molecules of the dissolved substance seem to move as through a vacuum, instead of through a space, which is occupied for a very great part by the molecules of the solvent.

Just on this most important point Prof. LORENTZ's paper leaves us in the dark, for so far as I have been able to see. And it seems to me beyond doubt, that in the first place this is due to an inaccurate interpretation of the term "kinetic pressure". According to Prof. LORENTZ it is always equal to $^2/_3$ of the kinetic energy of the centres of gravity of the molecules which are found in the unity of volume. It is therefore independent of the volume of those molecules. Now this would only be a question of nomenclature, if not that kinetic pressure was also defined as the quantity of motion, carried through the unity of surface in the unity of time by the motion of the molecules; and that this quantity is dependent on the number of collisions and so on the volume of the molecules does not seem open to doubt to me after KORTEWEG's proof [3]). In agreement with this the kinetic pressure is represented in the equation of state by $MRT/v—b$. In consequence of his definition LORENTZ replaces this

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[1]) Zsch. phys. Ch. **7**, 37 and Arch. Néerl. **25**, 107.

[2]) Zsch. phys. Ch. **6**, 474 and **7**, 88.

[3]) Verslagen Kon. Ak. Amst. (2) **10**, 363 and Arch. Néerl. **12**, 254. Compare also the simpler, perhaps even more convincing proof for one dimension in Nature **44**, 152. As the attentive reader will notice Prof. LORENTZ's proof (l. c. 39) does not take into account the collisions and the fact ensuing from them, that a quantity of motion skips a distance or moves with infinite velocity for a moment. And the admission of the validity of KORTEWEG's reasoning appears, as it seems to me, already from the fact, that Prof. LORENTZ has to assume for the solid bodies introduced by him, that they are immovable (l. c. 40) or of infinite mass (l. c. 42) which comes to the same thing in this case.

quantity by MRT/v, and so his paper cannot give any elucidation on the point which requires it most. But that notwithstanding we owe to LORENTZ's labour a considerable widening of our views, will as I hope, appear from the continuation of this communication.

Also BOLTZMANN's paper leaves us in the dark as to the question why the quantity b, which in other cases plays such an important part for liquids, seems to have no influence on the value of the osmotic pressure. In the equations, which he draws up, he never takes the size of the molecules into account [1]) and it does not appear why he does not do so. Further he stops at the result, that the osmotic pressure is equal to the sum of the pressures exercised by the two kinds of molecules, without discussing the part played by the different kinds. For these reasons I cannot see a satisfactory solution of our problem in BOLTZMANN's paper either.

§ 4. To arrive at a solution it seems in the first place necessary to give three definitions.

1st. Given a fluid. Placed in it a body of perfect elastic impermeable substance, which does not exert any attraction on the molecules of the fluid. The thickness of this body (or this surface) be infinitely small; let us suppose it to have an area of 1 cm^2. The "kinetic pressure" in that fluid is then the quantity of motion in unity of time transferred by the molecules of the fluid to this body (or obtained in the elastic collisions from this body).

2nd. In the second place I imagine a body [2]), which is distinguished

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[1]) See specially l. c. 475 equation (4), which is evidently incorrect, when part of the cylindre is not open to the centres of the molecules, because it is occupied by distance spheres of other molecules.

[2]) That I assume that the body does not attract the molecules of the fluid, is for simplicity's sake, but it is not essential. If we imagine a wall, which *does* attract the fluid, more molecules will reach its surface (cf. the footnote p. 739) and hence will impart a greater quantity of motion to the wall. But on the other hand the particles of the surface will now be drawn into the fluid with an equally greater force. The elastic displacement of the particles of the surface of the solid wall, and with it (with sufficient elasticity) that of the layers lying under it, in other words the pressure which propagates in the solid body, and which would be measured with a manometer of any kind, will be perfectly the same in the two cases. If we wish to take also negative external pressures into account, we shall even have to give the definition by means of an attracting body, because in this case a non-attracting body would not even be reached by the molecules of the fluid. (Cf. the well-known fact that for the observation of the negative pressure strongly adhering walls are required). In this case the impulse of the attraction of the molecules is simply greater than the quantity of motion which they impart to the wall (and which may still be very great), the elastic displacement is therefore not from the fluid, but towards it.

Also in the case that we wish to take capillary layers into account, our definition from the just mentioned body only by its being very thick compared to the sphere of action of the molecules. The quantity of motion transferred by this body per unity of time to the molecules, is called the "external pressure" in that fluid.

3nd. In the third place I place in the fluid (which I now suppose to be a mixture) a body, which is distinguished from that mentioned under 2 only by the fact that the molecules of one component (solvent) pass through it without any change in their velocity. I shall leave undiscussed here whether such a body can actually occur. The pressure to which this body is now subjected, and which might be measured e. g. by the elastic displacement of the particles of its surface, I call the "osmotic" pressure in that solution.

From these definitions it is already clear that in dilute solutions the osmotic pressure defined here must be of the order of the kinetic pressure exerted by the dissolved substance, and not of that of the external pressure. For these two differ, in that $\frac{a}{r^2}$ has disappeared for the kinetic pressure, and this will also be the case for the osmotic pressure defined here, as appears from the reasoning given above (§ 3). I shall further show, that in dilute solutions this osmotic pressure has the value indicated by the law of Van 't Hoff, and that in any case it is as great as the well known experimentally introduced and measurable osmotic pressure, i. e. the difference in external pressure of solution and pure solvent under the pressure of its own vapour in equilibrium through a semipermeable wall.

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calls for fuller discussion. First of all this applies to what we have just now said, for just as for negative pressures so also in the capillary layer, as **Van der Waals** has shown in his theory of capillarity, the attraction of the surrounding layers is a necessary condition for stable equilibrium. But further, as **Hulshoff** has shown (These Proc. **8**, 432 and Diss. Amsterdam 1900), the above defined quantity does not obey the law of Pascal any more, because measured in the direction of the layer and perpendicular to it, it has a different value. In this case we might perhaps speak of a total external pressure, which might be split into an external fluid pressure and an external elastic pressure. The consideration of capillary layers round a free floating sphere, teaches us further, that the "external" in the name "external pressure" must not be understood in such a way, as might easily be done, viz. that the reactive force of this pressure, as it prevails in a certain point, would act in points outside the system in question, which would always be more or less arbitrary, as we may choose the limits of our system arbitrarily. The assertion: the external pressure is in a point of the fluid so great, comes simply to this, that *when I should place a strange body at that place, without altering the condition more than necessary* for this, this body would experience a pressure of such a value, and would suffer an elastic modification in form which corresponds to it, so differing in the capillary layer in different directions.

§ 5. For this proof I must refer to a formula of CLAUSIUS used by me already before [1]. Imagine a point which can freely move in a space W. CLAUSIUS [2] shows — which is already plausible beforehand — that the number of collisions of this point per second against a wall of area S is proportional to S/W (the factor of proportion depends only on the velocity of the point).

Let us now consider a wall as defined under 2, and draw a plane parallel to that wall at a distance $\frac{1}{2}\sigma$ (σ is the diameter of the molecules, which we think spherical); this plane we call plane of impact, because the centre of a molecule, which strikes against the wall, lies in this plane. Now we apply CLAUSIUS' formula to this wall. In this we must allow for the fact that the centre of a molecule cannot move freely throughout the volume of the fluid; for within the distance spheres (spheres drawn round the centre of every molecule with a radius σ) it cannot come; instead of v we have therefore to put $v-2b$, when $2b$ [3] is the volume of the distance spheres. Now the whole plane of impact, however, is not accessible to collisions either, part of it also falls within the distance spheres. In order to fix this part we draw two planes at distances h and $h+dh$ parallel to the plane of impact. We determine how many centres of molecules are found between them and what part of the plane of impact is within their distance sphere. In order to find what part of the plane of impact falls at all within distance spheres, we must integrate with respect to h between 0 and $\frac{1}{2}\sigma$. It appears then, that instead of S we must put $S(1-b/v)$ in the formula for the number of collisions against the wall, so that the pressure becomes proportional to

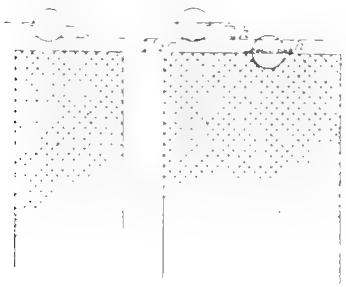

Fig. 1.

$$\frac{S\left(1-\frac{b}{v}\right)}{v-2b}$$

or in first approximation

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[1] These Proc. VI. 791.

[2] Kinetische Theorie der Gase, 60.

[3] For simplicity I confine myself to the first term, even if we have to deal with liquids; this is permissib'e here, because the other terms have no more influence on *our* question (the derivation of the law of VAN 'T HOFF) than the first.

$$\frac{S}{v-b}\ ^{1})$$

§ 6. Now we apply the reasoning of the preceding paragraph to the collisions of the dissolved substance on a wall defined as under 3. We assume the solution to be so diluted, that the volume of the molecules of the dissolved substance may be neglected compared with the whole volume. For simplicity — though it is not essential to the proof — we assume now also that the molecules are spheres. Then here too the available space must again be put equal to $v-2b$; but the part of the plane of impact, accessible to collisions, is now different. For as the molecules of the solvent pass through the wall, their centres may now just as well be on the other side of the plane of impact. We have therefore not to integrate with respect to h from 0 to $^1/_2\,\sigma$, but from $-\,^1/_2\,\sigma$ to $+\,^1/_2\,\sigma$, which evidently yields the double value. The pressure on the wall becomes therefore proportional to

$$\frac{S(1-2b/v)}{v-2b}=\frac{S}{v}\ ^{2})$$

so that the influence of the molecules of the solvent vanishes and VAN 'T HOFF's formula is proved for the quantity defined by us.

§ 7. That this quantity has further always the same value as the quantity which may be measured experimentally, is proved as follows. Let us think the action of the membrane in such a way that it suffers the molecules of the solvent to pass through freely, but repels those of the dissolved substance perfectly elastically. Something similar would take place when the membrane worked as a "molecule sieve", i.e. when the pores were such as to allow the molecules of the solvent (thought smaller) to pass, the others not. According to the definition the latter will then exert a pressure on the membrane equal to our osmotic pressure. The other molecules passing through the wall unmolested, there is no mutual action with the wall, and so they do not exert any force on it.

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1) If one should object to the train of reasoning followed here, one can find in BOLTZMANN's "Gastheorie" a proof for this formula which intrinsically agrees perfectly with that given in this paper, but will appear stricter to some. There one will also find the above given integration carried out.

2) It is clear that we shall get the same result, when we do not take $2b$, but $f\,(b/v.)$ for the volume of the distance spheres. For as the place of the plane of impact with respect to the molecules of the solvent is quite arbitrary in our present case, the part of the plane of impact, which lies within the distance spheres will stand to the whole area in the same proportion as the volume of the distance spheres to the whole volume.

The experimentally measurable difference in pressure on either side of the membrane must therefore have the same value as the quantity defined by us.

Lorentz [1]), however, has shown that the assumption made here concerning the membrane is by no means necessary. On the contrary; if we assume that the membrane is thick compared with the sphere of action, that its substance fills a volume large compared with the apertures present and that it feebly attracts the molecules of the dissolved substance, whereas these are strongly attracted by the solvent — none of which are improbable assumptions — we arrive at the result, that none of the dissolved particles reaches the membrane, much less exerts a pressure on it; the membrane is then quite surrounded by the pure solvent. And that this case is really the usual one in nature is made probable by the fact, that it is by no means always the smaller molecules which pass the membrane, as we assumed above. The membrane seems therefore not to work as a molecule-sieve. We are then easily led to suppose that the membrane does not exert a positive repulsion at all on the non-passing substance, but that it only attracts those particles much less strongly than the solvent, so that the dissolved particles do not pass through the membrane, because they occur but extremely rarely in its neighbourhood. This view is supported by the fact, that only those substances seem to be non-passing which are not easily converted to vapour, and so cannot reach the limits of the liquid in virtue of their own thermal motion alone.

However this be, also in this case our conclusion holds good. For when the molecules of the dissolved substance do not (or only in an infinitely small number) reach the membrane, two planes will be found not far from the membrane, A where the molecules of the dissolved substance still have their normal density, B where this density has diminished to zero. Between B and the membrane we find then pure solvent. If we wished to discuss such a layer fully, we should, of course, have to give a theory, as van der Waals has given for the transition liquid vapour [2]), extented to a mixture in the way van Eldik [3]) has done. But for our purpose this is fortunately not necessary. We need only observe, that the layer AB as a whole has now exactly the same influence on the condition of motion of the dissolved molecules as the mathematical upper surface of the membrane had just now. The layer AB as a whole will now,

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[1]) l. c.

[2]) Verh. dezer Ak. (2) **1**; Arch. Néerl. **28**, 121 and Zsch. phys. Ch. **13**, 657.

[3]) Diss. Leiden 1898.

just as the membrane just now, be pressed downward with a force equal to the osmotic pressure defined by us, and transfer this force to the underlying layer of the pure solvent, which is pressed outward with this force. But this pressing force is evidently equal to the difference in pressure which may be measured experimentally [1]).

§ 8. Thus it seems to me that VAN 'T HOFF's law for dilute solutions is kinetically explained in the same way as the law of BOYLE-GAY LUSSAC-AVOGADRO for dilute gases and that of VAN DER WAALS for liquids and gases, i.e. we have obtained an kinetic insight how these laws result from the condition of motion in the homogeneous mass, while we have left out of account what happens in the eventually (probably always) present unhomogeneous bounding layers.

It appears from the explanation convincingly, that VAN LAAR goes too far, when he states [2]), that we cannot speak of osmotic pressure in an isolated solution. Here too this notion has a clear physical signification, and the laws which govern it, are to be derived.

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[1]) This hydrostatic proof may easily be replaced by a purely kinetic one, though the latter is somewhat more elaborate. The layer AB, which (in consequence of course of the neighbourhood of the membrane) behaves as a layer of water, through which the dissolved substance cannot penetrate (Cf. NERNST's well-known osmotic experiment) imparts to the molecules of the dissolved substance per second a quantity of motion equal to the osmotic pressure defined by us, and receives itself an equally large quantity in opposite sense, which it transfers to the underlying layers, as the kinetic theory teaches. (See e. g. BOLTZMANN, Zsch. phys. Ch. **6**, 480). Now the whole mass of water, which is in the neighbourhood of the membrane, (on either side, reckoned on one side from B, on the other from a plane, so far from the membrane that the latter does not act on it any more), does not move downward, so it must receive an equally strong but opposed impulse, which, of course, cannot issue from anything but the membrane. Of what nature the forces acting here are is quite unknown. It cannot be the ordinary molecular attraction, for then the denser liquid found above the membrane would probably be drawn more strongly downward than that found under it upward. We might think of friction in the pores, but it would then have to be different in one direction from that in the other; in short I dare not venture on any conjecture about this. This alone is certain, such forces must exist, at least if the case put by us ever actually occurs. This appears already from the fact that the pure solvent above the membrane is subjected to a higher pressure, so has a greater density than under it. Such an equilibrium occurs for all kinds of kinetic questions (liquid vapour, gas under the influence of gravity), but the necessary condition is always a force, which at a cursory examination seems to have the result, that the *velocity* of the molecules in one part (so the temperature) would be higher than in the other, but in reality only proves to have influence on the *density*. The membrane, which furnishes this impulse, receives an equally strong one back from the reaction, and so here too, though indirectly, we see a force equal to the osmotic pressure defined by us, exercised on the membrane from the inside to the outside.

[2]) Chem. Weekblad 1905, N⁰. 9, § 3. Voordracht Bat. Gen. 3.

Whether this renders it desirable for us to give it a prominent place in the theory of solutions and make all the rest proceed from it, is a question to which I wish to revert in a separate paper.

First I must add this observation. The insight obtained in the nature of the osmotic pressure enables us to examine what quantities must occur in the formula for more concentrated solutions. In the first place it will no longer be true for concentrated solutions, that the term $^a/_{v^2}$ vanishes, both because on the two sides of the membrane the density v differs, and because the concentration and so the a will differ. Further — as appears from our proof — for higher concentrations the volume of the molecules will assert its influence, and not only that of the dissolved substance, but also of the solvent. For as on the two sides of the membrane the density differs, the part of the plane of impact that falls within the distance spheres of these molecules, will no longer be represented by the above given value. As finally the molecules are of different size, when the terms b_1 and b_2 occur, the term b_{12} is sure to appear. The formula found in this way will certainly not agree with the one found in the preceding communication by a thermodynamic method, for the latter is derived from the equation of state with constant b, whereas the kinetic considerations exclude all doubt that b is a function of the volume. If there should be a real diminishing of the size of molecules when passing beyond the membrane, then this fact is also to be taken into account.

Far be it from me to make an attempt to draw up such an equation. To achieve this, it would be required, as appears from what precedes, that one should be able to surmount at least all the obstacles which stand in the way of an accurate equation of state. And if this might be done — the preceding paper proves it — the final formula could be found in a way, which would not expose us again to the danger of making errors. I shall therefore not enter into the question either, in what way the formula derived in a kinetic way can satisfy the first requirement that may be put to every formula for concentrated solutions: that it yields the value ∞ for the case that the substance passing the membrane has perfectly vanished from the solution.

§ 9. I shall just add a single remark on the question whether our kinetic view implies that the so-called static theory of the osmotic pressure, which ascribes the cause of the phenomenon to attractive forces, is entirely wrong? It seems to me that from what LORENTZ has proved it appears that we must answer this question in the negative. It is true that we have seen that the attraction of solvent and dissolved substance begins to play a part only in sensibly concentrated solutions, and that we have to explain the osmotic pressure by a "moleculares Bombardement". But the case treated by LORENTZ shows that the whole osmotic phenomenon might possibly exclusively be the consequence, not so much of the presence of attractive forces, but just of the reverse, of the want of attraction between the molecules of most solid substances and certain other solid substances which form membranes. If the adherents of the static theory mean no more than this with their assertion: that the osmotic pressure must be explained from forces of attraction, then they seem to me for the present secured against every attack.

Physics. — "*Osmotic pressure or thermodynamic potential*". By Dr. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS).

§ 1. The theory of thermodynamic functions, through which GIBBS has enabled us to derive from the equation of state of a system in homogeneous condition, what heterogeneous equilibria will occur, has attracted attention only in a very limited circle during a series of years. However great the region opened for investigation by GIBBS was, the methods indicated by him seemed so abstract, that only very few dared to grapple with them. At a stroke this was changed, when in 1885 VAN 'T HOFF succeeded in replacing these methods in appearance so abstract, by another, that of the osmotic pressure, which strongly appeals to the imagination. The theory of solutions, which up to that time had only existed for a few, rapidly became one of the most frequently treated and discussed subjects of physics and chemistry; since then it has continued to enjoy undivided attention.

It stands to reason, that the attention, which now for twenty years has been so lavishly granted to the questions of heterogeneous equilibrium, have also been conducive to making GIBBS' methods for the solution of such questions known in a wider circle. But though GIBBS' name may be counted among the most famous and widely known names in the sciences of physics and chemistry, yet even now his methods cannot be said to have been universally accepted.

The adherent of a mechanical (or, if one prefers, statistical) natural philosophy has by no means reason exclusively to regret this course of affairs, for he sees in it a clear indication, that the views whose truth he advocates, are by no means so antiquated, nay even dead, as they are often declared to be. And if the current opinion — which certainly greatly contributes to the greater popularity of the osmotic pressure compared with that of the thermodynamic potential — were really correct, that we can form a clear idea of the physical meaning of the first quantity and *not* of the second, then there could not be any doubt for him which method to prefer, if for the rest the circumstances were quite the same.

But this current opinion seems to me hardly tenable and on the other hand I believe that in many respect the thermodynamical potential is preferable to the osmotic pressure, and that therefore it will be advisable to put the question whether it would not be better to return to the older method both for scientific investigation and for instruction?

§ 2. This question has lately again been put forward by Mr. VAN LAAR in an address for the "Bataafsch Genootschap" at Rotterdam[1]), which was followed by an article "Over tastbare en ontastbare grootheden" (On palpable and impalpable quantities)[2]). Though I readily admit, that these papers have induced me to consider the problem of the osmotic pressure specially, there would not be any reason for me to discuss Mr. VAN LAAR's views here, when only his address had appeared. For I can fully subscribe to the general tendency of this paper though of course I would not be responsible for every statement, as moreover has already appeared from my preceding communications in these Proceedings — and I should therefore only have to consider what in my opinion would have to be added to his address. His second paper, however — and in this I have specially in view § § 6 and 7, pointed out as the gist of his paper by the author himself — Mr. VAN LAAR seems to me to harm rather than to promote the good cause, which he has espoused with so much ardour, and already for this reason I feel it incumbent upon me to protest against this part of his reasoning. I think that I accurately represent the gist of it as follows: It is true that we cannot form a clear idea[3]) of the nature of the thermodynamic potential, but we cannot do so for the osmotic pressure either. Nor is this surprising, for the improved philosophical insight of the last years gives us the conviction that our natural philosophy never works with any but fictitious (though sharply defined) ideas,

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[1]) Also published in Chem. Weekblad, 1905, N⁰. 1.

[2]) Chem. Weekblad, 1905, N⁰. 9.

[3]) Mr. VAN LAAR speaks of a "palpable conception" (tastbaar begrip). It would lead me too far if I would account for the reason why I think that I may, nay even ought to substitute the term chosen here for it.

which must not and cannot claim in the least to represent the real nature of things. It is also owing to this insight, that several voices have been raised of late in favour of the use of the thermodynamical potential.

§ 3. Now I think that I have convincingly proved the incorrectness of the second thesis in the preceding paper, and as I gladly and with full conviction range myself with the "tastbaarheidsmenschen," (those who want to form a clear idea of the physical meaning of each term used), whose opinion Mr. VAN LAAR severely condemns, his reasoning would lead me to take side against the thermodynamic potential party when I could subscribe to his first and his last thesis more than to his second. This however, is by no means the case.

The last philosophical-historical thesis I can, naturally, not discuss here and I confine myself therefore to that concerning the physical meaning of the thermodynamical potential. It seems to me that we can form an idea of this quantity which need not be inferior to that of any other statistical quantity. That Mr. VAN LAAR has overlooked this fact seems chiefly owing to two circumstances of which it may appear that one can have hardly any influence, for it is simply a question of nomenclature. Following a common way of speaking, which does not seem to me the less reprehensible for the fact that it is of frequent occurrence, Mr. VAN LAAR does not give the name of "thermodynamical potential" to the quantity introduced by GIBBS into science by that name, but to one of the other functions introduced by GIBBS, the ζ-function. There are more reasons than only a feeling of deference, which make this undesirable. The real (GIBBS') potential *is* really a potential, i. e. it is constant in a space where equilibrium prevails, and its not being constant means, that there is no equilibrium. At least when there act no capillary or external forces; and in this case the resemblance of the thermodynamic potential with the potentials of other energies stands out perhaps the more clearly. For in this case we need only add to the (GIBBS') thermodynamic potential the other potentials, which exist in that space in order to get a quantity, the total potential, which now also is constant throughout the space in case of equilibrium. The ζ-function has neither the one property, nor the other, except when we have to deal with a simple substance without capillary layers, in which case it becomes identical with the thermodynamic potential.

If now also in §§ 6 and 7 Mr. VAN LAAR had directed his attention instead of to the ζ-function, to the real potential, as he has done in § 4, where he carries out his calculations by means of it, it would probably not have escaped his notice that he wrongly represents the thermodynamic potential (whether it be in one sense or in the other) as the last, most fundamental quantity, which determines the internal condition of a body. As such we cannot take others than v and T (if necessary of course x, y, etc.); that this is not only a subjective "point of view" appears perhaps most clearly from the study of the theory of capillarity, as VAN DER WAALS has given it.

§ 4. From this follows naturally, that we must try to form an idea on the relation between the thermodynamic functions and these fundamental quantities, and this does not seem so very difficult to me just with regard to the thermodynamic potential. Let us only consider the following. Thermodynamics teach, that however composite the equilibrium may be, the total potential of every component must be the same in two phases which are in equilibrium; the kinetic theory, or in plain language, common sense that in all those cases equilibrium is only possible when an equal number of particles of each substance passes from the first phase into the second phase and vice versa. Now VAN DER WAALS has shown [1]) that in the case of equilibrium of vapour and liquid, whether in a simple substance or a binary mixture, the two conditions are simply the same fact stated in different terms. It does not seem hazardous to me nor jumping to conclusions to conclude from this that these two conditions, which are always at the same time fulfilled or not fulfilled, also in other cases will agree in signification and that therefore the physical meaning of the thermodynamic potential [2]) of an homogeneous phase, on which no external forces act, is nothing but the number of particles which per second reach a wall as defined in the preceding communication § 4 under 2, if this wall is thought in the midst of that homogeneous phase.

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[1]) Verslagen Kon. Akad. Amsterdam (4) **3**, 205 and Arch. Néerl. **30**, 137.

[2]) I choose purposely the words "that the physical meaning of etc." and not "that the thermodynamic potential is equal to etc." For the equality of the two quantities would require an "absolute" scale of thermodynamic potential. For from the equality of the conditions mentioned follows only:

$$M\mu = F(N) + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where F is such a function, that $M\mu$ is a one-valued function of N and reversely N of $M\mu$. This however, is not of material influence, for formula (1) expresses only, that we begin to count the thermodynamic potential from another point than the number of particles (which agrees with the fact that our thermodynamic potentials always include an undetermined constant) and that we make use of another unity when measuring one quantity than when measuring the other. There is therefore perfect concordance of our case and that of the temperature measured e.g. according to Celsius and certainly nobody will object to the statement, also when he thinks of this temperature scale, that the physical meaning of the temperature is the mean vis viva of the centres of gravity of the molecules.

Yet this definition requires some further elucidation, because the number of molecules under consideration reaches a bounding plane of the phase, which does not exercise any attraction on those particles, whereas on the particles discussed above and whose number has been calculated by VAN DER WAALS, viz. those which pass from the one phase into the other, a force *does* work directed to the other phase. But this difference is in my opinion, only apparent. Also in the equations arrived at by VAN DER WAALS, one member refers exclusively to one phase, the other to the second phase: there are no terms in them consisting of factors, one of which refers to the first phase, another to the second. That we had to arrive at that result, may be easily understood, for the thermodynamic potentials themselves refer either to the one or to the other phase and are quite determined by the condition of that phase.

That at least in the definition of the thermodynamical potential one number may be put instead of the other, appears as follows. Let us consider a liquid in equilibrium with its vapour. The number of particles that now passes, per unit of area, through the bounding layer is that which VAN DER WAALS treats of; let us now place on this liquid a layer of a substance which does not attract the molecules; let this layer be thick with respect to the spheres of action and provided with narrow channels. The number of particles that penetrates into these channels on either side is the number, which we used in our definition. Now I assert that the introduction of this layer cannot disturb the equilibrium of the homogeneous phases [1]), i.e. their pressure and concentrations will not change. For if this had been the case we should have been able to construct with the aid of such a layer a so-called perpetuum mobile of the second kind, and should have come in conflict with the second law of the theory of heat. From this follows that equality of the number

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[1]) The equilibrium in the non-homogeneous, capillary layer *is* disturbed by introducing such a wall. For, as VAN DER WAALS has shown (cf. the footnote p. 735) the equilibrium in a plane of such a layer is only stable in consequence of the attractive forces exercised by the surroundings. When introducing the solid layer in question the condition in the transition layers will be considerably modified, which might also be anticipated. This does not affect our reasoning, for by the word "homogeneous" we have positively excluded these transition layers in our definition. That this was necessary in any case appears already from the fact, to which we have already called attention above, that the thermodynamic potential for such layers is no longer the quantity which determines the equilibrium, but that it is replaced by the total potential. We must therefore certainly not have recourse to such layers, in order to get acquainted with the thermodynamic potential in its simplest signification.

meant by VAN DER WAALS implies equality of that used by us in the definition, and that we may therefore substitute the latter for the former in the definition of the thermodynamic potential.

§ 5. In this way we have obtained a clear idea of the nature of the thermodynamic potential, which so far as I can see is in no respect second to that of temperature, external pressure, kinetic pressure, number of collisions, mean length of path etc. That for all this it is not always easy to derive in a special case the value of the thermodynamic potential from this kinetic meaning is self-evident, as well as that it will possibly always be more desirable to derive the thermodynamic potential by means of thermodynamic functions than from direct kinetic considerations. It is true that we do not avoid the latter in this way either, but we make use of the result of these considerations, as it is given in the equation of state. In these two respects, however, the thermodynamic potential is in no way inferior to the osmotic pressure, as appears from my two preceding communications, specially from § 8 of the second.

§ 6. Mr. VAN LAAR informs us, that in connection with his address he had been asked "to supply something as a substitute" for the osmotic pressure and the kinetic conception of it, something that "conveys some meaning". [1]) This request seems by no means so unreasonable to me as it seemed to Mr. VAN LAAR and I think that I have complied with it in the preceding pages. Now I may be allowed to prove that this "something else" is at the same time "something better".

First of all it seems not very appropriate to me to give a quantity of pressure such a prominent place in the theory of mixtures. As soon as we deal with this theory in general, i. e., include also external forces and capillary phenomena (which are very often of great importance, I need only mention critical points) it appears, that the pressure is a quantity we may only handle with great caution and which may certainly not be treated as fundamental variable. [2]) In a much higher degree this objection holds for the osmotic pressure. For this is, as we have seen, not a quantity which is characteristic for the state in which the solution is; the peculiar laws of the osmotic pressure are not due to the fact that matter in dilute solution is in a particular, peculiar condition, they originate — in their generality — only from our arbitrariness, which by means of fictitious ideas, calls peculiar conditions into existence on paper, which never exist in reality. For let us not close our eyes to this

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[1]) Chem. Weekblad 1905 No. 9, § 3. The inverted commas are Mr. VAN LAAR's.

[2]) Cf. the footnote on p. 735.

undeniable fact — and least of all should they do so who are so averse to "hypotheses" — that though all those semipermeable walls may be realised in a few cases, yet we have on the other hand thousands and thousands of cases, where we have not the slightest foundation for belief in their existence. What reason can there be for assuming, that there will ever be found a wall permeable to toluol, but not to benzol, and another wall, permeable to benzol and not to toluol, and what else is it but a fiction to speak of a wall, permeable to cane-sugar and not to water. (For also this is necessary, see VAN 'T HOFF, Vorlesungen II, 24). And let us even put the most favourable case: that such walls existed really, does it not remain perfect fiction then to try and treat the theory of concentrated solutions with them? We need only bear in mind that steel, our strongest material, however thick it is taken, can hardly bear pressures above 5000 atms, what to think then of a semipermeable wall for which such a pressure is but a trifle. And now I do not in the least object to such fictitious ideas when they are quite unavoidable — this is sufficiently proved by what precedes — but what is the use of using them, when we have another quantity of simple signification, which *is* characteristic of the condition in which the mixture is, which can be defined solely from the properties of the substance with which we have to deal?

To this comes another difficulty. He who works with the osmotic pressure — history teaches it — is but too apt to consider a mixture not as an individual, which must be examined in itself and must be known from itself, but as another substance (solvent), more or less modified by the presence of the "dissolved substance". In this way we lose quite sight of the fact, that the two components in a mixture are present in exactly the same condition (the singular theory of the "gaslike nature" of the dissolved substance proves it); we begin to overlook, that "dissolved substance" and "solvent" are perfectly arbitrary names, which have only a right to existence when we confine ourselves to one of the two extreme cases; we are led to try and explain the properties of a substance from those of another, which is often in quite different circumstances; we begin to apply all kinds of hazardous approximations and compromises; we get to the most extraordinary association and dissociation theories. How fruitful on the contrary the opposite method is, the whole work of VAN DER WAALS, the experimental and theoretic material (inter alia on the behaviour of mixtures with respect to the law of corresponding states) gathered specially at Leiden may prove.

§ 7. Now one may object to this, that all these are theoretical objections of more or less value, but that they are outweighed by the practical advantage that calculations with the osmotic pressure are so much simpler than with the thermodynamic potential, but this objection lacks all foundation. For kinetic calculation cannot be meant in this, and for the thermodynamic calculation it holds on the contrary, that when making use of the thermodynamic potential we need not take one step, which we are not obliged to take in exactly the same way when making use of the osmotic pressure. In order to prove this, I should like to reprint and follow step by step the proof given by VAN 'T HOFF in his Vorlesungen, but as this proof — carefully selected by VAN 'T HOFF from considerations partly from himself, partly from Lord RAYLEIGH, partly from Dr. DONNAN, so undoubtedly the finest and simplest to be found — covers two pages in print, I shall only indicate the principal operations and put in juxtaposition the operations, which are required for the thermodynamic potential with the same neglections.

1. Remove from a solution of osmotic pressure P a quantity of solvent, occupying a volume v. The substance yields an amount of work $\underline{-Pv}$.	1. The thermodynamic potential is: $M\mu = pv + \int_{v_0}^{v} pdv + MRTl(1-x) + F(T) + \int_{v_0}^{v} \left(\frac{\partial p}{\partial x}\right)_{vT} dv$ pv becomes here $\underline{p_0 v_0}$.
2. Neglect the change in vapour tension and the contraction of the solution. (This is not expressly stated, but is evidently necessary for the proof).	2. Neglect the variability of p with x and the compressibility of the liquid, then $\int_{v_0}^{v} \left(\frac{\partial p}{\partial x}\right) dv = 0$ en $\int_{v_0}^{v_{c_1}} pdv = 0.$
3. Let the quantity of dissolved substance, dissolved in v, evaporate diosmotically; let its volume be V, the work done is: $\underline{pV}$ (when we neglect v by the side of V).	3. $\int_{v_{c_1}}^{v_{c_2}} pdv = \underline{p_c (v_{c_2}} - v_{c_1})$

4. Let the vapour expand to infinite volume, the work done is: $\int_V^\infty p\,dv = \underline{MRTl\frac{V_\infty}{V}}$	4. $\int_{v_{e_2}}^{\gamma} p\,dv = \underline{MRTl\frac{\gamma}{v_{e_2}}}$.
5. Now press the vapour again into the solution, then a work is done by the substance: $-\int_V^\infty p\,dv = -\underline{MRTl\frac{V_\infty}{V}}$	5. The thermodynamic potential of pure water is: $M\mu = pv + \int_{v_g}^{v} p\,dv + F(T)$ $\int_{v_g}^{\gamma} p\,dv = \underline{MRTl\frac{\gamma}{v_{e_2}}}$; $pv = \underline{p_e v_{e_2}}$
6. The total quantity of work must be zero, so: $Pv = pV$	6. The two potentials are the same, so: $(p_0 - p_e)\, v_{e_1} = -MRTl(1-x)$

which in spite of the different notation is the same, when log $(1 - x)$ is replaced by $-x$.

So it is seen that to every integration on the right corresponds an operation on the left of exactly the same nature, though it does not always refer to the same substance. The only difference is that on the right the integration is carried out directly and that on the left pistons and membranes are worked with. Now I do not think that any one can easily set greater store by a clear physical meaning of operations than I do, but that we should not be able to carry out an integration along an isotherm without bringing in two pistons and three membranes, seems rather too much of a good thing.

§ 8. And now we have considered the most favourable case: dilute solutions; how is it with more concentrated ones? It will certainly be possible to devise also for them cycles so that the calculations introduced in my first paper may be carried out without mentioning the *name:* "thermodynamic potential", but it will not be found possible by a thermodynamic method to draw up a formula for the osmotic pressure without determining the integrals occurring in it.

In this way it would seem as if the two methods were essentially the same; it is not so, the osmotic pressure method has drawbacks, of which the other is free. For what is it that we really wish to learn by the *two* different methods? Not the osmotic pressure itself, and the properties of the solutions under that pressure, that is for concentrated solutions: in sensibly compressed state. What we aim at are the properties of solutions under the pressure of their saturated vapour: lowering of the freezing point and the vapour tension, rise of the boiling point and coefficient of division or more accurately (cf § 6 above) freezing point, boiling point, vapour tension of the mixture and the concentration of coexisting phases. And this does not only apply to physicists and chemists, who rarely if ever work with membranes, but also to biologists, to whom they are of the greatest importance. For differences in pressure of about ten atmospheres will probably hardly ever occur in biologic experiments and a fortiori not in the living organism either. The equilibrium between two solutions will therefore never be established by difference in *pressure,* but by the difference in *concentration* required to make the pressure equal. So we have not to deal here either with compressed solutions. [1])

For the calculation this implies that when making use of the thermodynamic potential we need extend the integration along the isotherm only to the pressure p_c and the thermodynamic potential may then be determined with sufficient approximation from the well-kwown formula for the vapour pressure:

$$-\log\frac{p_c}{p_k} = f\left(\frac{T_k}{T} - 1\right)$$

though it be with the factor 7 determined experimentally instead of the value 4 found theoretically. But if the osmotic pressure is used we can naturally not do without the integration up to p_0 $\left(\text{in the term} \int \frac{\partial p}{\partial x}\,dx\right)$ and it is exactly this part of the isotherm which is known the least, where e. g. the variability of b is felt strongest, even the only term, on which it has influence when the just mentioned formula for the vapour pressure is used. Quite unnecessarily therefore the result is made less reliable by the introduction of the osmotic pressure.

And supposed even that we had found the desired expression, of what use could it be to us? It is true that the quantities, which we really wish to know and which I mentioned before, are con-

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[1]) For this reason hardly anything would be lost when in the discussion of really osmotic questions it was made a rule to treat them without "osmotic pressure" and simply to introduce the concentrations on either side of the wall; whereas in this way there would be a great gain in lucidity of expression, witness the example cited by Mr. VAN LAAR (l.c. § 5). For the interpretation given there may be correct or incorrect, it can hardly be denied that the cited phrases may be easily misunderstood in the sense of the well-known question of PUPIN, which has so repeatedly been seriously discussed, how e. g. a $CaCl_2$ solution of no less than 53 atms. osmotic pressure could be kept in a thin glass vessel without making it burst asunder!

nected in a simple way with the osmotic pressure in dilute solutions, but we have not a single reason to assume this also for concentrated solutions, or rather we may state with almost perfect certainty that this will not be the case. How on the other hand those quantities may be determined with the aid of the thermodynamic potential, VAN DER WAALS taught us already fifteen years ago.

§ 9. And let us finally not forget that though solutions of non-volatile substances at low temperatures *do* play an important part in nature, yet they are not the *only* substances which exist, nor the only ones which deserve scientific consideration. And yet, the theory of the osmotic pressure must necessarily be confined to them. One is so customed to derive the laws of the rise of the boiling point and the decrease of the vapour tension from the osmotic pressure, but it is generally forgotten, that many mixtures have on the contrary lowering of the boiling point and rise of the vapour tension [1]), and that at any rate if the dissolved substance is but in the least volatile, the changes in boiling point and vapour tension cannot be derived any more from the osmotic pressure. And it is obvious why. It is inherent in every definition of the osmotic pressure, that it can only be applied to those cases, in which one component may be separated from the mixture in pure condition, as NERNST has clearly stated for the first time. Hence this does not only exclude the whole region of higher temperatures, at which all substances become more or less volatile, but also all cases of not perfect separation in the liquid or solid state. Also the lowering of the freezing point is touched by this objection. It is true that the lowering of the freezing point may be computed from the osmotic pressure, but only when, as in water and sugar, the solid substance, which deposits, is not of variable composition. Solid solutions and mixed crystals, which attract at present so much attention in chemistry, cannot be treated in this way.

Physical chemistry in its present state reminds us strongly with regard to its quantitative part, of the navigation of a people, which does not yet know the compass. The coasting-trade is carried on with great vigour, the same limited region is traversed again and again; but they do not dare to venture on the main sea far from the coast, and with reason, for great is the danger of ruin in the towering waves of random hypotheses. This can only be remedied by a trustworthy compass. Physical chemistry may obtain it if it will abandon the method of the osmotic pressure and adopt that of the thermodynamic potential in connection with a well-grounded equation of state.

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[1]) Cf. Théorie Moléculaire § 17.

Astronomy. — *"Approximate formulae of a high degree of accuracy for the relations of the triangles in the determination of an elliptic orbit from three observations."* By **J. WEEDER**. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN.)

The places in space occupied by the observed planet or comet at the instants t_1, t_2 and t_3 are indicated by P_1, P_2 and P_3, the position of the sun is indicated by Z.

For the determination of an elliptic orbit we mainly proceed as follows: first by means of successive approximation we derive the distances $P_1Z = r_1$, $P_2Z = r_2$, $P_3Z = r_3$ from the data of the observations, from which distances the elements of the orbit are directly computed without using the intervals of time. From the obtained ellipse we can again derive the intervals of time in order to test the accuracy of the results and compare them with the real ones. In case they perfectly agree, the ellipse found satisfies all the conditions of the problem, but as a rule this is not so. The cause of it is that, in order to calculate the distances r_1, r_2, and r_3, we use approximate formulae to express the relations $\dfrac{\text{triangle } P_1ZP_2}{\text{triangle } P_1ZP_3} = n_3$ and $\dfrac{\text{triangle } P_2ZP_3}{\text{triangle } P_1ZP_3} = n_1$ in terms of the intervals of time and of the three distances to be found, while neglecting the terms of the 2nd, 3rd or 4th order with respect to the intervals. Indeed, different expressions have been proposed for n_1 and n_3, some recommending themselves by greater simplicity, others by greater accuracy, but, so far as I know, in the general case of unequal intervals none of them contain the quantities of the fourth order with respect to the intervals.

The errors in the calculated distances r_1, r_2 and r_3 and those in the elements of the orbit derived from them are generally of the same order as that of the terms omitted in the expressions for n_1 and n_3.

Accurate and at the same time simple expressions for n_1 and n_3 have been given by J. W. GIBBS[1]).

The purpose of this paper is to develop, according to GIBBS' method, expressions for n_1 and n_3 which include the terms of the 4th order; at the same time a new derivation of GIBBS' relations is given.

In the ellipse sought let P be the position of the heavenly body at the time t, x and y its heliocentric rectangular coordinates in the

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[1]) J. W. GIBBS: On the determination of elliptic orbits from three complete observations. Memoirs of the national academy of sciences. Vol. IV, 2; p. 81. Washington 1889.

plane of the orbit, and $r = ZP$, then x and y satisfy the following differential equations

$$\frac{d^2x}{d\tau^2} = -\frac{x}{r^3} = \ddot{x} \qquad \frac{d^2y}{d\tau^2} = -\frac{y}{r^3} = \ddot{y}\,.$$

wherein we have put $\tau = k(t - t_1)$ as independent variable instead of the time t; τ is therefore the time reckoned from the epoch of the first observation and expressed in the unit for which, in the solar system, the acceleration $= 1$ at a distance from the sun which is adopted as unit of length; k is the constant of GAUSS [$\log k = 8.235\ 581\ 4414 - 10$].

While designating the rectangular coordinates of P_1, P_2, P_3 by corresponding indices I remark that $n = \frac{x_1 y - y_1 x}{x_1 y_3 - y_1 x_3} = \frac{\text{triangle } P_1ZP}{\text{triangle } P_1ZP_3}$ satisfies a similar differential equation as x and y, namely:

$$\frac{d^2n}{d\tau^2} = -\frac{n}{r^3} = \ddot{n}\,.$$

At the times $t_1\ (\tau = 0)$, $t_2\ (\tau = \tau_3)$, $t_3\ (\tau = \tau_2)$
the values of n are 0, $+n_3$, $+1$ and
the values of $\ddot{n}$ 0, $-\frac{n_3}{r_2^{\,3}}$, $-\frac{1}{r_3^{\,3}}$

Consequently in the development of n in a series of ascending powers of τ after MAC LAURIN, the terms of the power zero and 2 will be wanting. If in this expansion we do not go farther than the 4th power of τ, we require only 3 indefinite coefficients which may be eliminated from the following 4 relations:

$$\begin{aligned}
n_3 &= K_1\tau_3 + K_3\tau_3^{\,3} + K_4\tau_3^{\,4} + f_4 \\
1 &= K_1\tau_2 + K_3\tau_2^{\,3} + K_4\tau_2^{\,4} + F_4 \\
-\frac{n_3}{r_2^{\,3}} &= +6K_3\tau_3 + 12K_4\tau_3^{\,2} + f_2 \\
-\frac{1}{r_3^{\,3}} &= +6K_3\tau_2 + 12K_4\tau_2^{\,2} + F_2\,.
\end{aligned}$$

The remaining relation yields an expression for n_3 in τ_2, τ_3, r_2, r_3 and the remainders f_4, F_4, f_2 and F_2.

The indices which I have used for the remainders, indicate the order of these terms with respect to τ; F_4, for instance, which begins with $K_5\tau_2^{\,5}$ is of the 4th order of τ, which is evident when we express the coefficients K in terms of the derivatives of n for $\tau = 0$ and develop the latter by means of the differential equation for n as products of $\ddot{n}_0$. For clearness I shall here give this development:

$$\frac{d^3n}{d\tau^3} = -n\dot{z} - z\dot{n}\,, \quad \text{where } z \text{ is put for } \frac{1}{r^3}$$

$$\frac{d^4n}{d\tau^4} = (z^2 - \ddot{z})\,n - 2\dot{z}\,\dot{n}$$

$$\frac{d^5n}{d\tau^5} = (4z\dot{z} - \dddot{z}\,)\,n + (z^2 - 3\ddot{z})\,\dot{n}\,.$$

From the differential equation $\frac{d}{d\tau}(r^3\ddot{r} + r) = 0$, satisfied by r, we can derive the following differential equation for $z = \frac{1}{r^3}$:

$$\dddot{z} = \dot{z}\left(5\,\frac{\ddot{z}}{z} - \frac{40}{9}\,\frac{\dot{z}^2}{z^2} - z\right)$$

which may serve to eliminate $\dddot{z}$ from the higher derivatives.

$$\frac{d^5n}{d\tau^5} = 5\left(z - \frac{\ddot{z}}{z} + \frac{8}{9}\,\frac{\dot{z}^2}{z^2}\right)\dot{z}n + (z^2 - 3\ddot{z})\,\dot{n}\,.$$

For $\tau = 0$, n is equal to zero and $\dot{n} = K_1$, hence

$$K_3 = -\frac{1}{6}\,z_1K_1 \quad . \quad K_4 = -\frac{1}{12}\,\dot{z}_1K_1 \quad , \quad K_5 = \frac{z_1^{\,2}-3\ddot{z}_1}{120}\,K_1\,.$$

If we substitute the expressions for the coefficients K in the second of the 4 relations, this becomes:

$$1 = K_1\tau_2 \left\{1 - \frac{1}{6}\,z_1\tau_2^{\,2} - \frac{1}{12}\,\dot{z}_1\tau_2^{\,3} + \frac{z_1^{\,2}-3\ddot{z}_1}{120}\,\tau_2^{\,4}\ldots\right\}$$

and from this it clearly appears that K_1 and the other coefficients K, in so far as they depend on the intervals, are of the order $\frac{1}{\tau_2}$.

From the 4 relations with the indefinite coefficients K_1, K_3, K_4 we find by eliminating the latter:

$$\left\{n_3 - f_4 - \frac{\tau_2^{\,2}+\tau_2\tau_3-\tau_3^{\,2}}{12}\left(\frac{n_3}{r_2^{\,3}} + f_2\right)\right\}\tau_2 = \left\{1 - F_4 - \frac{\tau_3^{\,2}+\tau_3\tau_2-\tau_2^{\,2}}{12}\left(\frac{1}{r_3^{\,3}} + F_2\right)\right\}\tau_3\,.$$

From this equation I solve:

$$n_3 = \frac{\tau_3}{\tau_2}\,\frac{1 - \dfrac{\tau_3^{\,2}+\tau_3\tau_2-\tau_2^{\,2}}{12r_3^{\,3}}}{1 - \dfrac{\tau_2^{\,2}+\tau_2\tau_3-\tau_3^{\,2}}{12r_2^{\,3}}} + R_4$$

where

$$R_4 = \frac{f_4 + f_2 \dfrac{\tau_2^2+\tau_2\tau_3-\tau_3^2}{12} - \dfrac{\tau_3}{\tau_2}\left\{F_4 + F_2 \dfrac{\tau_3^2+\tau_3\tau_2-\tau_2^2}{12}\right\}}{1 - \dfrac{\tau_2^2+\tau_2\tau_3-\tau_3^2}{12 r_2^3}} .$$

This remainder is apparently of the 4th order with respect to the intervals. If we neglect the terms of higher order than the fourth we can replace in R_4: f_4 by $K_5\tau_3^5$, F_4 by $K_5\tau_2^5$, f_2 by $20K_5\tau_3^3$ and F_2 by $20K_5\tau_2^3$; and we obtain as supplementary term, accurate to the fourth order

$$+\frac{1}{3} K_5\tau_3 (\tau_2 + \tau_3)(\tau_2 - \tau_3)(2\tau_2 - \tau_3)(\tau_2 - 2\tau_3) ,$$

which expression vanishes on account of the last factor, in the case of equal intervals.

The corresponding approximate formula for n_1 can be derived by developing the relation $\dfrac{\text{triangle } PZP_3}{\text{triangle } P_1ZP_3}$, depending on the time, in ascending powers of $k(t_3 - t)$ and further by proceeding in the same manner as we have done for n_3. The result for n_1 is derived from the preceding result by interchanging the indices 1 and 3, in which case τ_1 stands for $k(t_3 - t_2)$, hence:

$$n_1 = \frac{\tau_1}{\tau_2} \frac{1 - \dfrac{\tau_1^2+\tau_1\tau_2-\tau_2^2}{12 r_1^3}}{1 - \dfrac{\tau_2^2+\tau_2\tau_1-\tau_1^2}{12 r_2^3}} - R_4 .$$

The remainder of n_1 is not only of the same order as that of n_3, but even in the 4th order it has the same absolute value, with a different sign however. This appears clearly when, using the relation $\tau_2 = \tau_1 + \tau_3$, we express the correction of the 4th order for n_3 in terms of τ_1 and τ_3; this correction takes the following form, which is symmetrical with respect to τ_1 and τ_3:

$$\frac{1}{3} K_5\tau_1\tau_3 (2\tau_1 + \tau_3)(\tau_1 + 2\tau_3)(\tau_1 - \tau_3) .$$

In the remainder of n_1 the coefficient L_5 may be assumed equal to K_5. Therefore these approximate formulae always give for $n_1 + n_3$ an accurate value (comp. p. 758), including the terms of the 4th order of the interval.

The denominators of these expressions for n_1 and n_3, although here different in form, are indeed identical; the expressions themselves agree with those derived from the fundamental equation adopted by GIBBS between the 3 vectors ZP_1, ZP_2 and ZP_3 which can be easily reduced to the form:

$$\frac{\tau_1}{\tau_2}\left(1-\frac{\tau_1{}^2+\tau_1\tau_2-\tau_2{}^2}{12r_1{}^3}\right)\overline{ZP}_1+\frac{\tau_3}{\tau_2}\left(1-\frac{\tau_3{}^2+r_3\tau_2-\tau_2{}^2}{12r_3{}^3}\right)\overline{ZP}_3=$$
$$=\left(1-\frac{\tau_2{}^2+\tau_2\tau_3-\tau_3{}^2}{12r_2{}^3}\right)ZP_2.$$

This equation is satisfied by the real places of the object when we neglect a residual of the 5th order with respect to the intervals of time. This signifies little, however, when compared with the accuracy of the places calculated after Gibbs' method, which rigorously satisfy them; for each set of vector corrections $\Delta\, ZP_1$, $\Delta\, ZP_2$ and $\Delta\, ZP$ does not lessen the agreement below the 5th order with respect to the intervals of time, provided they satisfy the condition

$$\frac{\tau_1}{\tau_2}\,\Delta\, ZP_1+\frac{\tau_3}{\tau_2}\,\Delta\,\overline{ZP}_3=\Delta\, ZP_2$$

and are not below the 3rd order with respect to those intervals.

Because in Gibbs' method the relations n_1 and n_3 contain errors of the 4th order, it would follow from this that the places computed after this method are inaccurate in the 4th order also. But thanks to the circumstance that Gibbs' method includes for $n_1 + n_3$ the terms of the 4th order in all cases, its results are yet correct in terms of the 4th order.

This special feature of Gibbs' method has been pointed out by E. Weiss [1]).

In order to obtain for n_1 and n_3 expressions including in all cases the 4th order of the intervals of time and containing besides them only $\frac{1}{r_1{}^3}=z_1$, $\frac{1}{r_2{}^3}=z_2$ and $\frac{1}{r_3{}^3}=z_3$, I have used the relation derived on p. 754 $K_3=-\frac{1}{6}z_1\,K_1$.

Starting from the development

$$n=K_1\,\tau+K_3\,\tau^3+K_4\,\tau^4+K_5\,\tau^5+\text{remainder of the 5th order}$$

I can make use of the following relations between the coefficients K, the quantities z_1, z_2, z_3 and n_3.

$$\begin{aligned}
n_3 &= K_1\,\tau_3+K_3\,\tau_3{}^3+K_4\,\tau_3{}^4+K_5\,\tau_3{}^5+f_5\\
1 &= K_1\,\tau_2+K_3\,\tau_2{}^3+K_4\,\tau_2{}^4+K_5\,\tau_2{}^5+F_5\\
-z_2\,n_3 &= +6K_3\,\tau_3+12K_4\,\tau_3{}^2+20K_5\,\tau_3{}^3+f_3\\
-z_3 \quad &= +6K_3\,\tau_2+12K_4\,\tau_2{}^2+20K_5\,\tau_2{}^3+F_3\\
0 &= K_1\,z_1+6K_3
\end{aligned}$$

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[1]) E. Weiss, Ueber die Bestimmung der Bahn eines Himmelskörpers aus drei Beobachtungen. Denkschriften der Mathem. Naturw. Classe der Wiener Akademie. Bd. LX (1893).

By eliminating K_1, K_3, K_4 and K_5 we derive from them the following equation:

$$\tau_2 \left\{ (n_3 - f_5)\left(1 + \frac{\tau_2^2(2\tau_2 - 5\tau_3)}{60\tau_3} z_1\right) - \right.$$

$$\left. - (n_3 z_2 + f_3)\left(\frac{2\tau_2^3 + 2\tau_2^2\tau_3 + 2\tau_2\tau_3^2 - 3\tau_3^3}{60\tau_3} - \frac{\tau_2^2\tau_3(4\tau_2 - 3\tau_3)}{720} z_1\right)\right\} =$$

$$= \tau_3 \left\{ (1 - F_5)\left(1 + \frac{\tau_3^2(2\tau_3 - 5\tau_2)}{60\tau_2} z_1\right) - \right.$$

$$\left. - (z_3 + F_3)\left(\frac{2\tau_3^3 + 2\tau_3^2\tau_2 + 2\tau_3\tau_2^2 - 3\tau_2^3}{60\tau_2} - \frac{\tau_3^2\tau_2(4\tau_3 - 3\tau_2)}{720} z_1\right)\right\}.$$

For shortness I replace the expressions which only depend on the intervals of time by single letters, putting

$$A_{2.3} = \frac{\tau_2^2(2\tau_2 - 5\tau_3)}{60\tau_3} \qquad A_{3.2} = \frac{\tau_3^2(2\tau_3 - 5\tau_2)}{60\tau_2}$$

$$B_{2.3} = \frac{-2\tau_2^3 - 2\tau_2^2\tau_3 - 2\tau_2\tau_3^2 + 3\tau_3^3}{60\tau_3} \qquad B_{3.2} = \frac{-2\tau_3^3 - 2\tau_3^2\tau_2 - 2\tau_3\tau_2^2 + 3\tau_2^3}{60\tau_2}$$

$$C_{2.3} = \frac{\tau_2^2\tau_3(4\tau_2 - 3\tau_3)}{720} \qquad C_{3.2} = \frac{\tau_3^2\tau_2(4\tau_3 - 3\tau_2)}{720}.$$

then the equation, solved with respect to n_3, yields for this relation the following expression:

$$n_3 = \frac{\tau_3}{\tau_2} \times \frac{1 + A_{3.2} z_1 + B_{3.2} z_3 + C_{3.2} z_1 z_3}{1 + A_{2.3} z_1 + B_{2.3} z_2 + C_{2.3} z_1 z_2} + R_5 \quad . \quad . \quad (I)$$

The remainder R_5 contains the quantities F_5, f_5, F_3 and f_3; for these I set, in order to form the value of R_5 in the 5th order with respect to the intervals of time, $f_5 = K_6\tau_3^6$, $F_5 = K_6\tau_2^6$, $f_3 = 30\,K_6\tau_3^4$ and $F_3 = 30\,K_6\tau_2^4$; I then find:

$$R_5 = \tfrac{1}{2} K_6 (\tau_2^4 - \tau_2^3\tau_3 - \tau_2^2\tau_3^2 - \tau_2\tau_3^3 + \tau_3^4)\,\tau_3(\tau_2 - \tau_3).$$

As the root of the 4th power equation $1 - x - x^2 - x^3 + x^4 = 0$ lies between zero and 1, viz. $x = 0{,}5806$, the terms of the 5th order will vanish from the residual, if $\tau_3 = 0.5806\,\tau_2$.

We obtain the corresponding approximation for n_1 when we derive an expression from that for n_3 by interchanging everywhere the indices 1 and 3, hence:

$$n_1 = \frac{\tau_1}{\tau_2} \times \frac{1 + A_{1.2} z_3 + B_{1.2} z_1 + C_{1.2} z_3 z_1}{1 + A_{2.1} z_3 + B_{2.1} z_2 + C_{2.1} z_3 z_2} \quad . \quad . \quad . \quad (II)$$

The meaning of the new letters agrees with the rules for the interchange of the indices 1 and 3.

$$A_{1.2} = \frac{\tau_1^{\,2}\,(2\tau_1 - 5\tau_2)}{60\,\tau_2} \qquad A_{2.1} = \frac{\tau_2^{\,2}\,(2\tau_2 - 5\tau_1)}{60\,\tau_1}$$

$$B_{1.2} = \frac{-2\tau_1^{\,3} - 2\tau_1^{\,2}\,\tau_2 - 2\tau_1\,\tau_2^{\,2} + 3\tau_2^{\,3}}{60\,\tau_2} \qquad B_{2.1} = \frac{-2\tau_2^{\,3} - 2\tau_2^{\,2}\,\tau_1 - 2\tau_2\,\tau_1^{\,2} + 3\tau_1^{\,3}}{60\,\tau_1}$$

$$C_{1.2} = \frac{\tau_1^{\,2}\,\tau_2\,(4\tau_1 - 3\tau_2)}{720} \qquad C_{2.1} = \frac{\tau_2^{\,2}\,\tau_1\,(4\tau_2 - 3\tau_1)}{720}.$$

In the remainder which belongs to this expression for n_1, the term of the 5th order:

$$\tfrac{1}{2}\,L_6\,(\tau_2^{\,4} - \tau_2^{\,3}\,\tau_1 - \tau_2^{\,2}\,\tau_1^{\,2} - \tau_2\,\tau_1^{\,3} + \tau_1^{\,4})\,\tau_1\,(\tau_2 - \tau_1)$$

will vanish if $\tau_1 = 0.5806\,\tau_2$, therefore the term can never vanish at the same time for n_1 and for n_3.

L_6 occurs as coefficient of τ_6 in the development of $\dfrac{\text{triangle } PZP_3}{\text{triangle } P_1ZP_3}$ in ascending powers of $\tau = k\,(t_3 - t)$, while K_6 indicates the coefficient of τ^6 in the development of $\dfrac{\text{triangle } P_1ZP}{\text{triangle } P_1ZP_3}$, where the variable τ means $k\,(t - t_1)$.

If the first of these developments were performed in powers of $k\,(t - t_3) = -\tau$, there would exist between each pair of corresponding coefficients a relation implying that its sum with regard to τ_2 would be of one order higher than the coefficients themselves. Therefore, neglecting terms of higher order than the 5th, we may assume that the coefficients K_6 and L_6 are identical in absolute value, yet differ in sign.

Of a similar relation I have made use on p. 755, where in the remainders of the 4th order I assumed the coefficients identical. In the new expressions for n_1 and n_3 we can now, by putting $L_6 = -K_6$, derive the following value for the remainder of the 5th order of $n_1 + n_3$:

$$\tfrac{1}{2}\,K_6\,\tau_1\tau_2\tau_3\,(\tau_1 - \tau_3)\,(2\tau_2^{\,2} + \tau_1\tau_3).$$

Therefore when the intervals of time are equal, the error in $n_1 + n_3$ is of the 6th order.

If according to the indicated method we include the terms of the 4th order, we find for the 3rd relation $\dfrac{\text{triangle } P_2ZP_1}{\text{triangle } P_3ZP_2} = \dfrac{n_3}{n_1}$

$$\frac{n_3}{n_1} = \frac{\tau_3}{\tau_1} \times \frac{1 + A_{3.1}z_2 + B_{3.1}z_3 + C_{3.1}z_2z_3}{1 + A_{1.3}z_2 + B_{1.3}z_1 + C_{1.3}z_2z_1}, \quad . \quad . \quad . \quad (III)$$

and with it as remainder of the 5th order

$$+\tfrac{1}{2}\,K_6\,\frac{\tau_3}{\tau_1}\,\tau_2^{\,2}(\tau_3^{\,4} + \tau_3^{\,3}\tau_1 - \tau_3^{\,2}\tau_1^{\,2} + \tau_3\tau_1^{\,3} + \tau_1^{\,4})$$

From one of the examples from GAUSS' *Theoria Motus* (Libr. II, Sect. I cc. 156—158) I have computed the 3 relations according to the formulae I, II and III. The rigorously correct values of those relations and the results of GIBBS' expressions for this example I borrow from P. HARZER's *Bestimmung und Verbesserung der Bahnen von Himmelskörpern nach drei Beobachtungen* p. 8.[1])

The heliocentric motion of the planet Pallas was from the 1st to the 3d observation 22°33′.

$$log\,\tau_1 = 9.8362703 \quad log\,\tau_2 = 0.0854631 \quad log\,\tau_3 = 9.7255594$$

$$log\,r_1 = 0.3630906 \quad log\,r_2 = 0.3507163 \quad log\,r_3 = 0.3369508$$

These values for $log\,r$ are also taken from HARZER and differ a little from those according to GAUSS.

Results for	$log\,n_1$	and for	$log\,n_3$
GIBBS	9.7572961	GIBBS	9.6480108
formula II	9.7572928	formula I	9.6480167
rigorous	9.7572923	rigorous	9.6480201.

Formula III yields: $log\,\dfrac{n_3}{n_1} = 9.8907237.$

With the given logarithms agree the following values:

	n_1		n_3		$n_3 : n_1$
rigorous	0.5718634		0.4446518		0.7775491
f. II	0.5718641	f. I	0.4446484	f. III	0.7775418
differences	— 0.0000007		+ 0.0000034		+ 0.0000073

From the expressions given for the remainders of the 5th order I calculated that they are in the ratio of — 9, + 72 and + 140. If we compare these numbers with the residuals, it appears that for our example they would vanish to the 7th decimal if we succeeded in including also the terms of the 5th order in the expressions.

As to the calculation of the quantities A and B dependent on τ_1, τ_2, and τ_3, I remark that it may be performed quickly if we modify these forms in the following way:

$$A_{12} = -\frac{\tau_3}{10}\left(\frac{1}{2}\frac{\tau_1^{\,2}}{\tau_3} + \frac{1}{3}\frac{\tau_1^{\,2}}{\tau_2}\right) \qquad B_{1.2} = +\frac{\tau_1}{10}\left\{\frac{1}{2}\frac{\tau_2^{\,2}}{\tau_1} - \frac{1}{3}\left(\tau_1 - \tau_2 + \frac{\tau_1^{\,2}}{\tau_2}\right)\right\}$$

$$A_{2.1} = -\frac{\tau_3}{10}\left(\frac{1}{2}\frac{\tau_2^{\,2}}{\tau_3} - \frac{1}{3}\frac{\tau_2^{\,2}}{\tau_1}\right) \qquad B_{2.1} = +\frac{\tau_2}{10}\left\{\frac{1}{2}\frac{\tau_1^{\,2}}{\tau_2} - \frac{1}{3}\left(\tau_1 + \tau_2 + \frac{\tau_2^{\,2}}{\tau_1}\right)\right\}$$

$$A_{32} = -\frac{\tau_1}{10}\left(\frac{1}{2}\frac{\tau_3^{\,2}}{\tau_1} + \frac{1}{3}\frac{\tau_3^{\,2}}{\tau_2}\right) \qquad B_{3.2} = +\frac{\tau_3}{10}\left\{\frac{1}{2}\frac{\tau_2^{\,2}}{\tau_3} - \frac{1}{3}\left(\tau_2 + \tau_3 + \frac{\tau_3^{\,2}}{\tau_2}\right)\right\}$$

$$A_{2.3} = -\frac{\tau_1}{10}\left(\frac{1}{2}\frac{\tau_2^{\,2}}{\tau_1} - \frac{1}{3}\frac{\tau_2^{\,2}}{\tau_3}\right) \qquad B_{2.3} = +\frac{\tau_2}{10}\left\{\frac{1}{2}\frac{\tau_3^{\,2}}{\tau_2} - \frac{1}{3}\left(\tau_2 + \tau_3 + \frac{\tau_2^{\,2}}{\tau_3}\right)\right\}$$

$$A_{3\,1} = -\frac{\tau_2}{10}\left(\frac{1}{2}\frac{\tau_3^{\,2}}{\tau_2} + \frac{1}{3}\frac{\tau_3^{\,2}}{\tau_1}\right) \qquad B_{3.1} = +\frac{\tau_3}{10}\left\{\frac{1}{2}\frac{\tau_1^{\,2}}{\tau_3} + \frac{1}{3}\left(\tau_1 - \tau_3 + \frac{\tau_3^{\,2}}{\tau_1}\right)\right\}$$

$$A_{1.3} = -\frac{\tau_2}{10}\left(\frac{1}{2}\frac{\tau_1^{\,2}}{\tau_2} + \frac{1}{3}\frac{\tau_1^{\,2}}{\tau_3}\right) \qquad B_{1\,3} = +\frac{\tau_1}{10}\left\{\frac{1}{2}\frac{\tau_3^{\,2}}{\tau_1} + \frac{1}{3}\left(\tau_3 - \tau_1 + \frac{\tau_1^{\,2}}{\tau_3}\right)\right\}$$

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[1]) Publication der Sternwarte in Kiel, XI.

Chemistry. — "*A few observations on autocatalysis and the transformation of γ-hydroxy-acids, with and without addition of other acids, conceived as an ion-reaction.*" By Dr. A. W. VISSER. (Communicated by Prof. H. J. HAMBURGER).

1. The general equation for catalytic processes as proposed by OSTWALD [1] is:

$$\frac{dx}{dt} = \{k_1 + \Sigma\, k f(x)\}\,(A - x)\,(B - x)\ .\ .\ .\ .$$

in which $\Sigma\, k f(x)$ indicates the changeable catalytic influences. He remarks here that he cannot give a general method for drawing a conclusion from the observed progress of a definite reaction, as to the form of the function $f(x)$.

Whilst studying the transformations of cane-sugar by invertase and of salicin by emulsin [2], I have shown, that, by introducing a correct measure for the *intensity* of a catalyzer, the changeable catalytic influences which occur here, could be indicated during the whole of the progress of the reaction and it appears to me, that the method given in my dissertation for determining that change in intensity during the progress of the reaction may be called a general method for determining the above mentioned function.

The most simple case imaginable is this, that the change in intensity of the catalyzer with the change in concentration of the substance acted upon is constant. In that case:

$$-\frac{dI}{dC} = k_2,$$

therefore:

$$I = k_1 - k_2\, C.$$

In this equation is $I = k_1$ when $C = 0$; therefore k_1 is the intensity of the catalyzer when all has been converted, whilst k_2 is the increase in intensity, when the concentration diminishes with the unity.

Schematically this may be represented as follows:

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[1] OSTWALD, Lehrbuch der Allgem. Chem. II, 2, p. 270.

[2] VISSER, Dissertatie, Amsterdam 1904. A translation will shortly appear in the Zeitschr. f. phys. Chem.

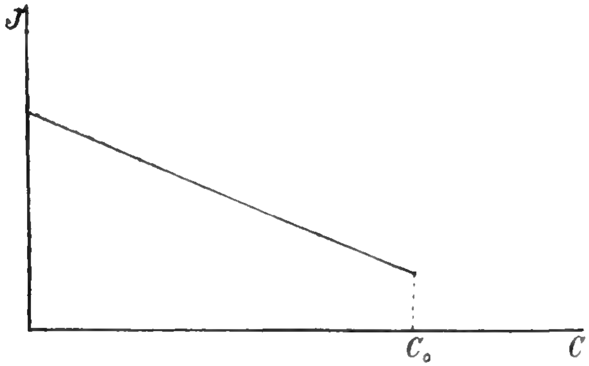

Fig. 1.

The reaction-equation for an unimolecular reaction, where the intensity of a catalyzer plays a rôle, may be represented by :

$$-\frac{dC}{dt} = k\,C\,I.$$

In the supposed case, therefore, by :

$$-\frac{dC}{dt} = k\,(k_1 - k_2\,C)\,C.$$

This is the same equation as the one proposed by OSTWALD [1]) for positive autocatalytic processes, but it seems to me that by introducing the intensity-idea the constants, occurring in the formulae obtain a more definite significance.

Then we have for the negative autocatalysis :

$$\frac{dI}{dC} = k_2$$

$$I = k_1 + k_2\,C$$

and here k_1 is again the intensity when all has been converted and k_2 the decrease in intensity when the concentration diminishes with the unity.

Schematically, this may be represented as follows :

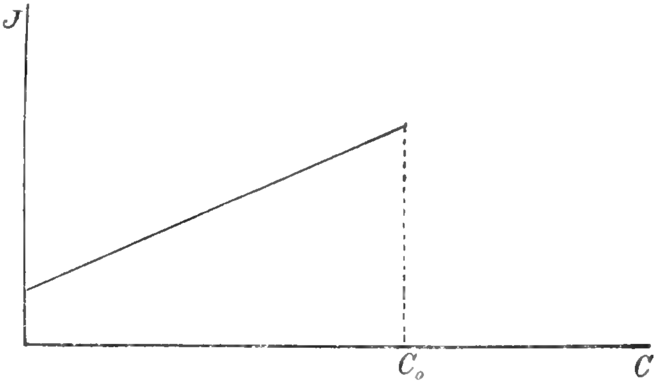

Fig. 2.

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[1]) Lehrb. der Allgem. Chem. II, 2 p. 263.

By positive autocatalysis must then be understood an increase in the intensity of the catalyzer during the progress of the reaction; by negative autocatalysis a decrease in that intensity.

2. As examples of reactions in which autocatalysis occurs, may be mentioned the spontaneous transformations of solutions of γ-hydroxy-acids into their lactones. The acid is split up into ions and according to PAUL HENRY[2]), who studied the transformation of γ-hydroxybutyric and hydroxyvaleric acids, these would convert the unaltered portion of the hydroxyacid and therefore act only catalytically. I have put to myself the question whether these transformations may be considered as being ion-reactions, as it seems to me that it is more rational to view them in this way and as such to bring them within the laws of the mass-action, as we are ignorant as to the true nature of catalysis. Profiting by the researches of PAUL HENRY, I have arrived at a very satisfactory result.

According to this view, the hydroxy-acid is at any moment in equilibrium with its ions and these are converted into the lactone according to the scheme:

$$\gamma\text{-hydroxy-acid} \rightleftarrows \text{positive ions} + \text{negative ions} \quad \text{I}$$
$$\text{positive ions} + \text{negative ions} = \text{lactone} + \text{water} \quad \text{II}$$

As has been stated, PAUL HENRY thinks that in this transformation the non-split portion of the hydroxy-acid only changes into lactone and that the ions exercise only a catalytic action, for he observes, that on addition of HCl or H_2SO_4 the dissociation-degree of the hydroxy-acid is diminished, that is to say, the equilibrium is shifted towards the side of the hydroxy-acid and the concentration of the negative ions of the hydroxy-acid diminishes and if now the dissociated portion of the acid were converted, the reaction-velocity would not rise quite so much under these circumstances. It seems to me that this argument is not correct; the concentration of the negative ions of the hydroxy-acid diminishes by addition of H-ions in the form of HCl, but on the other hand the concentration of the positive H-ions rises enormously and in order to construct the reaction-equation we must multiply these two concentrations by each other if we view the reaction as an ion-reaction.

3. In the first place the spontaneous transformations of the γ-hydroxy-acids must be considered. In constructing reaction-equations it must be borne in mind that the transformations of γ-hydroxy-acids into lactones is not complete.

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[1]) Z. f. phys. Chem. X, p. 111.

Suppose the initial concentration of the γ-hydroxy-acid $= C_0$
Suppose the concentration after a time t $= C$

Suppose that the portion p of the hydroxy-acid is then split into ions, the concentration of the hydroxy-acid will then be $(1-p)\,C$ and the concentration of the ions pC.

According to equation (1)

$$\frac{p^2C}{1-p} = k.$$

k is the dissociation-constant of the hydroxy-acid.

Suppose the concentration of the ions after a time $t = y$, then is:

$$y = pC = \tfrac{1}{2}\{\sqrt{4kC + k^2} - k\}$$

The scheme:

positive ions + negative ions $\rightleftarrows$ lactone + water,

gives as reaction-equation, when the concentration-change of the water is neglected

$$-\frac{dy}{dt} = k_1 y^2 - k_2\,(C_0 - C).$$

In this

$$(C_0 - C) = \frac{kC_0 - y^2 - ky}{k}$$

is the concentration of the formed lactone.

The above differential-equation gives, after introduction of this value for $C_0 - C$ and after integration

$$\gamma t = l\,(y-\alpha) - l\,(y-\beta) + const.$$

For $t=0$ is $y=y_0$, that is the initial concentration of the ions and the equation becomes:

$$\gamma = \frac{1}{t}\,l\,\frac{(y-\alpha)\,(y_0-\beta)}{(y-\beta)\,(y_0-\alpha)}$$

This equation is the same as the one deduced in my dissertation for all bimolecular reactions where an equilibrium is formed.

In this equilibrium:

$y_0 = \tfrac{1}{2}\{\sqrt{4kC_0 + k^2} - k\}$ the initial concentration of the ions,

$y = \tfrac{1}{2}\{\sqrt{4kC + k^2} - k\}$ the concentration of the ions after a time t,

$\beta = y_\infty = \tfrac{1}{2}\{\sqrt{4kC_\infty + k^2} - k\}$ the end-concentration of the ions,

$\alpha = \dfrac{-\beta C_0}{C_0 - \beta}$. (see p. 14 of my dissertation).

The C_0 and C were determined by titration with barium hydroxide.

k is the dissociation-constant of the hydroxy-acid and could be obtained by conductivity-determinations.

4. In the spontaneous transformation of the hydroxy-acids the C_∞ has not been determined and this is necessary in order to calculate β and α. The question therefore arises how these may be determined. In the condition of equilibrium $-\frac{dy}{dt} = 0$ therefore:

$$k_1 y_\infty^2 = k_2 (C_0 - C_\infty)$$

$$y_\infty = \tfrac{1}{2} \{\sqrt{4kC_\infty + k^2} - k\}, \text{ so}$$

$$2 \times \frac{k_2}{k_1} = \frac{2kC_\infty + k^2 - k\sqrt{4kC_\infty + k^2}}{C_0 - C_\infty}.$$

C_0, the initial concentration is known, also k the dissociation-constant. If now we know $\frac{k_2}{k_1}$ the reciprocal value of the equilibrium-constant of the transformation:

positive ions + negative ions $\rightleftarrows$ lactone,

C_∞ may be calculated.

This equilibrium-constant may be found from a series of determinations where the end-condition has been determined of a definite quantity of hydroxybutyric-acid when HCl was added, therefore having H-ions as active constituents. On pg. 112 of his treatise the author states that to 20 cc. of the hydroxy-acid was added 5 cc. of the acid to be investigated (HCl or H_2SO_4); according to table 64 on pg. 116 5 cc. of N HCl are added, the solution therefore becomes $N/_4$ HCl and in case of complete splitting of the HCl in that concentration also quadri-normal in H-ions.

In the condition of equilibrium the positive H-ions of the γ-hydroxy-acid and those of the HCl and the negative ions of the hydroxy-acid are therefore in equilibrium with the lactone.

From the data of the above mentioned table 64 we may calculate that

$$\frac{k_2}{k_1} = 1715 \times 10^{-9}.$$

The transformation of hydroxyvaleric-acid also leads to an equilibrium, but, whereas in the condition of equilibrium the hydroxybutyric-acid was converted to the extent of about $65\,^0/_0$, the hydroxyvaleric-acid had been converted to the extent of $93\,^0/_0$.

In this transformation was found for:

$$\frac{k_2}{k_1} = 15 \times 10^{-7}.$$

Paul Henry disregards in this transformation the occurring equilibrium as it is shifted so much towards the side of the decomposition-products. This should not happen if this transformation is regarded as an ion-reaction as shown from the data on pg. 766; then the end concentration of the ions is in the one case 0.000701 and the initial-concentration 0.002690 and in the second case the end-concentration of the ions is 0.000501 and the initial-concentration 0.001885.

The following tables derived from a series of determinations by Paul Henry show that the above reaction-equation is a correct one

For the spontaneous transformation of γ-hydroxybutyric-acid we find: (see table p. 766).

5. It has been shown by the writer, that, if so much of a foreign acid (HCl, H_2SO_4) is added that the concentration of the H-ions during the whole progress of the reaction may be taken as constant, the usual reaction-equation applies; therefore in this case that of the unimolecular reaction in which an equilibrium is formed.

If we consider these reactions as ion-reactions it may be easily proved, that in the supposed case that equation appears.

If the concentration of the hydroxy-acid at a definite period is C, that of the added H-ions C'' and p the part of the hydroxy-acid which has split up into ions, then $C_{\text{hydroxy-acid}} = (1 - p)\,C$; $C_{\text{H-ions}} = p\,C + C''$; $C_{\text{neg. ions}} = pC$.

This acid is in equilibrium with its ions, consequently,

$$\frac{p\,(pC + C'')}{1-p} = k.$$

If so many H-ions have been added that this concentration may be regarded as constant, $pC + C''$ is a constant and the above equation becomes:

$$\frac{p}{1-p} = k',$$

that is to say, whatever value the concentration of the hydroxy-acid (C) attains, p remains constant and during the whole of the progress of the reaction, the concentration of the negative ions will amount to the same part of the hydroxy-acid present. In this case we therefore, have:

negative ions + positive ions = lactone + water.

Suppose the concentration of the negative ions $= y$, and that of the positive ions $= C_H$, then if the concentration of the lactone $= C_L$ and that of the water $= C_W$ we have:

$$-\frac{dy}{dt} = k_1\, C_H\, y - k_2\, C_W\, C_L = k'_1\, y - k'_2\, C_L = k'_1\, y - k'_2\, (C_0 - C);$$

then C_H and C_W may be taken as constant.

It has been shown above that during the progress of the action

Tab. 92 and 93 PAUL HENRY p. 128. $C_0 = 0.17166$ $\beta = 0.000741$ $\alpha = -0.000703$			Tab. 94 and 95 PAUL HENRY p. 128 $C_0 = 0.3390$ $\beta = 0.001313$ $\alpha = -0.001318$		
t in hours.	y	γ.	t in hours.	y	γ.
0	0.001810	—	0	0.002549	—
25	0.001742	0.00067	24	0.002476	0.00085
66	0.001634	71	48	0.002372	97
120	0.001520	71	72	0.002274	107
$148^1/_2$	0.001476	68	123	0.002118	110
172	0.001448	66	$151^1/_2$	0.002049	109
219	0.001377	66	$174^1/_2$	0.002006	106
∞	0.000741	—	192	0.001925	119
			∞	0.001313	—

The following tables may serve for the spontaneous transformation of γ-hydroxyvaleric-acid.

Tab. 66. PAUL HENRY. p. 118. $C_0 = 0.3580$ $\beta = y_\infty = 0.000701$ $\alpha = -0.000703$			Tab. 72 and 73. PAUL HENRY. p. 121. $C_0 = 0.1769$ $\beta = 0.000501$ $\alpha = -0.000502$		
0	0 002690	—	0	0.001885	—
240	0.002607	0.000032	390	0.001830	0.0000193
450	0.002541	29	1170	0.001705	226
1170	0.002350	30	1860	0.001615	226
1500	0.002266	31	2640	0.001520	230
1890	0.002188	30	3300	0.001460	225
2840	0.002053	28	4080	0.001385	227
3530	0.001942	28	4710	0 001335	225
4310	0.001895	27	5550	0.001275	224
4940	0.001773	27	6900	0.001185	225
6170	0.001580	26	∞	0.000501	—
7740	0.001557	25			
∞	0.000701	—			

$$y = pC$$
$$\frac{dC}{dy} = \frac{1}{p}$$

From this and the previous equation follows:

$$-\frac{dC}{dt} = \frac{k_1'}{p}C - \frac{k_2'}{p}(C_0 - C) = k_1''C - k_2''(C_0 - C)$$

and this is the differential-equation for a unimolecular reaction in which an equilibrium is formed.

6. If we add instead of HCl or H_2SO_4 an acid like acetic-acid which is partly split into ions, then, although H-ions are being added, the concentration of the H-ions during the whole progress of the reaction must no longer be considered as constant.

Suppose the initial-concentration of the hydroxy-acid $= C_0$, that of the acetic-acid C' and that of the hydroxy-acid after a time t C and let us suppose that a portion a of the hydroxy-acid is split up into ions and a portion b of the acetic-acid then:

$$C_{\text{hydroxy-acid}} = (1-a)\,C; \qquad C_{\text{H-ions}} = aC + bC'$$
$$C_{\text{acetic-acid}} = (1-b)\,C'; \qquad C_{\text{neg. ions hydroxy-acid}} = aC$$
$$C_{\text{neg. ions acetic acid}} = bC'$$

At each period the hydroxy-acid is in equilibrium with the H-ions and its negative ions and the same applies to the acetic acid, therefore the two following equilibrium-equations apply:

$$\frac{a\,(aC+bC')}{1-a} = k_1 \quad \text{and} \quad \frac{b\,(aC+bC')}{1-b} = k_2.$$

The dissociation-constants k_1 and k_2 of the hydroxy-acid and the acetic acid are nearly alike, consequently $a = b$ and

$$\frac{a^2(C+C')}{1-a} = k \quad ; \quad k = 0.000207.$$

$$a = \frac{\sqrt{4k(C+C') + k^2} - k}{2\,(C+C')}$$

$$C_{\text{neg. ions hydroxy-acid}} = aC = \frac{C\,\{\sqrt{4k(C+C') + k^2} - k\}}{2\,(C+C')} = y.$$

$$C_{\text{H-ions}} = a\,(C+C') = \tfrac{1}{2}\,\{\sqrt{4k(C+C') + k^2} - k\} = \frac{C+C'}{C}\,y.$$

From this follows:

$$C = \frac{y}{2k}\,\{(y+k) + \sqrt{(y+k)^2 + 4kC'}\}.$$

We again have:

negative ions + positive ions ⇄ lactone, therefore:

$$-\frac{dy}{dt} = k_1\left(\frac{C+C'}{C}\right)y^2 - k_2(C_0 - C) =$$

$$= \frac{k\,k_1 + k_2}{2k}\left[(y+k) + \sqrt{(y+k)^2 + 4k\,C'}\right]y - k\,k_1\,y - k_2\,C_0.$$

Suppose $y + k + \sqrt{(y+k)^2 + 4k\,C'} = z,$

then:
$$y = \frac{z^2 - 4k\,C'}{2z} - k$$

and
$$\frac{dy}{dz} = \frac{z^2 + 4k\,C'}{2z^2}$$

and when we call $\frac{2k}{k\,k_1 + k_2} = N$

$$-\frac{1}{N}\cdot\frac{dt}{dz} = \frac{z^2 + 4k\,C'}{z\left\{(z^2 - 2k\,z - 4k\,C')(z - Nk\,k_1) - 2Nk_2\,C_0\,z\right\}} =$$

$$= \frac{z^2 + 4\,k\,C'}{z^3 - (Nk\,k_1 + 2k)\,z^2 + 2\,(Nk^2\,k_1 - 2k\,C' - Nk_2\,C_0)\,z + 4Nk^2\,k_1\,C'} =$$

$$= \frac{p}{z} + \frac{q}{z-\alpha} - \frac{r}{z-\beta} + \frac{s}{z-\gamma}.$$

Therefore:

$$\alpha + \beta + \gamma = Nkk_1 + 2k\ \ (a);\ \ \alpha\beta + \alpha\gamma + \beta\gamma = 2(Nk^2k_1 - 2kC'' - Nk_2C_0)\ \ (b);$$
$$-\alpha\beta\gamma = 4\,Nk^2k_1C'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

From (b) and (c) follows:

$$\alpha + \gamma = \frac{2\beta\,(Nk^2k_1 - 2kC'' - Nk^2C_0) + 4Nk^2k_1C'}{\beta^2} \quad . \quad . \quad . \quad (d)$$

$$\alpha\gamma = -\frac{4Nk^2k_1C''}{\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (e)$$

From (a) and (d) follows:

$$\beta^3 - (Nkk_1 + 2k)\beta^2 - 2\beta(Nk^2k_1 - 2kC'' - Nk^2C_0) - 4Nk^2k_1C' \quad . \quad (f)$$

If there is equilibrium $-\frac{dz}{dt}$ becomes 0 and this happens when the denominator of the above differential-equation becomes nought. The equation which we then obtain in z is the same as equation (f) in β, consequently $\beta = z_\infty$ (the value of z in case of an equilibrium being established).

Again introducing the value for N in equation (f) we obtain:

$$\beta^3 = \left\{\frac{2k^3}{k + \frac{k_2}{k_1}} + 2k\right\}\beta^2 - \left\{\frac{2k^3}{k + \frac{k_2}{k_1}} - 2kC'' - \frac{2k\,.\,\frac{k_2}{k_1}\,.\,C_0}{k + \frac{k_2}{k_1}}\right\}2\beta - \frac{8k^3C'}{k + \frac{k_2}{k_1}} \ . \ (g)$$

For the constants p, q, r and s we find:

$$p = -\frac{4kC'}{\alpha\beta\gamma}\ ;\ q = \frac{\alpha^2 + 4kC''}{\alpha(\alpha-\gamma)(\alpha-\beta)}\ ;\ r = \frac{\beta^2 + 4kC''}{\beta(\alpha-\beta)(\beta-\gamma)} \text{ and } s = \frac{\gamma^2+4kC''}{\gamma(\alpha-\gamma)(\beta-\gamma)}.$$

The following tables have been constructed from the observations of Paul Henry on the action of acetic-acid on hydroxyvaleric-acid.

For this, $k = 0.0000207$ and $\frac{k_2}{k_1} = 15 \times 10^{-7}$ (p. 764). Given the values of C_0, (initial concentration of the hydroxy-acid) and C'' (concentration of the acetic-acid) β may be calculated from equation (g) α and γ may then be calculated from (d) and (e).

For this transformation the reaction-equation becomes,

$$\frac{k\,k_1+k_2}{2k} \cdot t = p\,l\,\frac{z_0}{z} + q\,l\,\frac{z_0-\alpha}{z-\alpha} - r\,l\,\frac{z_0-\beta}{z-\beta} + s\,l\,\frac{z_0-\gamma}{z-\gamma}.$$

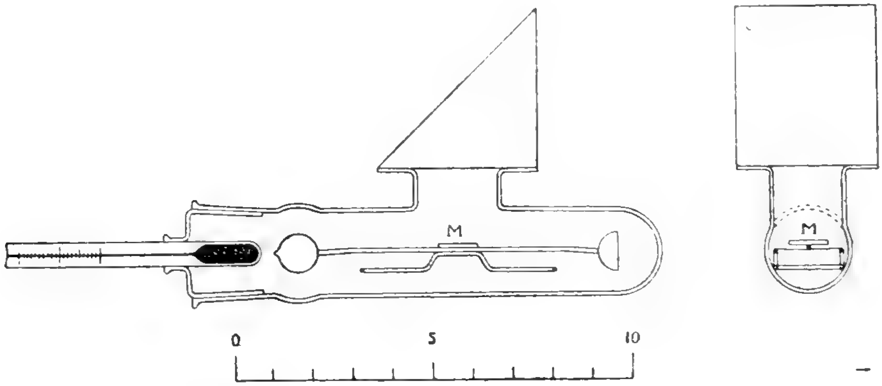
Tab. 74 and 75. PAUL HENRY. p. 123.		Tab 76 and 77. PAUL HENRY. p. 123.	
$C_0 = 0.4708$	$p = 26976,89$	$C_0 = 0.4795$	$p = 25905,42$
$C' = 0.2058$	$q = -232,46$	$C' = 0.01977$	$q = -497,543$
$\beta = 0.0041945$	$r = -233,84$	$\beta = 0.001653$	$r = -499,052$
$\alpha = -0.004153$	$s = -27005,45$	$\alpha = -0.001597$	$s = -25906,92$
$\gamma = 0.000035$		$\gamma = 0.000024$	

t in hours	z	$\frac{k\,k_1+k_2}{2k}$	t in hours	z	$\frac{k\,k_1+k_2}{2k}$
0	0.005495	—	0	0.004083	—
210	0.005439	0.014	390	0.003947	0.0126
390	0.005349	21	1170	0.003706	128
1170	0.005226	21	1860	0.003521	128
1860	0.004953	21	2640	0.003330	127
2640	0.004806	21	3300	0.003206	128
3300	0.004692	22	4080	0.003082	126
4080	0.004591	23	4710	0.002 87	125
4710	0.004529	23	5550	0.002859	127
5550	0.004435	25			

These tables also give satisfactory values for the reaction-constants.

Physics. — "*Application of the Baroscope to the Determination of the Densities of Gases and Vapors.*" By ARTHUR W. GRAY. [Preliminary Notice.] (Communication No. 94*a* from the Physical Laboratory at Leyden by Prof. H. KAMERLINGH ONNES).

For determining the densities of gases, especially while flowing continuously, the principle of the baroscope has been variously applied by FITZGERALD [1]), LOMMEL [2]), SIEGERT and DÜRR [3]), MESLANS [4]), PRECHT [5]), and others. In the apparatus here described the aim has been great sensitiveness combined with simplicity, ease of operation and small volume.



The accompanying figure illustrates the essential features. A capillary glass tube carries at one end a closed bulb, and at the other a hemispherical shell of the same diameter, weight, and kind of glass. This is fastened to a horizontal quartz fiber stretched on a glass frame, and carries a small mirror M, so that rotations about the quartz fiber [6]) as axis can be measured with telescope and scale. The whole is placed within a glass tube containing a sensitive thermometer of some sort, and communicating with a manometer.

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[1]) G. F. FITZGERALD. Fortschritte der Physik 41, 102, 1885.

[2]) E. LOMMEL. Wied. Ann. 27, 144, 1886.

[3]) A. SIEGERT and W. DÜRR. Zs. f. Instr.k. 8, 258, 1888.

[4]) M. MESLANS. Comptes Rend. 117, 386, 1893.

[5]) H. PRECHT. Zs. f. Instr.k. 13, 36, 1893.

[6]) The use of the quartz fiber was suggested by the delicate chemical balance of NERNST and RIESENFELD, Beibl. 28, 380, 1904, to which Prof. KAMERLINGH ONNES had drawn my attention. Much more delicate instruments are, however, the quartz thread gravity balance of THRELLFALL and POLLOCK R. S. Trans. 193, A, 215, 1900, and the magnetograph of WATSON, Proc. Phys. Soc. London. 19, 102, 1904.

If the instrument has once been calibrated, the scale reading gives immediately the density of the gas within; while the thermometer and the manometer permit the calculation of the density under standard conditions, if the compressibility of the gas is known. The calibration may be made either with a single gas whose density at various pressures is known with sufficient accuracy for any one temperature, or by employing in turn several different gases under known conditions of pressure, temperature and density, or with a rider. Counterpoising the closed sphere with the hemispherical shell of equal surface tends to eliminate errors that would be introduced if the apparatus contained a vapor which condensed on the glass. The instruments should, of course, be protected from changes of temperature by proper jacketing or by immersion in a liquid bath. A fixed reference mirror (not shown in the figure) is desirable to indicate any change in the leveling of the apparatus.

In order to get an idea of the sensitiveness that could be expected from such an instrument, some rough preliminary measurements were made.

The dimensions were as follows:

Diameter of bulb	1.0 cm.
,, ,, capillary beam	0.1 ,,
Length ,, ,, ,,	7.0 ,,
Mass of entire suspended system	0.67 gms.
Length of quartz fiber	1.4 cm.

The apparatus was filled with dry air, and the scale readings noted for various pressures ranging from 0.3 cm. to nearly 90 cm. of mercury. With a fiber about 0,005 cm. in diameter and the scale 255 cm. from the mirror, 0.1 mm. change in the deflection was found to indicate a change of about 0,0002 $\frac{\text{gm.}}{\text{liter}}$ change in the density; and this was the same for all densities tried; that is to say, a change of 0.1 mm. in the scale reading indicated a change of about one part in 6000 in the density of air under ordinary conditions. The scale might easily have been placed much farther from the mirror and the sensitiveness could have been greatly increased by using a larger bulb, a longer beam, and a longer and thinner fiber. And since the change in deflection is, in the first approximation at least, directly proportional to the change in density, an accurate knowledge of the deflections for a few densities is sufficient for the calibration of the instrument. Certain corrections, as, for instance, for the effects of changes of temperature on the quartz fiber, must, of course, be applied when the greatest accuracy is desired.

This instrument was devised in order to follow the course of a separation of atmospheric gases by fractional distillation at low temperature, which Prof. KAMERLINGH ONNES wished to be made and to be controlled by density measurements; but it is evident that its use is not confined to this field. It might be used for determining the densities of gases or vapors under various conditions, and therefore, their compressibilities; but it is especially useful as an indicator of minute changes of density. Professor KAMERLINGH ONNES has already suggested its use to determine the composition of coexisting vapor and liquid phases in cases where a chemical analysis would be difficult or impossible, for example, in a mixture of two of the inert gases of the atmosphere.

Constructional details and refinements, together with the results of more careful and more varied tests will be communicated in a later paper.

(May 25, 1905).

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