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# 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).

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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:

$$z = c_1 (x^2 + y^2) + d_1 x^3 + d_2 x^2 y + d_3 x y^2 + d_4 y^3 + e_1 x^4 + \ . \quad (1)$$

By a slight deformation we arrive for the new surface at the equation:

$$z = \alpha + \beta_1 x + \beta_2 y + c_1 x^2 + \gamma_2 x y + (c_1 + \gamma_3) y^2 + d_1 x^3 + d_2 x^2 y \ . \quad (2)$$

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:

$$\gamma_2 + 2\, d_2\, x + 2 d_3\, y = 0 ; \gamma_3 + (d_3 - 3 d_1)\, x + (3 d_4 - d_2)\, y = 0 \quad . \quad (4)$$

from which in general we deduce without difficulty the sought for displacement.

This however is different when the determinant

$$K_1 \equiv \begin{vmatrix} d_3 - 3 d_1 & 3 d_4 - d_2 \\ d_2 & d_3 \end{vmatrix} \equiv d_2^2 + d_3^2 - 3\, (d_1\, d_3 + d_2\, d_4) \quad (5)$$

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:

$$\begin{aligned}&(d_3 - 3 d_1) \gamma_2 - 2 d_2 \gamma_3 + [12 d_2 e_1 + 3 (d_3 - 3 d_1) e_2 - 2 d_2 e_3 - 8 c_1^3 d_2] x^2 + \\ &+ [6 d_2 e_3 + 4 (d_3 - 3 d_1) e_3 - 6 d_2 e_4 - 2 c_1^3 (d_3 - 3 d_1)] x y + [2 d_2 e_3 + 3 (d_3 - 3 d_1)\, e_4 - \\ &- 12 d_2 e_5 + 8 c_1^3 d_2] y^2 = 0 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (6)\end{aligned}$$

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).

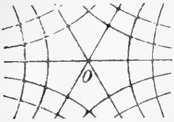

Fig. 1.

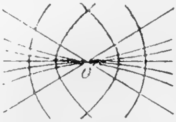

Fig. 2.

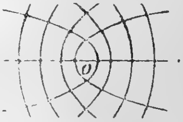

Fig. 3.

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

$$d_3\, n^3 + (2d_2 - 3d_4)\, n^2 + (3d_1 - 2d_3)\, n - d_2 = 0\ . \quad . \quad . \quad (7)$$

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

$$[d_2\, x + d_3\, y] \left[ 1 - \left( \frac{dy}{dx} \right)^2 \right] + [(d_3 - 3d_1)\, x + (3d_4 - d_2)\, y]\, \frac{dy}{dx} = 0\ \ ,\ (8)$$

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]).

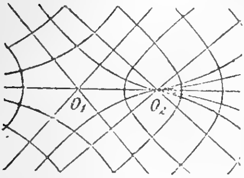

Fig. 4.

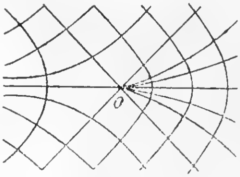

Fig. 5.

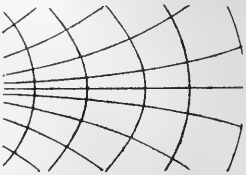

Fig. 6.

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:

$$ax^2 + by^2 + c\,z^2 + H_3 + H_4 + \ldots . = 0 \quad . \quad . \quad . \quad . \quad (9)$$

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* $\omega$, *a plane* $\alpha$, *and in that plane a conic c; to define on the surface* $\omega$ *the points* $\boldsymbol{\Omega}$ *which have the property that the two nodal tangents of the section of the tangent plane* $\varrho$ *in* $\boldsymbol{\Omega}$ *pass respectively through the points* $A_1$ *and* $A_2$ *where c is cut by* $\varrho$.

For this more general problem the plane at infinity has been replaced by the plane $\alpha$ and we have but to study the points $\boldsymbol{\Omega}$ which as singularities of the first order may appear in the section $d$ of $\boldsymbol{\Omega}$ and $\alpha$ 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 $\omega$ touches the plane $\alpha$, such a point of contact must be regarded as an $\boldsymbol{\Omega}$-point; for its tangents in the section of the tangent plane will certainly meet the conic $c$ in the plane $\alpha$. 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 $\boldsymbol{\Omega}$-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 $\omega$ touches $c$ the point of contact must be an $\Omega$-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 $\Omega$-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 $\omega$ cuts the plane $\alpha$, it is easy to see that this point must be regarded as an $\Omega$-point as often as the cuspidal tangent of the section of the tangent plane lies in plane $\alpha$, 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 $\Omega$-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 $\omega$ are $\Omega$-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:

$$z = c_1 (x^2 + y^2) + k_1 xz + k_2 yz + k_3 z^2 \quad . \quad . \quad . \quad . \quad (11)$$

Bringing the value of $z$ into the second member this furnishes the development in series

$$z = c_1 (x^2 + y^2) + k_1 c_1 x^3 + k_2 c_1 x^2 y + k_1 c_1 x y^2 + k_2 c_1 y^3 + \ . \quad (12)$$

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°.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 $2\,^{0}/_{0}$ of aniline and another portion with $2\,^{0}/_{0}$ 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 | |
|---|---|---|
| | $2\,^{0}/_{0}$ *p*-toluidine | $2\,^{0}/_{0}$ 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 $^{0}/_{0}$.

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 (1) 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 | 2.1 | 0.127 | 7 | 28 |
| | sensibility coefficient... | + 0.08 | | + 0.29 | | |

| | | *M* | *Q* | $\frac{Q}{M}$ | Minimum. | Maximum. |
|---|---|---|---|---|---|---|
| Scandix Pecten-Veneris.<br>IX. Number of lobes of the first leaf.. | *G* | 27.2 | 3.85 | 0.14 | 16 | 56 |
| | *B* | 25.4 | 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.<br>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.<br>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.<br>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.

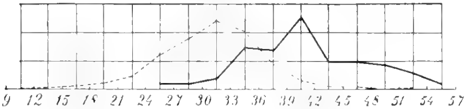
From these the curve of the number of branches of the third order of *Iberis amara*, grown on the sand, deviates entirely, being a semi-curve. For the culture on fertile earth, however, this same character gives a symmetrical curve. In fig. V this latter is very flat and extended in length, as the observations 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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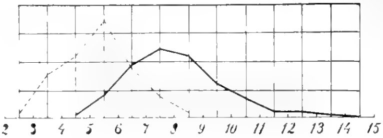

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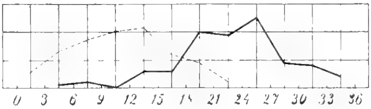

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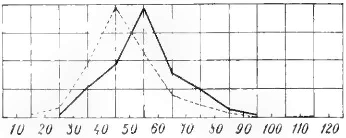

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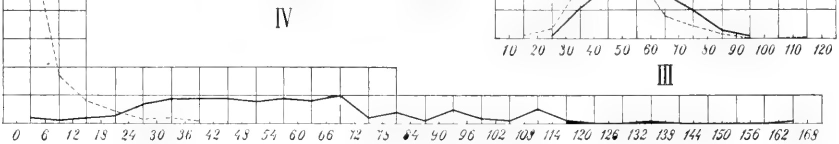

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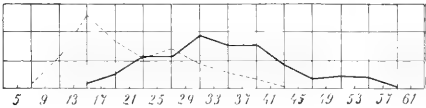

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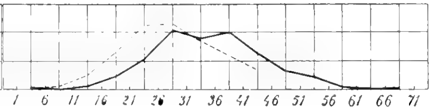

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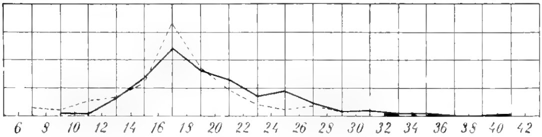

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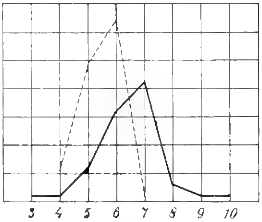

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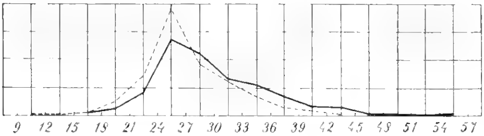

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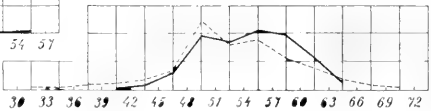

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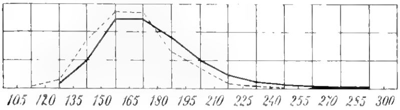

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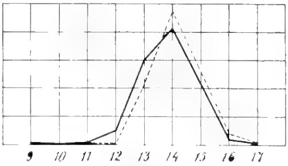

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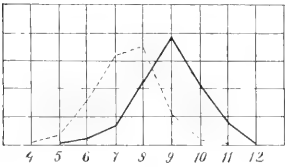

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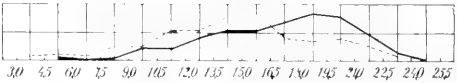

XV

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 $\mu$ 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. 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 GRÉGOIRÉ 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

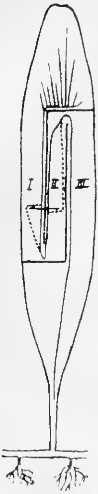

Fig. 1.

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.

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.

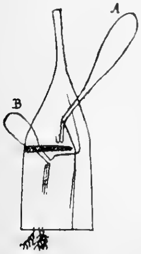

Fig. 2.

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.

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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:

$$\Delta = \frac{\omega_o \varepsilon l}{V^2} \left\{ \frac{4\delta^2 - d'^2 \vartheta_o^2}{(4\delta^2 - d'^2 \vartheta_o^2)^2 - 4c^2 R^2 \delta^2} - \frac{1}{4\delta^2 - d^2 \vartheta_o^2} \right\} .$$

In this formula $V$ indicates the velocity of light in the aether, $R$ the strength of the field, $\varepsilon, d, d'$ and $c$ being constants characteristic of the medium. Moreover $2\pi\vartheta_o = \tau_o$ 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.

**P. ZEE**

*Triplet.*

**P. ZEEMAN and J. GEEST.** Double refraction near the components of absorption lines magnetically split into several components.

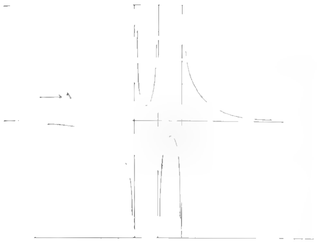

Fig. 1.
(theoretical curve)

Fig. 4.
(observed)

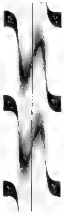

Fig. 5.
(observed)

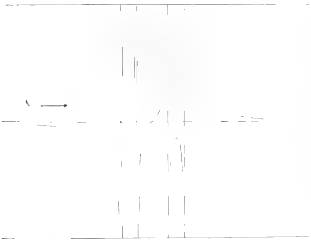

Fig. 2.
(theoretical curve)

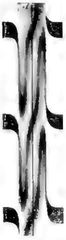

Fig. 6.
(observed)

Fig. 7.
(observed)

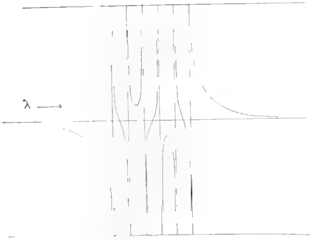

Fig. 3.
(theoretical curve)

Fig. 8.
(observed)

give the graphical representation of $\Delta$ as a function of $\sigma$ 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 $\alpha T$, where $\alpha$ 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 $\nu$ 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 $\nu$ 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 $\xi$, $\eta$, $\zeta$ 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 $(\xi, \eta, \zeta)$, 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

$$f(\xi, \eta, \zeta)\, dS\, d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is the number of electrons in the element $dS$, whose velocity-points lie in $d\lambda$; in particular

$$f(\xi, \eta, \zeta)\, dS\, d\xi\, d\eta\, d\zeta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is the number of electrons for which the values of the components of velocity are included between $\xi$ and $\xi + d\xi$, $\eta$ and $\eta + d\eta$, $\zeta$ 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 $\nu$ and $W$ mentioned in § 1. Integrating over the full extent of the diagram of velocities, we have

$$N = \int f(\xi, \eta, \zeta)\, d\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\nu = \int \xi f(\xi, \eta, \zeta)\, d\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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 $\xi dt$, $\eta dt$, $\zeta dt$. 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 $(x + \xi\, d\, t, y + \eta\, d\, t, z + \zeta\, d\, t)$ and their velocity-points in the element $d\lambda'$ at the point $(\xi + X d\, t, \eta + Y d\, t, \zeta + Z d\, t)$. Hence, since $dS' = dS$ and $d\lambda' = d\lambda$,

$$f(\xi, \eta, \zeta, x, y, z, t) + (b - a)\, dt =$$
$$= f(\xi + Xdt, \eta + Ydt, \zeta + Zdt, x + \xi dt, y + \eta dt, z + \zeta dt, t + dt),$$

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 $b\, d\, S\, d\, \lambda\, d\, t$, 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 $\vartheta$ 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 $\zeta, \eta, \xi$ by the coordinates $\xi', \eta', \zeta'$ of the image of the point $(\xi, \eta, \zeta)$ 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 $(\zeta, \eta, \xi)$ and $(\xi', \eta', \zeta')$ 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 $\xi', \eta', \zeta'$ in $\xi, \eta, \zeta$. 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 $\vartheta$ with the velocity $(\xi, \eta, \zeta)$. 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 $(\xi', \eta', \zeta')$, which I shall call $r'$, is equal to the magnitude $r$ of the velocity $(\xi, \eta, \zeta)$.

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 $(\xi, \eta, \zeta)$ 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 $r^3$ in the following way

$$A = N\sqrt{\frac{h^3}{\pi^3}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$r^2 = \frac{3}{2h}.$$

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 $\varphi$ 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

$$\left(-2\,h\,A\,X + \frac{dA}{dx} - r^2\,A\,\frac{dh}{dx}\right)\xi\,e^{-hr^2} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

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 $\xi$ in this last expression makes it probable that the same factor will also appear in the function $\varphi$. 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 $\mu$ the angle between the velocity $(\xi, \eta, \zeta)$, i. e. the line $OP$, and the axis of $x$, and by $\psi$ the angle between the planes $QOP$ and $XOP$, I find for (18)

$$-\,2nR^2r^3\,\chi\,(r)\int_0^{\frac{1}{2}\pi}\int_0^{2\pi}\cos^2\vartheta\,(\cos\vartheta\cos\mu + \sin\vartheta\sin\mu\cos\psi)\sin\vartheta\,d\,\vartheta\,d\,\psi =$$

$$= -\,\pi\,n\,R^2r^2\,\chi\,(r)\cos\mu = -\,\pi\,n\,R^2\,\xi\,r\,\chi\,(r).$$

If this is equated to (16), the factor $\xi$ 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

$$\frac{l\,\frac{dA}{dx}}{A} \text{ and } l\,\overline{r^2}\,\frac{dh}{dx},$$

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 $\varphi\,(\xi, \eta, \zeta)$ 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 $\nu$ 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 $\xi$; this integral vanishes, if taken over the full extent of the diagram of velocities. In the remaining integrals the factor $\xi^2$ occurs; these are easily found, if we replace $\xi^2$ 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

$$\int_0^\infty s\, e^{-hs}\, ds, \quad \int_0^\infty s^2\, e^{-hs}\, ds \text{ and } \int_0^\infty s^3\, e^{-hs}\, ds,$$

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* $\sigma$ 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

$$\nu = \frac{4\pi lAe}{3hm} E.$$

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

$$\sigma = \frac{4\pi lAe^2}{3hm}, \quad \dots\dots\dots \quad (23)$$

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,

$$\sigma = \sqrt{\frac{2}{3\pi}} \cdot \frac{lNe^2u}{\alpha T} \quad \dots\dots\dots \quad (24)$$

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 $\nu = 0$,

$$2hAX - \frac{dA}{dx} = -2\frac{A}{h}\frac{dh}{dx} \quad \dots\dots \quad (25)$$

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

$$k = \frac{8\pi l A a}{9h^2}, \quad \ldots \ldots \ldots \quad (26)$$

or

$$k = \frac{8}{9}\sqrt{\frac{2}{3\pi}}\, l\, N\, a\, u\,, \quad \ldots \ldots \ldots \quad (27)$$

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

$$\frac{k}{\sigma} = \frac{8}{9}\left(\frac{a}{e}\right)^2 T \quad \ldots \ldots \ldots \quad (28)$$

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 $\sigma$ and for which, using (28), I find

$$\frac{aT}{e} = \sqrt{\frac{9}{8}\frac{k}{\sigma}T}, \quad \ldots \ldots \ldots \quad (29)$$

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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 $\alpha T$, 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, $T = 273° + 18°$,

$$3p = 38.$$

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 $\varphi$ 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 $\varphi$ for the electric potential, the force $X$ divides into two parts

$$\left.\begin{array}{c} X = X_m + X_e, \\ X_m = -\dfrac{1}{m}\dfrac{dV}{dx},\ X_e = -\dfrac{e}{m}\dfrac{d\varphi}{dx} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

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) $v = 0$ 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

$$\varphi_Q - \varphi_P = \frac{1}{e}\left(V_P - V_Q\right) + \frac{m}{2\,e\,h}\left(\log A_P - \log A_Q\right) . \quad (33)$$

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,

$$F = \frac{m}{2e}\int_P^Q \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx \quad . \; . \; . \; . \; . \; . \; . \; . \quad (34)$$

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

$$\int_{R'}^{S'} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx = 0, \quad \int_{S''}^{R''} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx = 0,$$

$$\int_P^{R'} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx + \int_{R''}^{Q} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx = \int_{h''}^{h'} \log A_I \frac{d}{dh}\left(\frac{1}{h}\right) dh,$$

$h'$ and $h''$ being the values corresponding to $T'$ and $T''$, the temperatures in $R'$ and $R''$. Similarly

$$\int_{S'}^{S''} \log A \frac{d}{dx}\left(\frac{1}{h}\right) dx = \int_{h'}^{h''} \log A_{II} \frac{d}{dh}\left(\frac{1}{h}\right) dh.$$

If we combine these results, the formula (34) for the electromotive force becomes

$$F = \frac{m}{2e}\int_{h'}^{h''} \log \frac{A_I}{A_{II}} \frac{1}{h^2} dh,$$

or, if we use (13) and (14),

$$F = \frac{2\,a}{3\,e}\int_{T'}^{T''} \log \frac{N_{II}}{N_I} dT. \quad . \; . \; . \; . \; . \; . \; . \quad (35)$$

## **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 G$^{g}$ Gadoet $P 1$ — Poelau Satoe $P 2$ of the triangulation of the West Coast of Sumatra, is 49.

(2). The distance between the stations G$^{g}$ 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 G$^{g}$ Dempoe — G$^{g}$ 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 G$^{g}$ 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 (1) | (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″.165 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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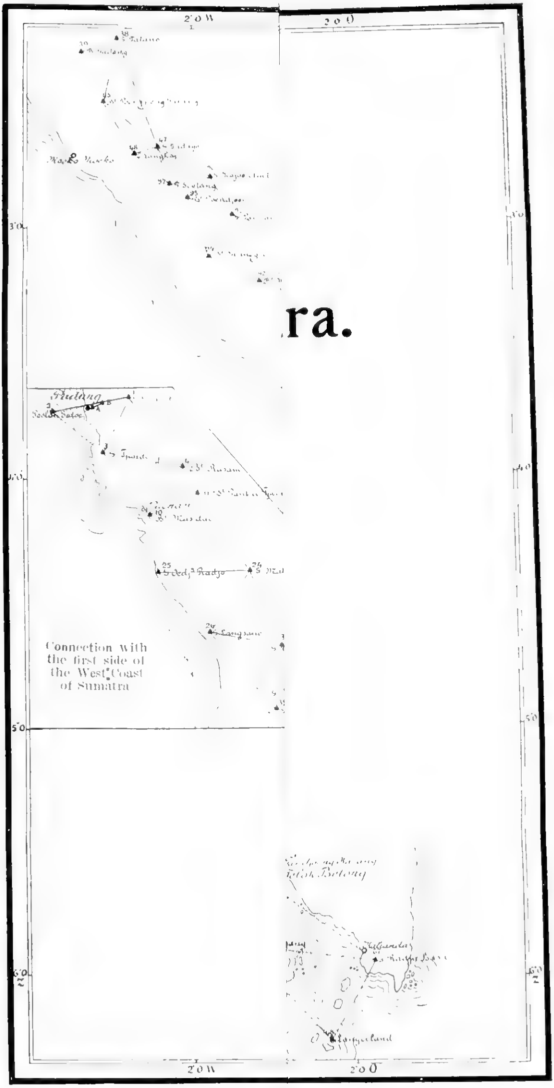
*) These triangles occur under the numbers 1, 2, 16, 17, 35, 36, 43, 50, 51 and 52 on pp. 603 and 604 of Comptes Rendus des séances de la dixième conférence générale de l'Association Géodésique Internationale.

## 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 | | $\Delta^2$ |
|---|---|---|---|---|---|---|---|
| | | | | | + | − | |
| 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 |

S. BLOK: The connection betw



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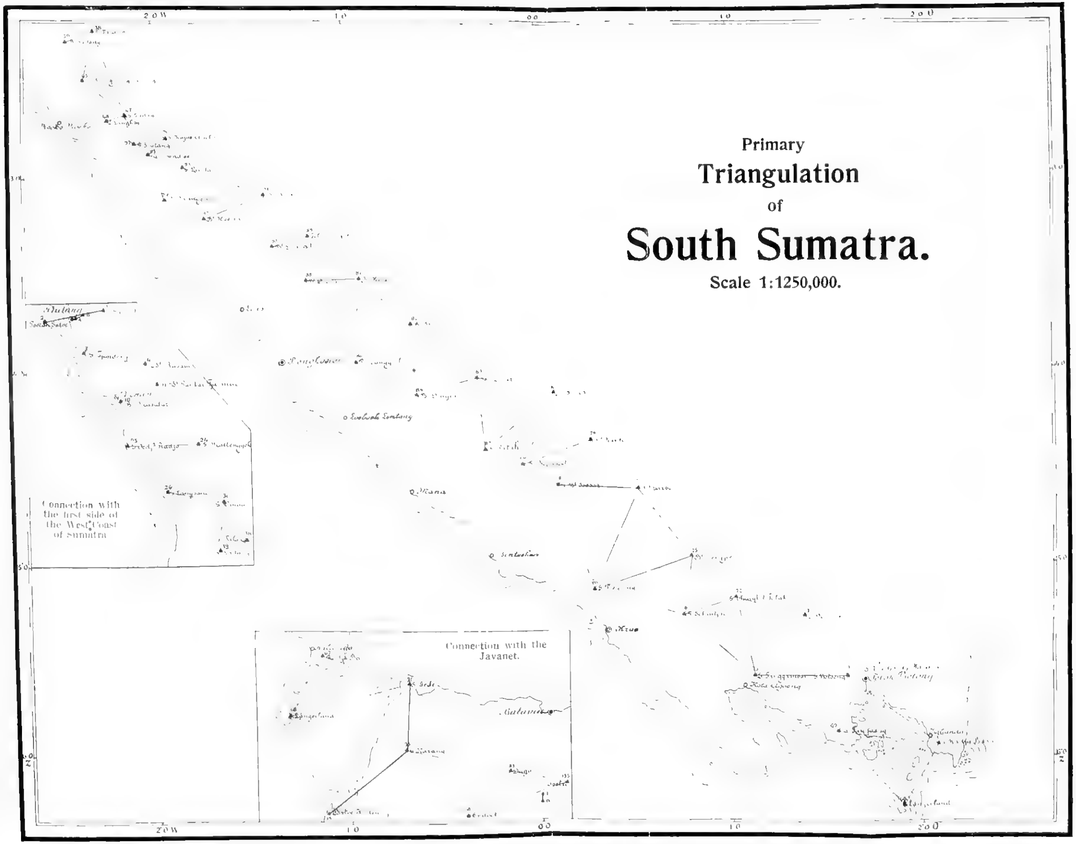
S. BLOK: The connection between the primary triangulation of South-Sumatra and that of the West Coast of Sumatra.



the geographical longitude of G$^{s}$ 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 $\left(4{,}1 + \frac{B}{27-0{,}027\,B}\right)$.

The smaller $B$ is, the more this relation approaches to about a fourth.

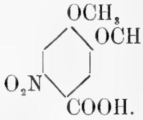
§ 10. *History.* A remark made two years ago by a pupil of the third year of the "Gymnasium Willem III" at Batavia to the writer suggested this paper. This pupil, called VAN ERPECUM, said that he had observed that a glass filled to the brim with water and floating ice, does not flow over, when the ice 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.

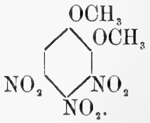
*Amsterdam*, Dec. 1904.

## **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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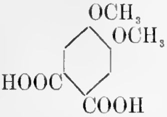
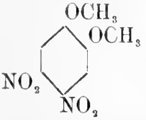
[1]) Recueil **23**, 114.

[2]) Ber. **9**, 937.

[3]) Ann. der. Chem. **293**, 175.

Dinitroveratrol prepared by nitration of veratrol [1]) and of meta-hemipinic acid [2]) and which is consequently formed as follows:



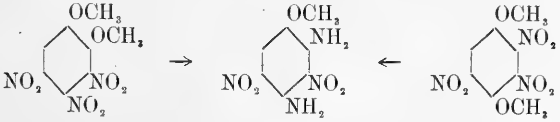


also gives on subsequent nitration the same trinitroveratrol, again showing that the constitution of that substance may be expressed by $C_6\,H(OCH_3)_2\,(NO_2)_3$ 1, 2, 3, 4, 5.

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.

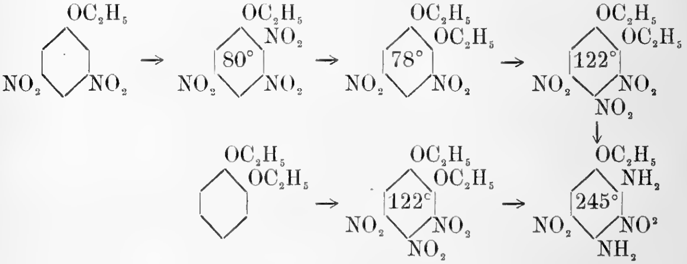
[3]) Ber. **9**, 937 ; **11**, 131.

[4]) Ber. **25**, 282.

This also shows that the $NO_2$ groups in trinitroveratrol are situated in the positions 3, 4 and 5.

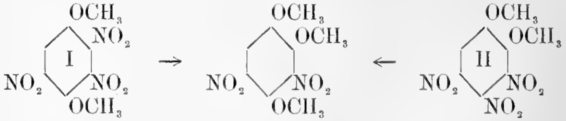
If this dinitrodiamidoanisol is treated with KOH we obtain the monomethylether of dinitrotrioxybenzene, a substance already obtained by Nietzki and Kurtenbacher from the said reaction-product of trinitrohydroquinonedimethylether and ammonia.

In quite an analogous manner the same result was obtained for the oxyethyl compound :

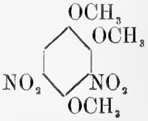


This latter substance has been formerly obtained by Nietzki [1]) by treating trinitrohydroquinonediethylether with alcoholic ammonia.

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 nitrocompounds) 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).

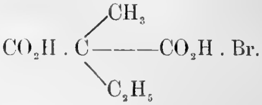
LOBRY DE BRUYN. Rec. **23**. 47.

[2]) Ber. 37, 349.

[3]) Ber. 37, 1012.

wards, Marckwald [1]) defended his standpoint in such a manner that no further controversy has 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:



$$CO_2H \,.\, C\overset{CH_3}{\underset{C_2H_5}{\text{———}}}CO_2H \,.\, Br.$$

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 $10^0/_0$ 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.

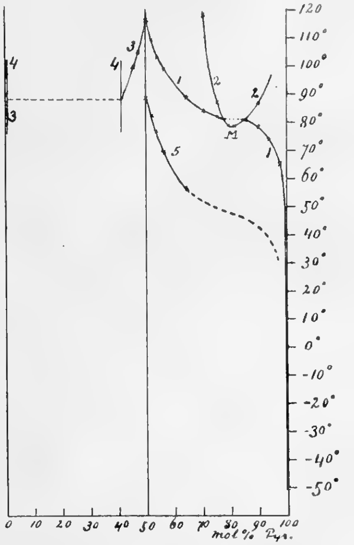
## **Chemistry.** — "*On the system pyridine and methyl iodide.*" By Dr. A. H. W. Aten. (Communicated by Prof. Bakhuis Roozeboom).

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 $C_6H_5N.CH_3I$ 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. °/₀ 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. °/₀ 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' $\psi$-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 $\alpha$, $\beta$, 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:

$$T_{xk} = T_k(1 + \alpha x),\ p_{xk} = p_k(1 + \beta x),\ v_{xk} = v_k(1 + \gamma x).$$

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 $\frac{T'}{T} = \frac{T_k}{T_{xk}}$; 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 $\frac{T_k}{p_k}\left(\frac{\partial p}{\partial T}\right)_{v_k} = \left(\frac{\partial \mathfrak{p}}{\partial \mathfrak{t}}\right)_k = 7.3$ [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 $M_1(1-x)+M_2x$ gr., $M_1$ and $M_2$ representing the molecular weights of the pure substance and the admixture. Thence follows the density $\frac{M_1(1-x)+M_2x}{v}$, 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 $p$, $\varrho$ 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 $\alpha$ and the $\beta$ 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 $\alpha$ and the $\beta$ 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. $CH_3Cl$ | , $\alpha = 0.378$ | , $\beta = 0.088$ | , $\Delta = 34\%$ | of the critical density. |
| $CH_3Cl$ ,, ,, ,, $CO_2$ | , $\alpha = -0.221$ | , $\beta = 0.281$ | , $\Delta = 31\%$ | |
| $CO_2$ ,, ,, ,, $H_2$ | , $\alpha = -1.17$ | , $\beta = -1.62$ | , $\Delta = 42\%$ | |
| $CO_2$ ,, ,, ,, $O_2$ | , $\alpha = -0.66$ | , $\beta = -1.09$ | , $\Delta = 36\%$ | |

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 | $\Delta = 36\%$ | $\Delta = 30\%$ | $\Delta = 17\%$ |
| 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."

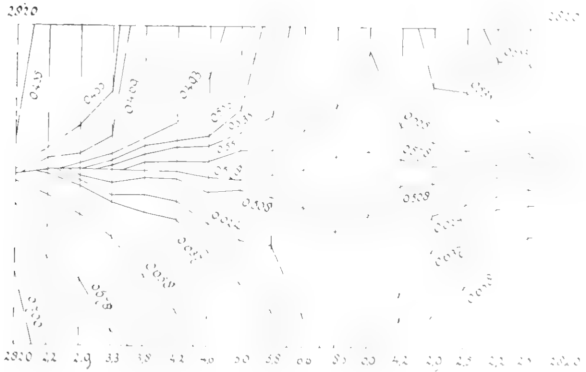

Fig. 1.

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.

| $\frac{1}{2}(x_2 + x_1) =$ | $\Delta =$ |
|---|---|
| 0.0005 | 36 °/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°
$\Delta =$ $50\,^0/_0$ $40\,^0/_0$ $30\,^0/_0$ $25\,^0/_0$ $20\,^0/_0$ $15\,^0/_0$ $15\,^0/_0$ $20\,^0/_0$ $25\,^0/_0$ $30\,^0/_0$

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 $\Delta$ 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 $\alpha$ and $\beta$ 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, $\alpha$ and $\delta$ 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 $x_{lpT}$, $x_1$, $x_{vpT}$.

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**(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).

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P. H. SCHOUTE: "The formulae of GULDIN in polydimensional space", p. 487.

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H. G. JONKER: "Contributions to the knowledge of the sedimentary boulders in the Netherlands. I. The Hondsrug in the province of Groningen. 2. Upper Silurian boulders. — First communication: Boulders of the age of the Eastern Baltic zone G". (Communicated by Prof. K. MARTIN), p. 500.

J. J. VAN LAAR: "On some phenomena, which can occur in the case of partial miscibility of two liquids, one of them being anomalous, specially water". (Communicated by Prof. H. A. LORENTZ), p. 517. (With one plate).

J. CARDINAAL: "The equations by which the locus of the principal axes of a pencil of quadratic surfaces is determined", p. 532.

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 $\overline{PQ}^{n-p}$ 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 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $v_n$ | $\pi$ | $\frac{4}{3}\pi$ | $\frac{1}{2}\pi^2$ | $\frac{8}{15}\pi^2$ | $\frac{1}{6}\pi^3$ | $\frac{16}{105}\pi^3$ | $\frac{1}{24}\pi^4$ | $\frac{32}{945}\pi^4$ | $\frac{1}{120}\pi^5$ | $\frac{64}{10395}\pi^5$ | $\frac{1}{720}\pi^6$ |
| $s_n$ | $2\pi$ | $4\pi$ | $2\pi^2$ | $\frac{8}{3}\pi^2$ | $\pi^3$ | $\frac{16}{15}\pi^3$ | $\frac{1}{3}\pi^4$ | $\frac{32}{105}\pi^4$ | $\frac{1}{12}\pi^5$ | $\frac{64}{945}\pi^5$ | $\frac{1}{60}\pi^6$ |

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 $x$, 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 $\varrho$ as radii of spherical and base boundary generates a segment of revolution $Sp(r, \varrho, \alpha)_n$ by rotation round a diametral space $S^{(a)}_{n-2}$, situated in its space $S_{n-1}$, having no point in common with it and forming an angle $\alpha$ 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 $\varrho$ 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 $S^{(a)}_{n-2}$."

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 $\alpha$. 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 $\alpha$, 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 $S^{(\alpha)}_{n-2}$, 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 $S^{(\alpha)}_{n-2}$ 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

$$V = 2\pi\, v_{n-2} \int_0^{\varrho} y^{n-1}\, dy = \frac{2\pi}{n}\, v_{n-2}\, \varrho^n = v_n\, \varrho^n,$$

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

$$Su = 2\pi r\, s_{n-2} \int_0^{\rho} y^{n-3}\, dy = \frac{2\pi}{n-2}\, r\, s_{n-2}\, \varrho^{n-2} = 2\pi r\, .\, v_{n-2}\, \varrho^{n-2},$$

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 $\alpha$ 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

$$\left.\begin{aligned} V_{n,k} &= v_{n-k-1}\, s_{k+1} \cos^k \alpha \int\limits_{x=\sqrt{r^2-\rho^2}}^{x=r} y^{n-k-1}\, x^k\, dx \\ Su_{n,k} &= r s_{n-k-1}\, s_{k+1} \cos^k \alpha \int\limits_{x=\sqrt{r^2-\rho^2}}^{x=r} y^{n-k-3}\, x^k\, dx \end{aligned}\right\}$$

and from this ensues the general relation

$$Su_{n,k} = 2\pi\, r \cos^3 \alpha\ V_{n-2,k}\,,$$

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

$$\left.\begin{aligned} V(r,a)_{n,k} &= s_{k+1}\, v_{n-k-1} \int\limits_{-a}^{a} \sqrt{r^2-x^2}^{\,n-k-1} (a+x)^k dx \\ Su(r,a)_{n,k} &= r\, s_{k+1}\, s_{n-k-1} \int\limits_{-a}^{a} \sqrt{r^2-x^2}^{\,n--k-3} (a+x)^k dx \end{aligned}\right\} \quad . \quad . \quad (3),$$

from which ensues again the formula of reduction

$$Su_{n,k} = 2\,\pi\, r\, V_{n-2,k} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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 $\pi$ 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

$$\frac{du}{d\alpha} = -\int_0^{\pi}\frac{cos^2\varphi\, sin\,(\alpha\, sin\,\varphi)}{1-2\,t^2\, cos\,2\varphi + t^4}\, sin\,\varphi\, d\varphi,$$

$$\frac{d^2u}{d\alpha^2} = -\int_0^{\pi}\frac{cos^2\varphi\, cos\,(\alpha\, sin\,\varphi)}{1-2\,t^2\, cos\,2\varphi + t^4}\, sin^2\varphi\, d\varphi$$

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

$$\frac{d^2u}{d\alpha^2} = m^2 u - \frac{1}{4\,t^2}\int_0^{\pi} cos^2\varphi\, cos\,(\alpha\, sin\,\varphi)\,d\varphi,$$

where $m = \frac{1-t^2}{2t}$.

If we replace $cos^2\varphi$ by $\frac{1+cos\,2\varphi}{2}$, we can easily reduce this differential equation to

$$\frac{d^2u}{d\alpha^2} - m^2 u = -\frac{\pi}{8t^2}\left(I_0(\alpha) + I_2(\alpha)\right)$$

$$= -\frac{\pi}{4t^2}\,\frac{I_1(\alpha)}{\alpha}.$$

Let us now determine the integral of this equation satisfying the conditions that for $\alpha = 0$

$$u = \int_0^{\pi} \frac{\cos^2 \varphi \, d\,\varphi}{1 - 2\,t^2 \cos^2 \varphi + t^4} = \frac{\pi}{2\,(1 - t^2)},$$

and

$$\frac{du}{d\alpha} = 0.$$

We then find

$$u = \frac{\pi}{4\,(1-t^2)} \left[ e^{m\alpha} + e^{-m\alpha} \right] - \frac{\pi}{8\,t^2\,m} \int_0^{\alpha} \frac{I_1(\beta)}{\beta}\, d\beta \left[ e^{m(\alpha-\beta)} - e^{-m(\alpha-\beta)} \right]$$

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

$$I_1(x+\alpha) = \frac{1}{\pi}\int_0^\pi \sin\varphi \sin(x\sin\varphi + \alpha\sin\varphi)\, d\varphi$$

follows

$$I_1(x-\alpha) + I_1(x+\alpha) = \frac{2}{\pi}\int_0^\pi \sin\varphi \sin(x\sin\varphi)\cos(\alpha\sin\varphi)\, d\varphi.$$

If we write

$$\sin(x\sin\varphi) = 2\, I_1 \sin\varphi + 2\, I_3 \sin 3\varphi + \dots$$

we obtain

$$\begin{aligned} I_1(x-\alpha) + I_1(x+\alpha) = {} & \frac{4}{\pi} I_1(x) \int_0^\pi \sin^2\varphi \cos(\alpha\sin\varphi)\, d\varphi \\ & + \frac{4}{\pi} I_3(x) \int_0^\pi \sin\varphi \sin 3\varphi \cos(\alpha\sin\varphi)\, d\varphi \\ & + \frac{4}{\pi} I_5(x) \int_0^\pi \sin\varphi \sin 5\varphi \cos(\alpha\sin\varphi)\, d\varphi \\ & + \dots\dots \end{aligned}$$

or as

$$\begin{aligned} 2\int_0^\pi \sin\varphi \sin(2n+1)\varphi \cos(\alpha\sin\varphi)\, d\varphi = {} & \\ & = \int_0^\pi [\cos 2n\varphi - \cos(2n+2)\varphi] \cos(\alpha\sin\varphi)\, d\varphi \\ & = \pi\, [I_{2n}(\alpha) - I_{2n+2}(\alpha)] \\ & = 2\pi \frac{d\, I_{2n+1}(\alpha)}{d\alpha} \end{aligned}$$

we get

$$I_1(x-\alpha) + I_1(x+\alpha) = 4\left[ I_1(x)\frac{dI_1}{d\alpha} + I_3(x)\frac{dI_3}{d\alpha} + I_5(x)\frac{dI_5}{d\alpha}\dots \right].$$

Substituting here

$$\alpha\frac{dI_n}{d\alpha} = n\, I_n(\alpha) - \alpha\, I_{n+1}(\alpha)$$

we arrive finally at

$$I_1(x-\alpha) + I_1(x+\alpha) = \frac{4}{\pi}\sum_{1.3}^{\infty} n\, I_n(\alpha)\, I_n(x) - 4\sum_{1.3}^{\infty} I_{n+1}(\alpha)\, I_n(x).$$

With this equation the result (1) may be written

$$\sum_{1.3}^{\infty} I_{n+1}(\alpha)\, I_n(x) = \frac{1}{4}\int_0^{\alpha} \frac{I_1(\beta)}{\beta}\, d\beta \left[I_0(x-\alpha+\beta) - I_0(x+\alpha-\beta)\right] \quad (2)$$

If here we develop

$$I_0(x-\alpha+\beta) = I_0(x)\, I_0(\alpha-\beta) + 2I_1(x)\, I_1(\alpha-\beta) + 2I_2(x)\, I_2(\alpha-\beta) + \dots$$

$$I_0(x+\alpha-\beta) = I_0(x)\, I_0(\alpha-\beta) - 2I_1(x)\, I_1(\alpha-\beta) + 2I_2(x)\, I_2(\alpha-\beta) - \dots$$

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

$$\sum_{1.3}^{\infty} n\, I_n(\alpha)\sin\frac{n\pi}{2} = \frac{\alpha}{2}\cos\alpha + \frac{\alpha}{2}\int_0^x \frac{I_1(\beta)}{\beta}\sin(\alpha-\beta)\, d\beta$$

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$^o$. 16; 3, p. 269, n$^o$. 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 $G_3$, 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 ellipti-frons* 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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## **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 $\psi$-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:

$$\left.\begin{aligned} \mu_1 &= \frac{\partial Z}{\partial n_1} = C_1 - \frac{\partial \omega}{\partial n_1} + RT\, log\, \frac{n_1}{\Sigma n_1} \\ \mu_1 &= \frac{\partial Z}{\partial n_2} = C_2 - \frac{\partial \omega}{\partial n_2} + RT\, log\, \frac{n_2}{\Sigma n_1} \end{aligned}\right\},$$

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 $\omega$ is given by

$$\omega = \int p dv - RT\,\Sigma n_1\,.\,log\,\Sigma n_1 - pv\,. \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

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 $\omega$ is, just as $Z$, a *homogeneous* function of the *first* degree with respect to $n_1$ and $n_2$, we may write:

$$\left.\begin{aligned} \mu_1 &= C_1 - \left(\omega - x\frac{\partial \omega}{\partial x}\right) + RT\, log\,(1 - x) \\ \mu_2 &= C_2 - \left(\omega + (1 - x)\frac{\partial \omega}{\partial x}\right) + RT\, log\, x \end{aligned}\right\} \quad . \quad . \quad . \quad . \qquad (2)$$

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, $\mu_1$ 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

$$RT = x\,(1 - x)\frac{\partial^2 \omega}{\partial x^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

If we use the equation of VAN DER WAALS:

$$p = \frac{\Sigma n_1 \, . \, RT}{v-b} - \frac{a}{v^2},$$

then we obtain:

$$\omega = \Sigma n_1 \, . \, RT \, log\,(v-b) + \frac{a}{v} - RT \, \Sigma n_1 \, . \, log \, \Sigma n_1 - pv \, ^{1)}.$$

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 $\omega$, 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

$$RT = \frac{x\,(1-x)\,\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right)}{1 + x\,(1-x)\,\frac{\partial^2}{\partial x^2} log \frac{a}{v^2}} \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

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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 $\gamma$ 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):

$$T = \frac{fx\,(1-x)\,\frac{\partial^2 T_c}{\partial x^2}}{1 + x\,(1-x)\,\frac{\partial^2\,log\,p_c}{\partial x^2}} \quad . \; . \; . \; . \; . \; . \; . \quad (4a)$$

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:

$$\left.\begin{array}{l} a = (1-x)^2\,a_1 + 2x\,(1-x)\,a_{12} + x^2\,a_2 \\ v = (1-x)\;\;v_1 + xv_2 \end{array}\right\},$$

since for liquids at low temperatures $v$ can be supposed dependent on $x$ in entirely the same manner as $b = (1-x)\,b_1 + xb_2$. 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 $b = (1-x)\,b_1 + xb_2$, 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 $b$, $v = (1-x)\,v_1 + xv_2$. 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

$$\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right)=\frac{2}{v^3}\left(a_1v_2{}^2+a_2v_1{}^2-2a_{12}v_1v_2\right),$$

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

$$\frac{\partial^2}{\partial x^2} \log \frac{a}{v^2} = 2\left[\frac{(v_2-v_1)^2}{v^2} - \frac{(\sqrt{a_2}-\sqrt{a_1})^2}{a}\right] \quad . \quad . \quad . \quad . \quad (6)$$

This expression can be reduced to a different form, and then we find:

$$\frac{\partial^2}{\partial x^2} \log \frac{a}{v^2} = \frac{2}{av^2}\left(v_2\sqrt{a_1}-v_1\sqrt{a_2}\right)\left[\left(v_2\sqrt{a_1}-v_1\sqrt{a_2}\right) + 2\,v\left(\sqrt{a_2}-\sqrt{a_1}\right)\right],$$

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:

$$\left.\begin{aligned} RT &= 2\,x\,(1-x)\,\frac{\left(v_2\sqrt{a_1}-v_1\sqrt{a_2}\right)^2}{v^3} : (1+\Delta), \\ \text{where} \qquad & \\ \Delta &= 2\,x\,(1-x)\left[\frac{(v_2-v_1)^2}{v^2} - \frac{(\sqrt{a_2}-\sqrt{a_1})^2}{a}\right] \end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

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 $1 + \Delta$ is supposed independent of $x$, which will be certainly permitted, in consequence of the small values of $\Delta$ in the case of normal substances:

$$R \frac{dT}{dx} = \frac{2\,(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{1+\Delta} \left\{ \frac{1-2\,x}{v^3} - \frac{3\,x\,(1-x)}{v^4}\,(v_2 - v_1) \right\},$$

as $v = v_1 + x\,(v_2 - v_1)$. This expression becomes $= 0$, when

$$(1-2x)\,(1+rx) - 3\,rx\,(1-x) = 0,$$

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 $\Delta$ should still be in any way dependent on $x$.

We will reduce now the equation (7) somewhat. With $a_1 = f\,RT_1 v_1$ and $a_2 = f\,RT_2 v_2$, where $T_1$ and $T_2$ are the critical temperatures of the components, these equations pass, after substituting $x_c$ for $x$, into

$$\left. \begin{aligned} RT_c &= 2\,x_c\,(1-x_c)\,\frac{[v_2 \sqrt{f\,RT_1 v_1} - v_1 \sqrt{f\,RT_2 v_2}]^2}{v_1^{\,3} \left(1 + x\,\frac{v_2 - v_1}{v_1}\right)^3} : (1 + \Delta_c) \\ \Delta_c &= 2\,x_c\,(1-x_c) \left\{ \frac{(v_2 - v_1)^2}{v_1^{\,2} \left(1 + x\,\frac{v_2 - v_1}{v_1}\right)^2} - \frac{(\sqrt{T_2 v_2} - \sqrt{T_1 v_1})^2}{[\sqrt{T_1 v_1} + x\{\sqrt{T_2 v_2} - \sqrt{T_1 v_1}\}]^2} \right\} \end{aligned} \right\},$$

or with $\underline{T_2 = \theta T_1}$ and $\underline{v_2 = \varphi v_1}$ into

$$\left. \begin{aligned} T_c &= 2\,f\,x_c\,(1-x_c)\,\frac{\varphi\,(\sqrt{\varphi} - \sqrt{\theta})^2}{(1 + (\varphi - 1)\,x_c)^3}\,T_1 : (1 + \Delta_c) \\ \Delta_c &= 2\,x_c\,(1-x_c) \left\{ \frac{(\varphi - 1)^2}{(1 + (\varphi - 1)\,x_c)^2} - \frac{(\sqrt{\theta\varphi} - 1)^2}{(1 + (\sqrt{\theta\varphi} - 1)\,x_c)^2} \right\} \end{aligned} \right\}, \quad . \quad (8)$$

since $(\varphi - \sqrt{\theta\varphi})^2 = \varphi\,(\sqrt{\varphi} - \sqrt{\theta})^2$.

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:

$$\begin{array}{l|l} CS_2 & T_1 = 548^\circ \quad ; \quad p_1 = 76 \textit{ atm.} \\ \textit{ether} & T_2 = 467^\circ \quad ; \quad p_2 = 35 \textit{ atm.} \end{array}$$

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 $\varphi = \theta\, \pi$, where the proportion $\frac{p_1}{p_2}$ is represented by $\pi$.

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

$$x_c = \frac{1}{\varphi - 1} \left(\varphi - \sqrt{\varphi^2 - \varphi + 1}\right), \quad . \quad . \quad . \quad . \quad . \quad (9)$$

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 $288 : 1{,}17 = 246 = -27^\circ$ 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 $\Delta$, 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 $\beta$ 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 $\Delta$ 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).

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[1]) Many anomalous substances namely can be regarded as normal ones, because the variation of $v$ 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 be expected the case of fig. 4,

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[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

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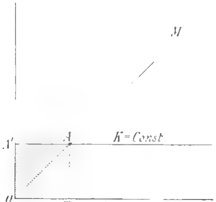

fig 1.

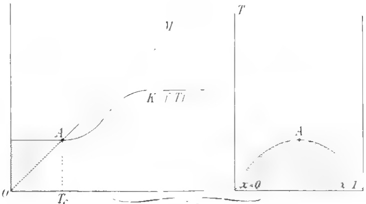

fig 2.

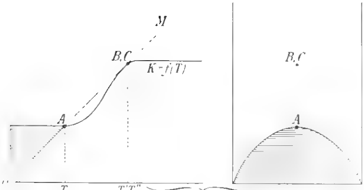

fig 3.

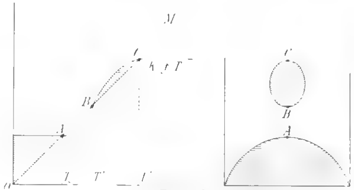

fig 4.

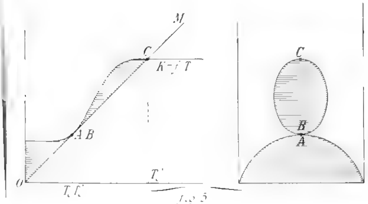

fig 5.

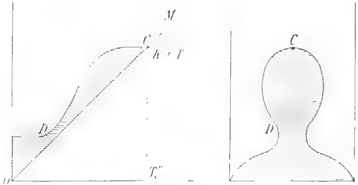

fig 6.

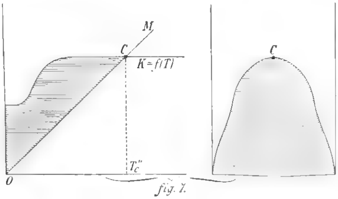

fig. 7.

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 $\beta$ 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 $\beta = 1$ ($T = 230°$) 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 $\beta$ 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 $\beta$ 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 $P_\infty$, and besides the isotropic circle situated in this plane; then we have the three equations in rectangular cartesian coordinates:

$$A \equiv a_{11}x^2 + a_{22}y^2 + a_{33}z^2 + 2a_{12}xy + 2a_{13}xz + 2a_{23}yz = 0,$$
$$B \equiv b_{11}x^2 + b_{22}y^2 + b_{33}z^2 + 2b_{12}xy + 2b_{13}xz + 2b_{23}yz = 0,$$
$$C \equiv x^2 + y^2 + z^2 = 0.$$

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

$$A + \lambda B = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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 $\lambda$ 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 $S_9$ is obtained by eliminating $p, q, r, k, \lambda$ 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:

$$kp = A_1 + B_1\lambda + kx,$$
$$kq = A_2 + B_2\lambda + ky,$$
$$kr = A_3 + B_3\lambda + kz.$$

Let us multiply each of the equations (2) by $k$ and replace the values $kp, kq, kr$; we then obtain:

$$(a_{11} + \lambda b_{11})(A_1 + B_1\lambda + kx) + (a_{12} + \lambda b_{12})(A_2 + B_2\lambda + ky) +$$
$$(a_{13} + \lambda b_{13})(A_3 + B_3\lambda + kz) + ka_{14} + kb_{14}\lambda = 0,$$

or:

$$(A_1 + B_1\lambda)k + (a_{11} + b_{11}\lambda)(A_1 + B_1\lambda) + (a_{12} + b_{12}\lambda)(A_2 + B_2\lambda) +$$
$$(a_{13} + b_{13}\lambda)(A_3 + B_3\lambda) = 0.$$

We likewise find: (5)

$$(A_2 + B_2\lambda)k + (a_{12} + b_{12}\lambda)(A_1 + B_1\lambda) + (a_{22} + b_{22}\lambda)(A_2 + B_2\lambda) +$$
$$(a_{23} + b_{23}\lambda)(A_3 + B_3\lambda) = 0,$$

and finally:

$$(A_3 + B_3\lambda)k + (a_{13} + b_{13}\lambda)(A_1 + \lambda B_1) + (a_{23} + b_{23}\lambda)(A_2 + B_2\lambda) +$$
$$(a_{33} + b_{33}\lambda)(A_3 + B_3\lambda) = 0.$$

If we reduce these equations and if we regard $k$ and $\lambda$ as variables, we shall get as result three quadratic equations, out of which $k$ and $\lambda$ 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):

$$(a_{11} + b_{11}\lambda)(A_1 + B_1\lambda)(A_2 + B_2\lambda) + (a_{12} + b_{12}\lambda\ (A_2 + B_2\lambda)^2 +$$
$$(a_{13} + b_{13}\lambda)(A_3 + B_3\lambda)(A_2 + B_2\lambda) = (a_{12} + b_{12}\lambda)(A_1 + B_1\lambda)^2 +$$
$$(a_{22} + b_{22}\lambda)(A_2 + B_2\lambda)(A_1 + B_1\lambda) + (a_{23} + b_{23}\lambda)(A_3 + B_3\lambda)(A_1 + B_1\lambda)$$

and (6)

$$(a_{12} + b_{12}\lambda)(A_1 + B_1\lambda)(A_3 + B_3\lambda) + (a_{22} + b_{22}\lambda)(A_2 + B_2\lambda)(A_3 + B_3\lambda) +$$
$$(a_{23} + b_{23}\lambda)(A_3 + B_3\lambda)^2 = (a_{13} + b_{13}\lambda)(A_1 + B_1\lambda)(A_2 + B_2\lambda) +$$
$$(a_{23} + b_{23}\lambda)(A_2 + B_2\lambda)^2 + (a_{33} + b_{33}\lambda)(A_3 + B_3\lambda)(A_2 + B_2\lambda).$$

When reduced these equations prove to be of order three in $\lambda$; we can write them in an abridged form:

$$\left.\begin{array}{l} M\lambda^3 + N\lambda^2 + P\lambda + Q = 0, \\ M'\lambda^3 + N'\lambda^2 + P'\lambda + Q' = 0, \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

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 $b_{12} = 0$, $b_{13} = 0$,

$b_{23} = 0$, $b_{14} = 0$, $b_{24} = 0$, $b_{34} = 0$, 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 $X\,O\,Y$ 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 $M, N \ldots.$ 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).

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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 ‰ 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 bonescissors. 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 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<br>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 | 1 spec. from Bergen. |
| | 0.540 | 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<br>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<br>0.526<br>0.530 | Resp. 4, 5 and 3 freshly caught spec. from Utrecht, Sept. andOct., 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 △ 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<br>0.500 | Observations at Leyden, on six, resp. five specimens in tolerably good condition, made in 1899. |
| Frog, Rana esculenta L. | 0.464<br>0.465 | id. $\genfrac{}{}{0pt}{}{8}{11}$ 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°/$_0$ which would point to a freezing point of only 0°.01. According to the figures collected by DUBOIS (see *Verslagen* 1900 p. 12 and 30) $\Delta$ 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 $\Delta$ 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; $\Delta$'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 $\Delta$ 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 $\Delta$ for the whole quantity of 24 hours varies from about 1.3 to 2.4. For normal man SCHOUTE [4]) found that $\Delta$ 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 $\Delta = 0.24$. 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 % 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 $\Delta$ 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 | △ Seawater, Gulf of Naples, in Nov. 1903, 2.105.<br>△ 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 „ „<br>(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—$4^0/_{00}$, $\Delta$ 0.159 to 0.212, $P_0$ 1.9 to 2.54 atm., north of Stockholm resp. $5^0/_{00}$, $0^\circ.265$, 3.18 atm., at Stockholm $6^0/_{00}$, $0^\circ.318$, 4 atm., on the north coast of Gothland $7^0/_{00}$, $0^\circ.37$, 4.45 atm.. and till Rügen—Schonen 7 to $8^0/_{00}$, $0^\circ.424$, 5 atm. At Bohuslän the salinity of the surface is in summer $13^0/_{00}$, $\Delta = 0^\circ.69$, but in the depth North sea water occurs of 32 to $33^0/_{00}$ and 1.8°.

*Gadus aeglefinus* L. Haddock. $\overset{\Delta}{0.767}$ 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 — $0^\circ.837$ and — $0^\circ.838$ were abnormal.

*Gadus merlangus*, L. Whiting $\overset{\Delta}{0.760}$ 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.

*Molva vulgaris*, Flemm. Ling, $\overset{\Delta}{0.716}$ Bergen. 3 fine spec.

Remark. The ling no more than G. virens penetrates into the Baltic Sea.

*Molva byrkelange* (Walb.), Trade Ling, $\overset{\Delta}{0.730}$ 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.

*Motella tricirrata* (Bloch), Whistler, $\overset{\Delta}{0{,}605}$ Bergen.

Remark. Motella tricirrata has only once been caught near Göteborg

Δ
*Hippoglossus vulgaris*, Flemm., Halibut, 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,

Δ
*Pleuronectes platessa* L., Plaice. 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.

Δ
*Pleuronectes microcephalus* Donovan, Lemon Dab 0.681 Bergen.

REMARK. P. microcephalus very rarely comes as far as Eckernförde.

Δ
*Labrus bergylta* Ascan., Ballan Wrasse 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.

Δ
*Labrus mixtus* L. Blue lipfish, Striped Wrasse 0.681 Bergen. 4 spec. } all ♀
„ „ 0.714 „ 5 „

REMARK. L. mixtus (♂ red, ♀ blue) seldom comes as far as the Sound.

Δ
*Conger vulgaris* Cuv. Conger-eel. 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.

Δ
*Salmo trutta* L. Sea or Bull trout. 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.

Δ
*Labrax lupus* Cuv. Bass, 0.720 1 spec. Aquar. Amsterdam.

REMARK. Rare in the western part of the Baltic sea.

Δ
*Trigla hirundo* Bloch. The gurnard, 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 $\Delta = 0\ .7245$ 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?)* $\Delta = 0°.76$, 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 $\Delta$ 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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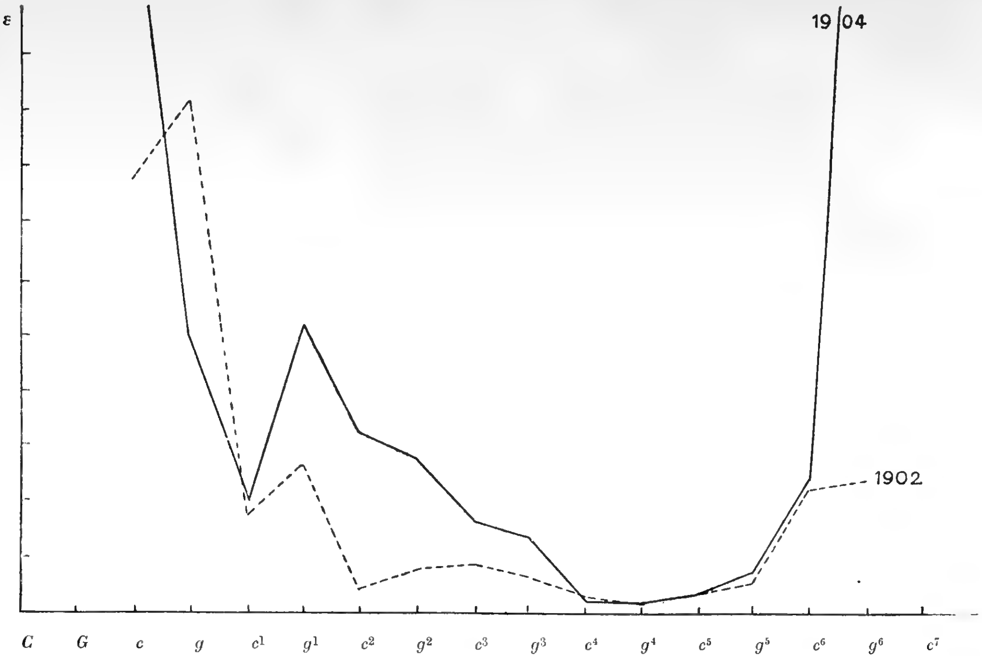
[1]) A. G. WEBSTER Boltzmann's Festschrift 1904 p. 870

[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 | $15.9\ 10^1$ | 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 | 43.1 | 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 | 58.1 | 1 25 | 7.1 » | 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 | 116.1 » | 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 woolen organ-pipes | *C* | 64 | 166.6 | 0.57 | $9.3\ 10^{4}$ | 18 | $0.2\ 10^{8}$ | $457.8\ 10^{-5}$ | $4768\ 10^{-8}$ | 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 » | 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 | $c^5$ | 4096 | 28.6 | 1.25 | 3.5 » | 71 | 3.2 » | 11.1 » | 2.3 » | 2.5 | |
| whistle. | $g^5$ | 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.

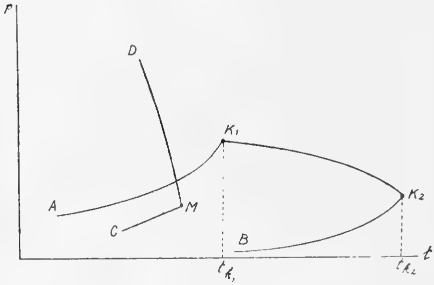

Fig. 1.

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.

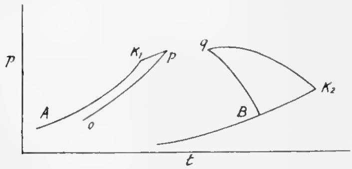

Fig. 2.

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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].

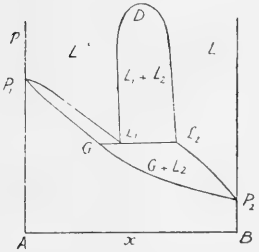

Fig. 3.

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 $BK_2$.

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.

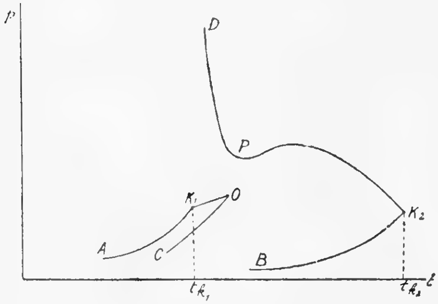

Fig. 4.

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

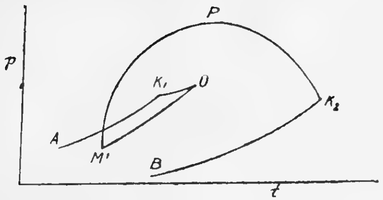

Fig. 5.

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.

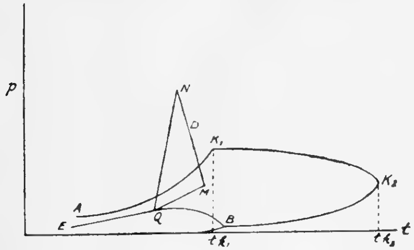

Fig. 6.

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.

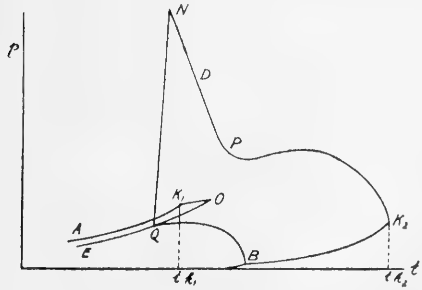

Fig. 7.

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 $L_1L_2$S 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.

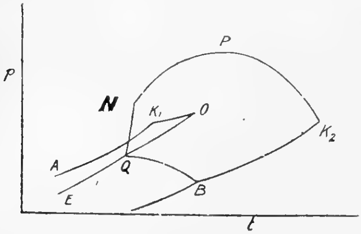

Fig. 8.

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.

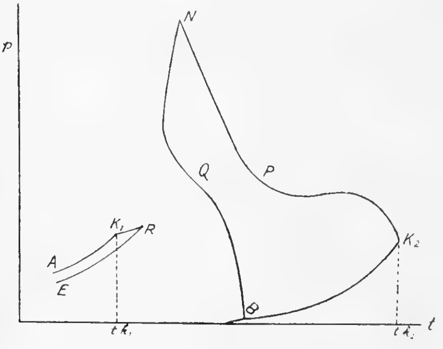

Fig. 9.

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.

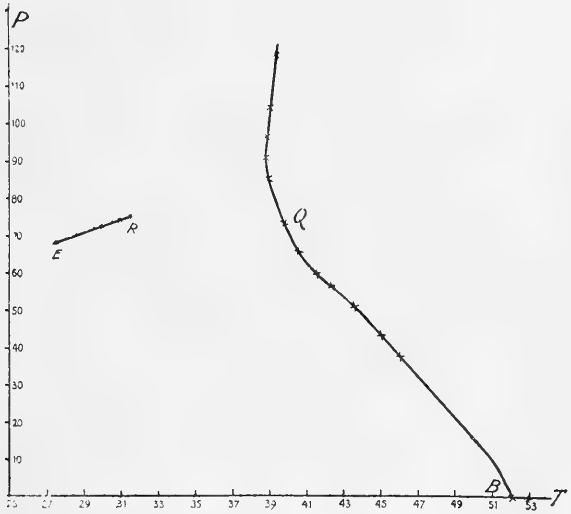

Fig. 10.

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

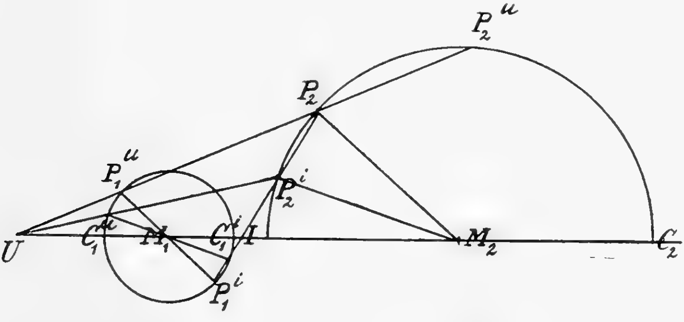

Fig. 1.

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 $Sp_n^{(1)}, Sp_n^{(2)}, \ldots Sp_n^{(n+1)}$ 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

$$\pm \quad \pm \quad \pm \quad \cdots\cdots\cdots \quad \pm,$$

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 $Sp_4^{(1)}$, $Sp_4^{(2)}, \ldots Sp_4^{(5)}$ 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 $\varepsilon_1$ 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 $\varepsilon_1$ 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 $Q_1, Q_2, \ldots Q_5$ and $Q_1', Q_2', \ldots Q_5'$. 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 $\varepsilon_1$ 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 $\varepsilon_1$, 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 $Sp_n(M_k, r_k)$, $(k = 1, 2, \ldots n)$ 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 $\varepsilon_0$ as locus of centres, whilst the other is an $n$—2-fold series with the space $S_{n-2}$ perpendicular in $M_0$ to $\varepsilon_0$ 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 $\sigma$ through $M_0$, $O'$ and the projection $O''$ of $O'$ on $S_{n-2}$. This plane $\sigma$ forming the plane of fig. 2 has with $\varepsilon_0$ 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 $\varepsilon_0$; so it is a plane of symmetry for $Sy'_1$. It has moreover with $S_{n-2}$ the line $M_0 O''$ 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 $\sigma$ (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 $M'O'.M'O = r_1^2$. Then point $A$ of $a$, which is at an equal distance from $O'$ and $O$, 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 $\varepsilon$ perpendicular to $O'A$, intersecting $\sigma$ according to a line $m$ normal to $O'A$; this plane $\varepsilon$ 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

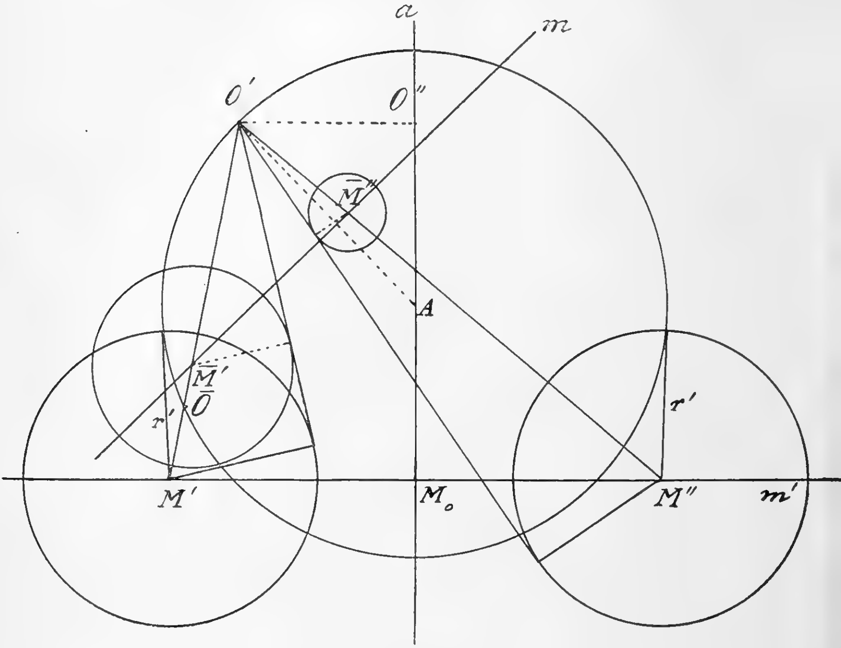

Fig. 2.

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 $\varepsilon$. Of this conic $m$ is an axis of symmetry and the points $\bar{M}'$ and $\bar{M}''$, 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 $Sp_n(\bar{M}', r')$ and $Sp_n(M'', \bar{r}'')$ 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 $M\bar{M}'M''$

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 $u - v = \pm(\bar{r}' - \bar{r}'')$. So the locus of the centres of the spherical spaces $Sp_n(M, \bar{r})$ of the system $Sy_{n-2}$ is the figure of revolution, which is generated when the hyperbola $H$ with $\overline{M}'$ and $\overline{M}''$ 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 series 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 $Sp_n^{(0)}$ 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.

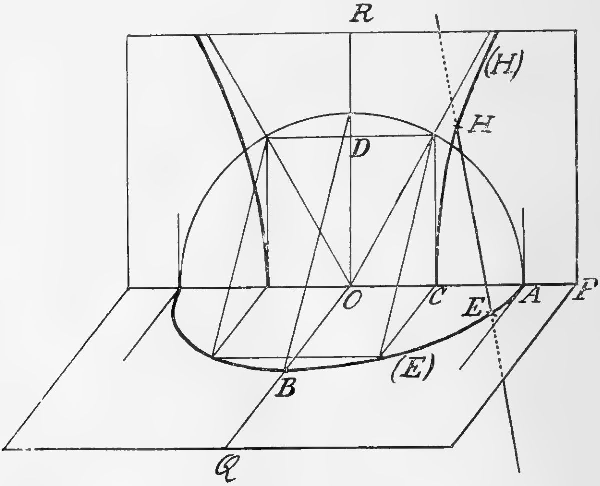

Fig. 3.

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
$E \ldots . \; x_1 = a \cos \varphi, \quad x_2 = b \sin \varphi, \quad x_3 = 0 \quad , \quad x_4 = 0, \ldots, x_n = 0,$
$H \ldots . \; x_1 = c \sec \psi, \quad x_2 = 0 \quad , \quad x_3 = b \; tg \; \psi, \quad x_4 = 0, \ldots, x_n = 0$
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 $\varrho$ 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 $\varrho$ represents an arbitrary constant and $\varphi$ and $\psi$ 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

| $E$ | $H$ |
|---|---|
| $x_1 = a \cos \varphi$ | $x_1 = c \sec \psi$ |
| $x_2 = b \sin \varphi \cos \varphi_1$ | $x_2 = 0$ |
| $x_3 = 0$ | $x_3 = b \, tg \, \psi \cos \psi_1$ |
| $x_4 = b \sin \varphi \sin \varphi_1 \cos \varphi_2$ | $x_4 = 0$ |
| $x_5 = b \sin \varphi \sin \varphi_1 \sin \varphi_2 \cos \varphi_3$ | $x_5 = 0$ |
| . . . . . . . . . . . . . . | . . . . . . . . . . . . . . |
| $x_{k+1} = b \sin \varphi \sin \varphi_1 \sin \varphi_2 \ldots . \sin \varphi_{k-2} \cos \varphi_{k-1}$ | $x_{k+1} = 0$ |
| $x_{k+2} = b \sin \varphi \sin \varphi_1 \sin \varphi_2 \ldots . \sin \varphi_{k-2} \sin \varphi_{k-1}$ | $x_{k+2} = 0$ |
| $x_{k+3} = 0$ | $x_{k+3} = b \, tg \, \psi \sin \psi_1 \cos \psi_2$ |
| $x_{k+4} = 0$ | $x_{k+4} = b \, tg \, \psi \sin \psi_1 \sin \psi_2 \cos \psi_3$ |
| . . . . . . . . . . . . . . | . . . . . . . . . . . . . . |
| $x_{n-1} = 0$ | $x_{n-1} = b \, tg \, \psi \sin \psi_1 \sin \psi_2 \ldots . \sin \psi_{n-k-3} \cos \psi_{n-k-2}$ |
| $x_n = 0$ | $x_n = b \, tg \, \psi \sin \psi_1 \sin \psi_2 \ldots . \sin \psi_{n-k-3} \sin \psi_{n-k-2}$ |

and

$$(x_1 - a\cos\varphi)^2 + (x_2 - b\sin\varphi\cos\varphi_1)^2 + x_3{}^2 + (x_4 - b\sin\varphi\sin\varphi_1\cos\varphi_2)^2 + \dots$$
$$+ (x_{k+2} - b\sin\varphi\sin\varphi_1\sin\varphi_2\dots\sin\varphi_{k-2}\sin\varphi_{k-1})^2 + x^2{}_{k+3} + \dots + x_n{}^2 =$$
$$= (c\cos\varphi + \varrho)^2$$

is the equation of the spherical space $Sp_n(E, c\cos\varphi + \varrho)$. If we write this equation in the form.

$$\sum_{i=1}^{n} x_i{}^2 + b^2 - \varrho^2 =$$
$$= 2\{ax_1\cos\varphi + b\sin\varphi\,[x_2\cos\varphi_1 + x_4\sin\varphi_1\cos\varphi_2 + \dots + x_{k+2}\sin\varphi_1\dots\sin\varphi_{k-1}]\}$$

and underneath the $k$ equations formed out of it by differentiation according to $\varphi, \varphi_1, \dots \varphi_{k-1}$, 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 $\varrho$ 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

$$x=\frac{a^2+u}{a^2}x_1\ ,\quad y=\frac{b^2+u}{b^2}y_1\ ,\quad z=\frac{c^2+u}{c^2}z_1\,.\quad .\quad .\quad .\qquad (2)$$

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

$$p_1=\frac{u'-u}{a^2}x_1 \text{ etc.}\qquad p_4=\frac{(b^2-c^2)(u'-u)}{b^2c^2}y_1 z_1 \text{ etc.}$$

From this ensues that the $\infty^3$ normals of the system of ellipsoids form a quadratic complex with the equation

$$a^2p_1p_4+b^2p_2p_5+c^2p_3p_6=0.\quad .\quad .\quad .\quad .\quad .\quad .\qquad (3)$$

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 $\infty^1$ 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 $X_\infty$, $Y_\infty$, $Z_\infty$ 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

$$x=\frac{a^2x_0}{a^2+v},\ y=\frac{b^2y_0}{b^2+v},\ z=\frac{c^2z_0}{c^2+v},\quad .\quad .\quad .\quad .\quad .\quad .\qquad (4)$$

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 $\omega^3$. 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 $\infty^1$ curves $\omega^3$; 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

$$x = \frac{(a^2+u)x_1}{a^2+v},\ y = \frac{(b^2+u)y_1}{b^2+v},\ z = \frac{(c^2+u)z_1}{c^2+v}, \quad . \quad . \quad . \quad (6)$$

or also by the equation obtained from these by elimination of $u$ and $v$

$$\begin{vmatrix} a^2(x-x_1) & x & x_1 \\ b^2(y-y_1) & y & y_1 \\ c^2(z-z_1) & z & z_1 \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

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 $\omega^3$ 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 $\omega^3$ through $P_1$.

4. Out of the preceding ensues that all bisecants of a curve $\omega^3$ 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 $\omega^3$ consists now of the hyperbola

$$z = 0, \quad (a^2-b^2)\,xy + b^2y_1x - a^2x_1y = 0 \quad . \quad . \quad . \quad . \quad (9)$$

and the right line cut by it

$$(a^2-c^2)\,x=a^2x_1 \quad , \quad (b^2-c^2)\,y=b^2y_1, \quad . \quad . \quad . \quad . \quad (10)$$

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 $(\lambda, \mu, \nu)$. 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

$$\sum_3 \frac{a^2+u'}{a^4}\,x_1x=k_0{}^2.$$

For all values of $u'$ this plane passes through the line of intersection of the planes

$$\frac{x_1x}{a^2}+\frac{y_1y}{b^2}+\frac{z_1z}{c^2}=k_0{}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\frac{x_1x}{a^4}+\frac{y_1y}{b^4}+\frac{z_1z}{c^4}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

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

$$\frac{(a^2-b^2)\,y_1y}{b^4}+\frac{(a^2-c^2)\,z_1z}{c^4}=k_0{}^2,$$

which becomes identical with the equation

$$\frac{b^2y}{y_2}-\frac{c^2z}{z_2}=b^2-c^2$$

of a projecting plane of the normal $n_2$ with footpoint $P_2$, if the conditions are satisfied

$$\frac{(a^2-b^2)\,y_1}{k_0{}^2b^4}=\frac{b^2}{(b^2-c^2)\,y_2}\;,\quad \frac{(a^2-c^2)\,z_1}{k_0{}^2c^4}=\frac{-c^2}{(b^2-c^2)\,z_2}.$$

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

$$xx' = \alpha^2 \;,\quad yy' = \beta^2 \;,\quad zz' = \gamma^2 \;. \quad . \quad . \quad . \quad . \qquad (15)$$

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

$$\frac{\alpha^2}{x_1} = x_0 \;,\quad \frac{\beta^2}{y_1} = y_0 \;,\quad \frac{\gamma^2}{z_1} = z_0 \;, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

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 $\omega^3$ 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* $\omega^3$.

In connection with this the cone of the complex of $P_1$ passes into the locus of the curves $\omega^3$ 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

$$\frac{\partial U}{\partial x} \equiv U_1 \frac{\partial U_2}{\partial x} + U_2 \frac{\partial U_1}{\partial x} - 2 U_{12} \frac{\partial U_{12}}{\partial x},$$

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 $\varrho^2$.

## **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 $\sigma$, and in a second plane $\tau$ a system of rays $[t]_n$ with index $n$ (thus the system of the tangents of a rational curve $\tau_n$) 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 $(S, \sigma)$ is projected on the plane $\tau$ in a pencil $(S', \tau)$, 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 $\tau_n$ 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* $\Sigma$ *of order* $2(n-1)$ *projecting the envelope* $\tau_n$ *out of* $S$.

The $3(n-2)$ cuspidal edges of $\Sigma$ 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 $\Sigma$ form the locus of the points $P$, for which two pairs of tangent planes of $P$ coincide along $PS$.

The cone $\Sigma$ is a part of the *singular surface* of the complex; the remaining parts are planes.

To these belongs in the first place the plane $\sigma$. Each right line of $\sigma$ is cut by $n$ rays $t$, can thus be regarded $n$ times as ray of the complex. Consequently $\sigma$ is an *n-fold principal plane.* In connection with this the cone of the complex of a point $P$ assumed in $\sigma$ degenerates into $n$ planes coinciding with $\sigma$ and into the plane through $P$ and the right line $t$ corresponding to the ray $s$ determined by $P$.

On the contrary $\tau$ 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 $\tau$ degenerates into $\tau$ 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* $\gamma_k$, $(k=1$ to $n+1)$, each connecting two homologous rays $s, t$. For the points of the line of intersection of $\sigma$ and $\tau$ 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 $\tau$ two homologous rays coincide.

§ 3. The *curve of the complex* $(\pi)$ in the arbitrary plane $\pi$ 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 $\pi$ passes through one of the $2(n-1)$ points of intersection of $\sigma$ with the envelope $\tau_n$ two of the points of contact of $(\sigma \pi)$ coincide. Regarded as locus of points $(\pi)$ 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* $\sigma$ *and* $\tau$.

If $\pi$ passes through a ray $s_1$, then $(\pi)$ as envelope consists of a pencil having its vertex in the trace of the homologous ray $t_1$ and of the pencil $(S, \pi)$ of which each ray belongs $n$ times to the complex, because it is intersected by $n$ rays $t$. As locus of points $(\pi)$ is here the line connecting the vertices of the pencils counted $2n$ times.

If $\pi$ contains a ray $t_1$ the envelope $(\pi)$ 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 $(\pi)$ 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 $\pi$ through one of the coincidences $C_k$, then $(\pi)$ 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 $A$ of an arbitrary right line $l$, thus the envelope of the rays of the complex resting on $l$. The rays in a plane $\pi$ brought through $l$ envelop a curve $(\pi)$ of order $2n$ (§ 3). If $\pi$ 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 $(\pi)$ coincide, so that $P$ is a point of $(\pi)$. So each point of $l$ belongs to $2n$ curves of the complex; consequently $l$ is a $2n$-fold right line of $A$.

*The surface of the complex is of order* $4n$.

In the planes connecting $l$ with the principal points $C_k$ the curve $(\pi)$ breaks up into a curve of order $2(n-1)$ and two right lines. This also takes place when $\pi$ passes through one of the $n$ rays $t$ resting on $l$. In the plane through $l$ and $S$ the curve $(\pi)$ degenerates into a right line to be counted $2n$ times.

In each of the planes connecting $l$ with the points of intersection of $\tau_n$ and $\sigma$ the curve $(\pi)$ consists of a curve of order $(2n-1)$ and a right line (§ 3).

*On $A$ lie besides the $2n$-fold right line and a $2n$-fold torsal right line $6n$ single right lines more.*

The plane $\sigma$ contains $2(n-1)$ right lines of $A$ and touches $A$ in the points of a curve of order $(n+1)$, which is the locus of the points where the curve of the complex $(\pi)$ touches its $n$-fold tangent $(\sigma\pi)$. For, if the ray $s_0$ resting on $l$ corresponds to the ray $t_0$ cutting $\sigma$ in $T_0$, then one of the points of contact of the curve of the complex of the plane $(l T_0)$ with $\sigma$ lies in the trace $L_\sigma$ of $l$; consequently the indicated points of contact lie on a curve of order $(n+1)$. This curve is generated by the pencils $(L_\sigma)$ and $(S)$ arranged in a $(1, n)$ correspondence; so it has in $S$ an $n$-fold point.

The plane $\tau$ touches $A$ according to a curve of order $(n+1)$ which is the locus of the points of contact of the curves $(\pi)$, in planes $\pi$ through $l$, with the traces $(\pi\tau)$. This curve has an $n$-fold point in the trace $L_\tau$ of $l$ on $\tau$; the tangents in this multiple point are the traces of the planes $\pi$ cutting $(\sigma\tau)$ on the $n$ rays $s$ conjugate to the rays $t$ drawn out of $L_\tau$.

The plane $\tau$ has farthermore the envelope $\tau_n$ in common with $A$. For, while a point $P$ of the right line $(\pi\tau)$ bears in general $n$ tangents of the curve of the complex $(\pi)$ 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 $\tau_n$; then however $P$ belongs to the curve $(\pi)$, thus to the surface of the complex $A$.

## **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 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 $\mu$, 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 $\mu$.

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 zincchloride 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 fcr 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 anaerobics, 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 $\varphi_P$ and $\varphi_Q$ will then become equal, but the stream of electrons $\boldsymbol{v}$ will no longer be 0. We shall have on the contrary, denoting by $\Sigma$ the normal section, which may slowly change from point to point, as has already been observed,

$$i = e\,\boldsymbol{v}\,\Sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

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

$$\varphi_P = \varphi_Q \;,\; V_P = V_Q \quad , \quad h_P = h_Q,$$

we find

$$-\frac{m}{2e}\int\limits_P^Q \frac{1}{h}\frac{d\,log\,A}{dx}\,dx - i\int\frac{dx}{\sigma\Sigma} = 0.$$

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, $\sigma$ 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

$$q = w - \frac{d}{dx}(W\Sigma)\,dx\ . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

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 $\Sigma dx$ 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

$$X = \frac{1}{2h}\frac{d\,log\,A}{dx} + \frac{d}{dx}\left(\frac{1}{h}\right) + \frac{e\,i}{m\sigma\Sigma}, \quad . \quad . \quad . \quad . \quad (38)$$

so that

$$w = w_1 + w_2\,,$$

if we put

$$w_1 = \frac{mi}{e}\left[\frac{1}{2h}\frac{d\,log\,A}{dx} + \frac{d}{dx}\left(\frac{1}{h}\right)\right]dx. \quad . \quad . \quad . \quad . \quad (39)$$

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

$$W_1 = \frac{2\pi m l A}{3h^4} \frac{dh}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

and

$$W_2 = \frac{m}{h} \mathbf{r} = \frac{mi}{e \Sigma h}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

§ 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

$$q'_{i=1} = \frac{2\,\alpha\,T}{3\,e}\,\frac{d\,log\,A}{d\,T}\,d\,T$$

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

$$\mu_{II} - \mu_I = T\,\frac{d}{dT}\left(\frac{\Pi_{I,\,II}}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

and

$$F = -\int_{T'}^{T''} \frac{\Pi_{I,\,II}}{T}\,dT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

in which $\mu_I$ and $\mu_{II}$ 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

$$F_{I,\,II} + F_{II,\,III} + F_{III,\,I} = 0 \; . \quad . \quad . \quad . \quad . \quad . \qquad (47)$$

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)

$$F_{1^\circ} = \frac{2\,a}{3\,e}\,log\,\frac{N_{II}}{N_I},$$

$$log\,\frac{N_{II}}{N_I} = \frac{3\,e}{2\,a}\,.\,F_{1^\circ}.$$

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

$$log\,\frac{N_{II}}{N_I} = 0{,}00011\,F_{1^\circ}.$$

In the case of bismuth and antimony, $F_{1^\circ}$ 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 $\Pi$.

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).

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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 $M_\nu$ of order $\nu$ 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 $\nu$ is a positive integer. If $\nu$ 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 | 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

$$r^\nu = [E*]^\nu . p^\nu \quad \text{resp.} \quad r^\nu = [A*|A*]^{\frac{\nu}{2}} . p^\nu$$

or

$$r^\nu = L p^\nu ,$$

where the expression $L$ (furnished with $\nu$ gaps) is equal to $[E*]^\nu$ in the first case and to $[A*|A*]^{\frac{\nu}{2}}$ 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

$$M_\nu = L . \int p^\nu \, dm = L p^{(\nu)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

This has reduced our problem to the determination of the "point-quantity of order $\nu$"

$$p^{(\nu)} = \int p^\nu \, dm , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

belonging to the given material figure. (The $\nu^{\text{th}}$ power of a point $p$ we have to imagine as the $\nu$-fold point $p$. The algebraic product of $\nu$ 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 $\nu$, 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 $A$ 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.

$$v^2 = \frac{dp}{dt} \mid \frac{dp}{dt},$$

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 $\lambda_1, \lambda_2, \ldots \lambda_n$:

$$\int \lambda_1^{\nu_1} \lambda_2^{\nu_2} \ldots \lambda_n^{\nu_n} d\lambda_2\, d\lambda_3 \ldots d\lambda_n = \frac{\nu_1!\, \nu_2! \ldots \nu_n!}{(\nu_1 + \nu_2 + \ldots + \nu_n + n-1)!} =$$

$$= \frac{\nu_1!\, \nu_2! \ldots \nu_n!}{(\nu + n-1)!},$$

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 $0.2725 \times$ 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 | $G$ | $G \triangle L$ | $\varepsilon$ | $G \varepsilon^2$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | s | | s | s | |
| Sept. 19 | O. | Arg. Z. 223, No. 75 | *D* | *D* | +2.26 | 0 70 | +1.58 | +3.18 | 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 | +2.19 | 1 34 |
| » 4 | O. | $(\alpha = 9^h0^m39^s.60)$<br>$(\delta = +22°57'38'',7)$ | *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. | $(\alpha = 18^h6^m41^s.75)$<br>$(\delta = -28°0'56'',8)$ | *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. | $(\alpha = 19^h2^m35^s.76)$<br>$(\delta = -27°54'17''75)$ | *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* | +1.15 | 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. | $(\alpha = 21^h2^m24^s.71)$<br>$(\delta = -21°33'15'',1)$ | *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 | $\dot{m} = \pm 4^s 25$ | |

$$\triangle L = -\frac{16.85}{18.305} = -0^s.92 \pm 0^s.99,$$

## 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: $+\ 0^s.97$

| $\varepsilon$ | $\varepsilon^2$ | $G$ | $G^2$ |
|---|---|---|---|
| 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:

$24 m^2 = 408.47$

$m^2 = 17.02$

$m = \pm\, 4^s.13$

$\frac{m^2}{16.115} = 1.056$  $\sqrt{\phantom{x}} = \pm\, 1^s.03,$

$\frac{m^2}{2.19} = 7.78$  $\sqrt{\phantom{x}} = \pm 2.79.$

8 84

4 | 2.21  $\sqrt{\phantom{x}} = \pm 1.49.$

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 $sin^2\ \psi$, $2\psi$ 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 $9^m20^s,932 \pm 0^s006$; by the French observers $9^m20^s,974 \pm 0^s008$. Mean $9^m20^s953$. (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, 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 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 $CaCl_2$ 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. $4^{3}/_{4}\,{}^{0}/_{0}$ 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. $1\,{}^{0}/_{0}$ $Cu\,SO_4$ 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 coagulation 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 $\psi$-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 $\psi$-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 $\psi$-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 $\psi$-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 $A'B'CA'$ 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,

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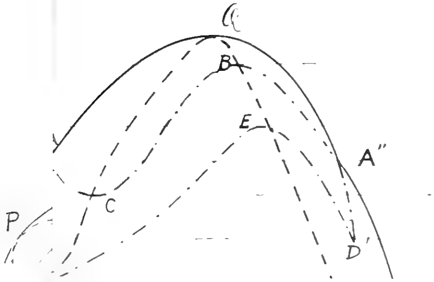

Fig 1

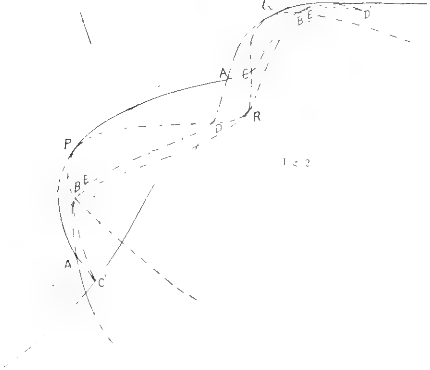

Fig 2

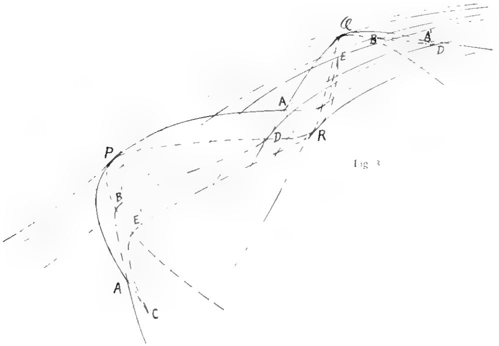

Fig 3

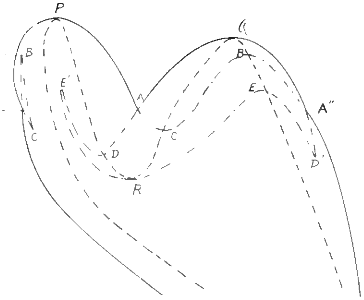

Fig 4

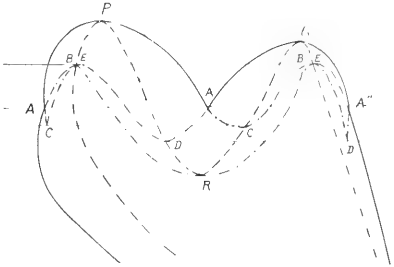

Fig 5

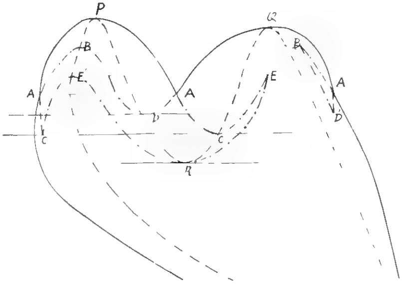

Fig 6

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, 5$^{de}$ 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 $(A, \alpha)$ to be projective to the curves $b^n$ of order $n$, passing through $n^2$ fixed points, $B_k$, of the plane $\beta$, 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 $(A, \alpha)$ on $\beta$ in a pencil $(A', \beta)$, 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 $\infty^3$ cones of the complex $(P)$ with the plane $\beta$ belong to a system $\infty^2$. 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 $\beta$. 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 $\beta$.

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 $\beta$ and cutting the plane $\alpha$ 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* $\Delta$ *of order* $n\ (3n-1)$ *having* $A$ *as vertex and passing twice through each edge* $AB_k$.

§ 3. If $P$ moves along the plane $\alpha$ then the cone of the complex $(P)$ consists of the plane $\alpha$ and a cone of order $n$ cut by $\alpha$ along the right lines $AC_k$. So $\alpha$ is a *principal plane* and at the same time part of the singular surface.

The plane $\beta$ belongs to this too. For, if $P$ lies in $\beta$ 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 $\beta$. So $\beta$ is an *n-fold principal plane* and *the singular surface* consists of a simple plane, an $n$-fold plane and a cone $\Delta$ 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 $\beta$ 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* $\Delta$.

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 $\pi$ with the planes $\alpha$ and $\beta$ 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 $\pi$ 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 $(\pi)$ can break up in three different ways.

First the point $\alpha\beta\pi$ may correspond to itself, so that $(\pi)$ breaks up into a *pencil* and into a *curve of class n*. This evidently takes place when $\pi$ 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 $\pi$ passes through one of the principal points $B_k$.

Thirdly the curve $\pi$ 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 $\pi$ is then replaced by $(n+1)$ *pencils*.

In a plane through $\alpha\beta$, thus through all principal points $C_k$, the curve $(\pi)$ 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 $\pi$ 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 $\alpha$ and $\beta$ 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 $\lambda$, 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 $\beta$ 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

$$y_1\,a_x^n + y_2\,b_x^n + y_3\,c_x^n = 0$$

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 basepoints, 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 $\delta''$ 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).

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A. W. Visser: "A few observations on autocatalysis and the transformation of $\gamma$-hydroxyacids, with and without addition of other acids conceived as an ion-reaction". (Communicated by Prof. H. J. Hamburger), p. 760.

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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; $\Delta M$ 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 $\psi$-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. $9a$), 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. $3a$ and $9a$). 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 $\psi$-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 $\Delta M$ 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 threephasepressure 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 three-phase-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 $\psi$-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 $p_2$ | $\underline{C_2H_6 + CH_3OH}$<br>$C_2H_6 + H_2O$<br>$SO_2 + H_2O$ |
| | $p_3 > p_1$ and $p_2$ | $\underline{\text{Ether} + H_2O}$ |
| Type II (fig. 7). | $p_3$ between $p_1$ and $p_2$ | $\underline{C_2H_6 + C_2H_5OH}$, $C_3H_7OH$,<br>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 $p_2$ | $CO_2 + H_2O$<br>$S$ + Xylol, Toluol |
| | $p_3 > p_1$ and $p_2$ | $\underline{C_3H_8 + CH_3OH}$ ($^{dp}/_{dT}$ –)<br>$C_5H_{12}$ and $C_6H_{14}$ + id. ($^{dp}/_{dT}$ +)<br>$C_6H_{14} + C_2H_5OH$<br>$H_2O$ + Phenol ($^{dp}/_{dT}$ +)<br>$H_2O$ + Aniline; id + isobutylalcohol.<br>$Br_2 + H_2O$ ; $CS_2 + H_2O$, $CH_3OH$, $C_2H_5OH$,<br>$C_8H_7OH$, $C_4H_9OH$. |

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.

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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.

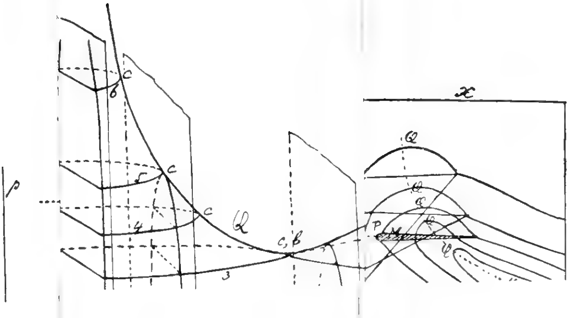
In a following communication it will be shown theoretically, that the three types may be deduced from the ordinary equation of state of Prof. VAN DER WAALS, even in the case of *normal* components. In connexion with this we must not forget, that in the neighbourhood of the critical points of each of 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 $\zeta$-surface, corresponding to points of the spinodal curve on the $\psi$-surface, are given by the simple relation

J. J. V



**J. J. VAN LAAR** "On the different forms and transformations of the boundary-curves in the case of partial miscibility of two liquids."

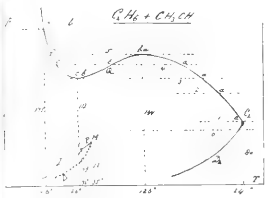


Fig 1.

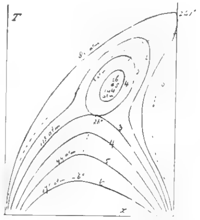


Fig 2.

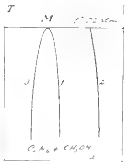


Fig 3.

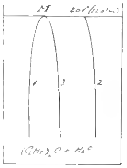


Fig 3a.

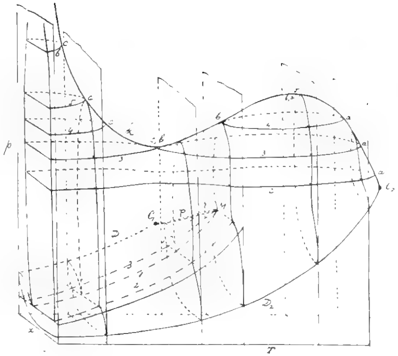


Fig 4.

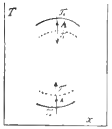


Fig 5.

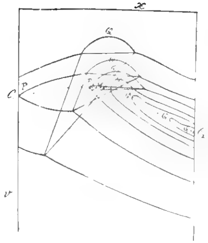


Fig 6.

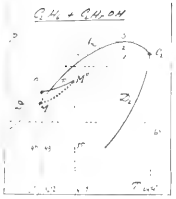


Fig 7.

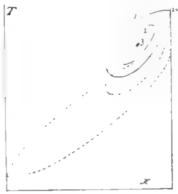


Fig 8.

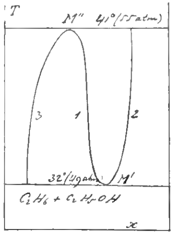


Fig 9a.

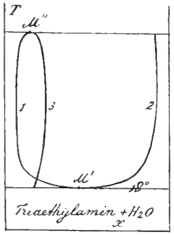


Fig. 9b.

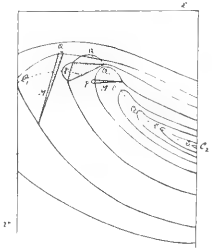


Fig 10.

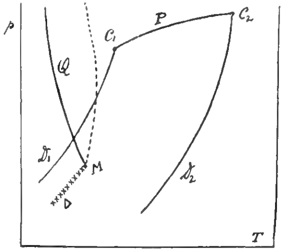


Fig 11.

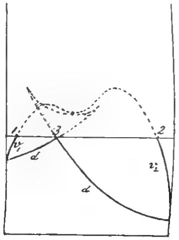


Fig. 12a.

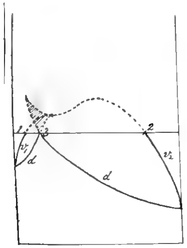


Fig 12b.

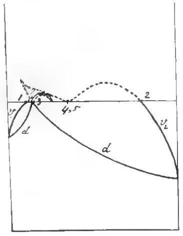


Fig. 12c.

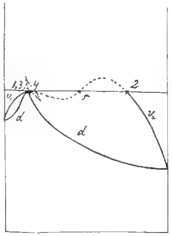


Fig 12d.

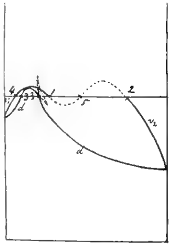


Fig 12e.

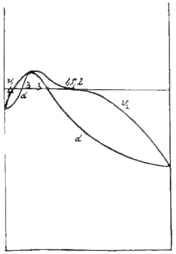


Fig 12f.

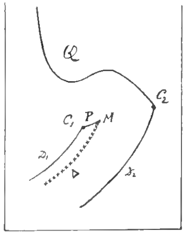


Fig. 13a.

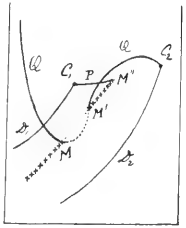


Fig 13b.

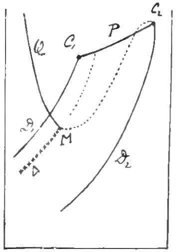


Fig. 13c.

$$\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{p,T} = 0,$$

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 $\omega$ 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

$$\underline{RT = x\,(1-x)\frac{\partial^2 \omega}{\partial x^2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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 $\omega$:

$$\underline{\omega = RT\,log\,(v-b)+\frac{a}{v}-pv} \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

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

$$\underline{\frac{\partial \omega}{\partial x} = \frac{1}{v}\frac{da}{dx} - \left(p + \frac{a}{v^2}\right)\frac{db}{dx}}, \quad \ldots\ldots\ldots \quad (3)$$

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:

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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.

$$a = ((1-x)\sqrt{a_1} + x\sqrt{a_2})^2.$$

Further we admit for $b$ the ordinary linear relation

$$b = (1-x)\, b_1 + x b_2 \,.$$

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 $a_{12} = \sqrt{a_1 a_2}$.

From the expressions for $a$ and $b$ used results:

$$\left\{ \begin{array}{l} \dfrac{da}{dx} = 2\left((1-x)\sqrt{a_1} + x\sqrt{a_2}\right)(\sqrt{a_2} - \sqrt{a_1}) = 2\sqrt{a} \,.\, (\sqrt{a_2} - \sqrt{a_1}) \\[2ex] \dfrac{d^2a}{dx^2} = 2\,(\sqrt{a_2} - \sqrt{a_1})^2 \\[2ex] \dfrac{db}{dx} = b_2 - b_1 \quad ; \quad \dfrac{d^2b}{dx^2} = 0. \end{array} \right.$$

If we did not put $a_{12} = \sqrt{a_1 a_2}$, 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 $\alpha$ is written for $\sqrt{a_2} - \sqrt{a_1}$, and $\beta$ 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

$$\frac{\partial v}{\partial x}=\frac{\frac{db}{dx}-\frac{1}{RT}\frac{(v-b)^2}{v^2}\frac{da}{dx}}{1-\frac{2^a/_v}{RT}\frac{(v-b)^2}{v^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Substituting this in the last equation for $\frac{\partial^2\omega}{\partial x^2}$, we obtain:

$$\frac{\partial^2\omega}{\partial x^2}=\frac{2}{v}\left[\left(\alpha^2-\alpha\beta\frac{\sqrt{a}}{v}\right)\left\{1-\frac{2^a/_v}{RT}\frac{(v-b)^2}{v^2}\right\}+\right.$$
$$\left.+\frac{\sqrt{a}}{v}\left(\beta\frac{\sqrt{a}}{v}-\alpha\right)\left(\beta-\frac{2\alpha\sqrt{a}}{RT}\frac{(v-b^2)}{v^2}\right)\right]:\left(1-\frac{2^a/_v}{RT}\frac{(v-b)^2}{v^2}\right),$$

since $\frac{da}{dx}=2\alpha\sqrt{a}$ and $\frac{db}{dx}=\beta$. Further treatment yields after important simplification:

$$\frac{\partial^2\omega}{\partial x^2}=\frac{2}{v}\frac{\left(\alpha-\beta\frac{\sqrt{a}}{v}\right)^2}{1-\frac{2^a/_v}{RT}\frac{(v-b)^2}{v^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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

$$RT=\frac{2x\,(1-x)}{v^3}\frac{(\alpha v-\beta\sqrt{a})^2}{1-\frac{2^a/_v}{RT}\frac{(v-b)^2}{v^2}},$$

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):

$$\underline{RT = \frac{2}{v^3}\left[x(1-x)\left\{(b_1\sqrt{a_2} - b_2\sqrt{a_1}) + \alpha(v-b)\right\}^2 + a(v-b)^2\right]}, \ldots (6)$$

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 $T =$ 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:

$$RT = \frac{2}{b^3}\,x\,(1-x)\,(b_1\sqrt{a_2} - b_2\sqrt{a_1})^2\,, \quad . \quad . \quad . \quad . \quad (6a)$$

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 (6a) 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 $\psi$-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.

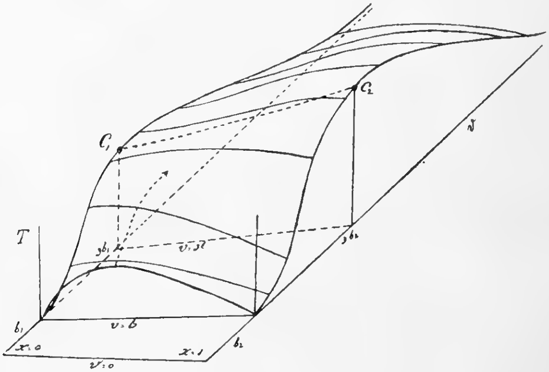
$$RT = \frac{2a_1}{v^3}(v - b_1)^2 \quad \text{and} \quad RT = \frac{2a_2}{v^3}(v - b_2)^2.$$

With $v = 3\,b_1$ (resp. $3b_2$) these two curves yield duly:

$$RT_1 = \frac{8}{27}\frac{a_1}{b_1} \quad ; \quad RT_2 = \frac{8}{27}\frac{a_2}{b_2}, \quad . \quad . \quad , \quad . \quad . \quad . \qquad (6^b)$$

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 $\psi$-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 $b_1\sqrt{a_2} - b_2\sqrt{a_1} = \pi$, by which the second member of (6) passes into

$$f = \frac{2}{v^3}\left[x\,(1-x)\,\Big\{\pi + \alpha\,(v-b)\Big\}^2 + a\,(v-b)^2\right].$$

The value of $\left(\frac{\partial v}{\partial x}\right)_{p,T}$ will be found from (4), viz.

$$\left(\frac{\partial v}{\partial x}\right)_{p,T} = \frac{\beta - \frac{2\alpha\sqrt{a}}{RT}\frac{(v-b)^2}{v^2}}{1 - \frac{2\,{}^{a}/{}_{v}}{RT}\frac{(v-b)^2}{v^2}}\,.$$

And since the denominator of this expression cannot become $\infty$, (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:

$$\left.\begin{aligned}
{}^1\!/_2\, v^3 \frac{\partial f}{\partial x} &= \theta^2(1-2x)-2x(1-x)\theta\alpha\beta-2a(v-b)\beta+2\alpha\sqrt{a}(v-b)^2 \\
{}^1\!/_2\, v^3 \frac{\partial f}{\partial v} &= \qquad 2x(1-x)\theta\alpha+2a(v-b) \qquad -\frac{3\varphi}{v}
\end{aligned}\right\},$$

where $\theta$ is written for $\pi+\alpha(v-b)$, and $\varphi$ for ${}^1\!/_2\, v^3 f$.

The equation (7$a$) becomes consequently:

$$\left\{1-\frac{2a/_v}{RT}\frac{(v-b)^2}{v^2}\right\}\left\{\theta^2(1-2x)+2\alpha\sqrt{a}(v-b)^2\right\}-\left\{\beta-\frac{2\alpha\sqrt{a}}{RT}\frac{(v-b)^2}{v^2}\right\}\frac{3\varphi}{v}+$$

$$+2\left\{x(1-x)\theta\alpha+a(v-b)\right\}\left[\left\{\beta-\frac{2\alpha\sqrt{a}}{RT}\frac{(v-b)^2}{v^2}\right\}-\beta\left\{1-\frac{2a/_v}{RT}\frac{(v-b)^2}{v^2}\right\}\right]=0.$$

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 $\alpha v-\beta\sqrt{a}=\pi+\alpha(v-b)=\theta$. 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 $\varphi$:

$$x(1-x)\theta^2\left[\theta^2(1-2x)+\underline{2\alpha\sqrt{a}(v-b)^2}\right]-3\frac{x(1-x)\theta^2+a(v-b)^2}{v}\left\{\beta\varphi-\alpha\sqrt{a}.v(v-b)^2\right\}-$$

$$-2\theta\sqrt{a}(v-b)^2\left[\underline{x(1-x)\theta\alpha}+a(v-b)\right]=0.$$

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 $\theta$, 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:

$$x(1-x)\theta^3\Big[(1-2x)\,v-3x(1-x)\,\beta\Big]+\sqrt{a}\,(v-b)^2\Big[3x(1-x)\,\theta(\theta-\beta\sqrt{a})+$$
$$+\,a\,(v-b)\,(v-3b)\Big]=0\,, \quad . \quad . \quad . \quad (8)$$

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 $\psi$-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 $x_c = \dfrac{1}{r}\Big[(r+1) - \sqrt{r^2+r+1}\Big]$, 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. $\dfrac{2a\,(v-b)^2}{v^3}$. 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.*

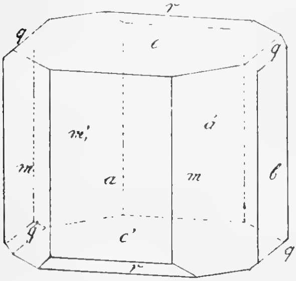
First of all I have extended the investigations *paranitrodiethylaniline* by Schrauf and myself [1]). As I could only get proper crystals of the *nitroso*-derivative from ethyl-acetate + ligroïne it was necessary to obtain the crystals of the *nitro*-derivative from the same solvent in order to get strictly comparable preparations.

### 1. p-Nitrodiethylaniline.

$C_6H_4.(NO_2).N(C_2H_5)_2$; *meltingpoint*: 73°,6.

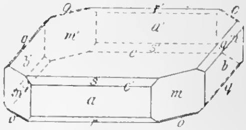
Crystals from ethyl-acetate + ligroïne. (Fig. 1).

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).

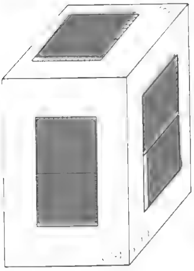

Fig. 3.

Pleochroism of p-Nitro-diaethyl-aniline.

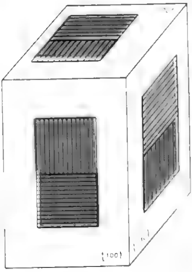

Fig. 5.

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.

$$a : b : c = 1,0342 : 1 : 1,9788.$$
$$\beta = 80°34'.$$

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 ago¹) 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.

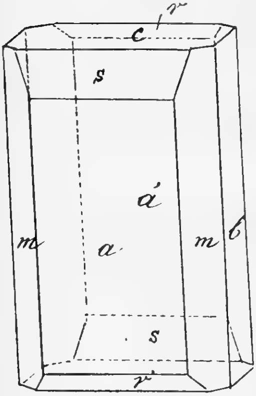
More accurate investigations have, as will be shown, practically confirmed these data. I obtained the improved material from a mixture of ethyl-acetate and ligroine, in which the compound was dissolved on warming. On slow evaporation small rectangularly bounded, thicker plates or also emerald green prisms 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:

$$a : b : c = 1{,}0178 : 1 : 1{,}9611.$$

$$\beta = 85°43'.$$

Fig. 4.



*p*-Nitroso-diethylaniline.

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.

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 $25^1/_2$ | — |
| $c : r = (001) : (\bar{1}02) =$ | *45 $59^1/_2$ | — |
| $r : a = (\bar{1}02) : (\bar{1}00) =$ | 48 19 | 48° $17^1/_2$′ |
| $a : s = (100) : (101) =$ | 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 $34^1/_2$ |
| $m : r = (\bar{1}10) : (\bar{1}02) =$ | 62 11 | 62 $9^2/_3$ |
| $m : s = (110) : (101) =$ | 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 $\rho < r$, 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: $\gamma, \beta, \alpha$ 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: $\gamma, \beta, \alpha$. | Optical orientation: $\gamma, \beta, \alpha$, |
| 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.

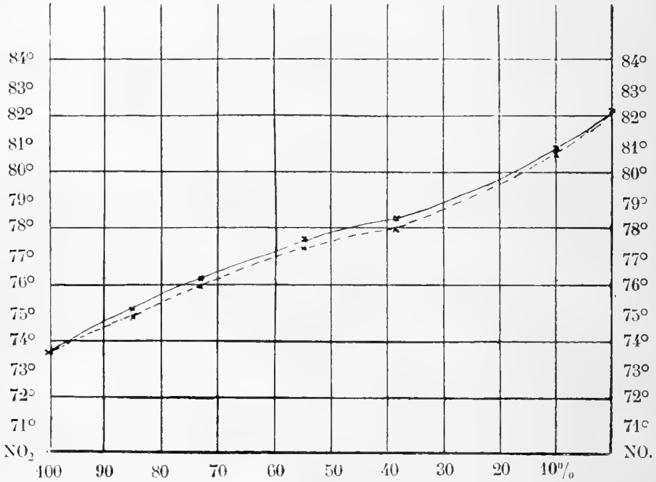


Fig. 6.

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)).

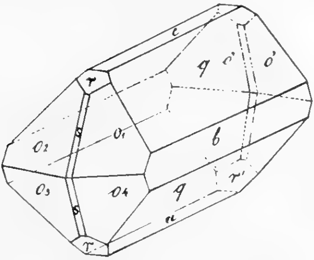
Recrystallised from acetone in which the compound (m. p. 96°) is very soluble, the substance forms very large, transparent, pale yellow or rather pale greenish-yellow crystals possessing a strong lustre and assuming a more brownish tinge on prolonged exposure to the air. Elongated, prismatic needles 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.*

$\underset{(1)}{C_6H_3 . Cl} . \underset{(2)}{Cl} . \underset{(3)}{(NO_2)}$ ; 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.

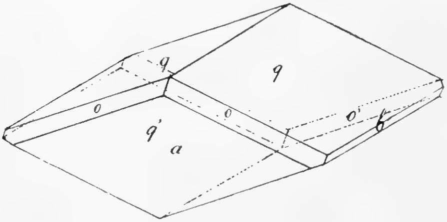
The specific gravity of the needles as determined by means of a solution of mercuric-potassium-iodide was 1,721 at 14°. The equivalent-volume is therefore 111.56 and the topical axes become;

$$\chi : \psi : \omega = 5{,}5190 : 8{,}5272 : 2{,}3706..$$

b. 1-3-*Dichloro*-2-*Nitro*-*Benzene*.

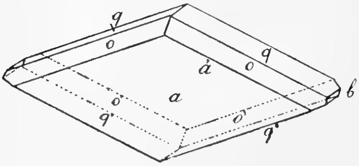
$C_6H_3 . \underset{(1)}{Cl} . \underset{(3)}{Cl} . \underset{(2)}{(NO_2)}$ ; melting point: 71° C.

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; $q \triangleq \{011\}$, 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 $\beta$ 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 $1^1/_2$ that of the first derivative.

c. 1-3-*Dichloro-5-Nitro-Benzene.*

$C_6 H_3 . \underset{(1)}{Cl} . \underset{(3)}{Cl} . \underset{(5)}{(NO_2)}$ ; 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}.

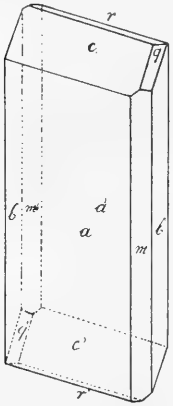
| | *Measured:* | *Calculated:* |
|---|---|---|
| $b : m = (010) : (110) =$ | * 63 5 | |
| $a : c = (100) : (001) =$ | * 58 43 | — |
| $a : m = (100) : (110) =$ | 26 58 | 26°55′ |
| $m : m = (110) : (\bar{1}10) =$ | 126 15 | 126 10 |
| $m : c = (110) : (001) =$ | — | 62 25 |
| $b : c = (010) : (001) =$ | 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 isorceles 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.*

$$a : b : c = 0{,}8072 : 1 : 0.8239$$

$$A = 79^\circ\, 33' \qquad \alpha = 92^\circ\, 48'$$
$$B = 114^\circ\, 51\tfrac{1}{2}' \qquad \beta = 112^\circ\, 51'$$
$$C = 58^\circ\, 35' \qquad \gamma = 60^\circ\, 5'$$

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:* |
|---|---|---|---|
| $a : c$ | $= (100) : (001) =$ | * $65^\circ\ 8^1/_2{}'$ | -- |
| $a : b$ | $= (100) : (010) =$ | *121 25 | — |
| $b : c$ | $= (010) : (001) =$ | *100 27 | — |
| $a : r$ | $= (\bar{1}00) : (\bar{1}01) =$ | * 50 $12^1/_2$ | — |
| $c : q$ | $= (001) : (011) =$ | * 45 39 | — |
| $q : b$ | $= (011) : (010) =$ | 54 44 | 54°48′ |
| $c : r$ | $= (001) : (\bar{1}01) =$ | 64 $40^1/_2$ | 64 $40^1/_2$ |
| $m : b$ | $= (110) : (010) =$ | 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.

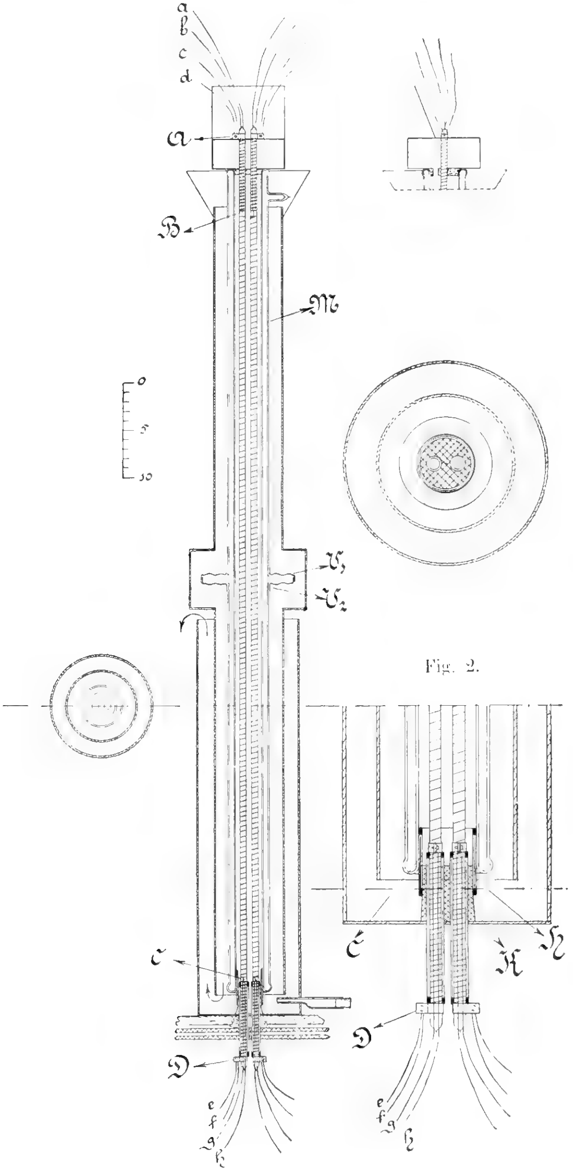

Fig. 2.

already, and the lower rim cracked off. Later we made the connection tube and the stopper more elastic (cf. *H* 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 $\mu$. The levels on the telescopes were carefully calibrated; at the distance used, one division on the levels corresponded to from 4 to 6 $\mu$ and the uncertainty in reading was less than 0.2 division or about 1 $\mu$. 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 $\omega$ and a sensitiveness of $2.5 \times 10^{-7}$. 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 | | | | 16.74 |
| Millimeter | | | 116<br>117 | 34.23<br>20.07 | 5.2<br>5.1 | |
| Point above | 19.44 | 6.1 | | | | 16.70 |
| Millimeter | | | 1127<br>1128 | 33.33<br>17.14 | 5.8<br>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<br>117 | 34.30<br>20.15 | |
| Point above | 19.43 | | | 16.63 |
| Millimeter | | 1127<br>1128 | 33.35<br>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* | *B* | *C* | *D* | *E* | *F* | | *G* | *H* | *I* |
|---|---|---|---|---|---|---|---|---|---|
| Date | Mean time. | Tempe scale. | $L_T$ | $L_{(16°)}$ | $W_t$ | | $W_0$ | $\vartheta$ | |
| 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 | | $\lambda_s =$ 5.61 |
| | | 17.82 | .836 | .868 | middle | 22.15 | 33.95 | - 87.87 | |
| | | 18.00 | .844 | .880 | bottom | 6.98 | 10.17 | | $\lambda_i =$ 78.1 |
| 22 V | $5^h20$ | 18.32 | 1011.827 | 1011.868 | top | 5.01 | 6. 29 | | $\lambda_s =$ 9.86 |
| | | 18.41 | .815 | .858 | middle | 22.13 | 33.95 | - 87.87 | |
| | | | | | bottom | 6.91 | 10.17 | | $\lambda_i =$ 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 | | $\lambda'_s =$ 2.18 |
| | | .13 | .411 | .413 | middle | 8.77 | 33.95 | -182.99 | |
| | | .17 | .406 | .409 | bottom | 4.37 | 10.17 | | $\lambda_i =$ 51.0 |
| 25 V. | $1^h15$ | 16.38 | 1011.407 | 1011.414 | top | 4.68 | 6.29 | | $\lambda'_s =$ 18.3 |
| | | .55 | .401 | .411 | middle | 8.77 | 33.95 | -182.99 | |
| | | | | | bottom | 4.34 | 10.17 | | $\lambda_i =$ 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

$$w_t = w_0\,(1 + 0.003864\,t - 0.0_5103\,t^2)$$

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 $17.8 \times 10^{-6}$. 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. | $2^h45$ | 15.12 | 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 | | $\lambda =$ 26.6 |
| | | .33 | .238 | .262 | middle 22.55 | 34.53 | -87.71 | |
| | | .37 | .239 | .263 | bottom 6.51 | 9.68 | | $\lambda =$ 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 | | $\lambda =$ 1.0 |
| | | .12 | .748 | .768 | middle 8.95 | 34.53 | -182.79 | |
| | | .19 | .740 | .761 | bottom 5.29 | 9.68 | | $\lambda =$ 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.

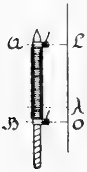

Fig. 2.

Let us suppose that the level of the liquid reaches to a position $\lambda$, fig. 2, and hence that the upper portion of $AB$ is outside the liquid. We may suppose that, for the length $\lambda$, the rod has the temperature of the bath. The resistance of the wire between $B$ and $\lambda$ 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 $\lambda$ 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 $\lambda$ 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 $\lambda$, $t_x = t_1$, between $\lambda$ 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 $\lambda$, 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 $1 \mu$.

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 $\lambda$ and 0° from $\lambda$ to $L$, in place of the distribution assumed above. The change was hardly $0.1 \mu$ 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 $\bar{a} = \frac{L_t - L_{t_1}}{L_t} \; \frac{1}{t - t_1}$.

The accuracy of the cathetometer reading can be put at $2 \mu$ (the whole contraction being $1200 \mu$). 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 $d\bar{a} = 1.5 \times 10^{-8}$, and for that of the ends we found $1 \mu$. Hence a greater uncertainty than $d\bar{a} = 4 \times 10^{-8}$ 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 $\lambda$, 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 $\lambda'$ 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 $16^{III}$** $\left\{ \begin{array}{l} \mathbf{a = 7.74.\ 10^{-6}, b = 0.00882.\ 10^{-6}} \\ \mathbf{k_1 = 23.21.\ 10^{-6}, k_2 = 0.0265.\ \ 10^{-6}} \end{array} \right.$

**Thüringer glass (n°. 50)** $\left\{ \begin{array}{l} \mathbf{a = 9.15\ 10^{-6}, b = 0.0119\ \ 10^{-6}} \\ \mathbf{k_1 = 27.45\ 10^{-6}, k_2 = 0.0357\ 10^{-6}} \end{array} \right.$

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

$$e_2 = -e_1 \quad \ldots \ldots \ldots \ldots \quad (48)$$

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.

$$\nu = \frac{4\pi l A e}{3hm} E.$$

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)

$$\sigma_1 = \sqrt{\frac{2}{3\pi}} \cdot \frac{l_1\, N_1\, e_1^2\, u_1}{\alpha T} \quad , \quad \sigma_2 = \sqrt{\frac{2}{3\pi}} \cdot \frac{l_2\, N_2\, e_2^2\, u_2}{\alpha T} \quad . \; . \quad (50)$$

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

$$\boldsymbol{\nu}=\frac{2}{3}\pi l\left[\frac{1}{h^2}\left(-\frac{2hA}{m}\frac{dV}{dx}+\frac{2heA}{m}E-\frac{dA}{dx}\right)+2\frac{A}{h^3}\frac{dh}{dx}\right]. \quad (51)$$

This will be 0, if the electric force $E$ has a certain particular value, which I shall denote by $\mathrm{E}$ 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

$$\boldsymbol{\nu}=\frac{4}{3}\pi l\,\frac{eA}{hm}(E-\mathrm{E}),$$

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

$$\left.\begin{aligned} \mathrm{E}_1 &= \frac{1}{e_1}\frac{dV_1}{dx} + \frac{2}{3}\frac{\alpha T}{e_1}\frac{d\log A_1}{dx} + \frac{4}{3}\frac{\alpha}{e_1}\frac{dT}{dx} \\ \mathrm{E}_2 &= \frac{1}{e_2}\frac{dV_2}{dx} + \frac{2}{3}\frac{\alpha T}{e_2}\frac{d\log A_2}{dx} + \frac{4}{3}\frac{\alpha}{e_2}\frac{dT}{dx} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (53)$$

If the area of a normal section is again denoted by $\Sigma$, the intensities of the partial currents are given by

$$i_1 = \sigma_1 (E - \mathrm{E}_1)\,\Sigma, \quad i_2 = \sigma_2 (E - \mathrm{E}_2)\,\Sigma, \quad . \quad . \quad . \quad . \quad (54)$$

and that of the total current, on account of (49), by

$$i = i_1 + i_2 = (\sigma E - \sigma_1 \mathrm{E}_1 - \sigma_2 \mathrm{E}_2)\,\Sigma. \quad . \quad . \quad . \quad . \quad (55)$$

Putting

$$j_1 = \frac{\sigma_1}{\sigma} i \quad , \quad j_2 = \frac{\sigma_2}{\sigma} i,$$

we may also write

$$i_1 = j_1 + \frac{\sigma_1\sigma_2}{\sigma}(\mathrm{E}_2 - \mathrm{E}_1)\,\Sigma, \quad i_2 = j_2 + \frac{\sigma_1\sigma_2}{\sigma}(\mathrm{E}_1 - \mathrm{E}_2)\,\Sigma.$$

It appears from these formulae that, whenever $\mathrm{E}_1$ differs from $\mathrm{E}_2$, the partial currents $i_1$ and $i_2$ will *not* be proportional to the conductivities $\sigma_1$ and $\sigma_2$.

§ 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 $\varphi$, so that

$$E = -\frac{d\varphi}{dx},$$

we get

$$\frac{d\varphi}{dx} = -\frac{\sigma_1}{\sigma}\mathrm{E}_1 - \frac{\sigma_2}{\sigma}\mathrm{E}_2. \quad . \quad . \quad . \quad . \quad . \quad (56)$$

and finally, taking into account the values (53), in which we now have $\frac{dT}{dx} = 0$, and integrating from $P$ to $Q$,

$$\varphi_Q - \varphi_P = -\frac{1}{e_1}\int_P^Q \frac{\sigma_1}{\sigma}\frac{dV_1}{dx}\,dx - \frac{1}{e_2}\int_P^Q \frac{\sigma_2}{\sigma}\frac{dV_2}{dx}\,dx -$$

$$-\frac{2}{3}\frac{aT}{e_1}\int_P^Q \frac{\sigma_1}{\sigma}\frac{d\log A_1}{dx}dx - \frac{2}{3}\frac{aT}{e_2}\int_P^Q \frac{\sigma_2}{\sigma}\frac{d\log A_2}{dx}dx \quad . \quad . \quad . \quad (57)$$

At the same time the intensities of the partial currents are given by

$$i_1 = \frac{\sigma_1\sigma_2}{\sigma}(\mathrm{E}_2 - \mathrm{E}_1)\,\Sigma \quad , \quad i_2 = \frac{\sigma_1\sigma_2}{\sigma}(\mathrm{E}_1 - \mathrm{E}_2)\,\Sigma.$$

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 $\mathrm{E}_1 = \mathrm{E}_2$, or in virtue of (53)

$$\frac{1}{e_1}\frac{dV_1}{dx} + \frac{2}{3}\frac{aT}{e_1}\frac{d\log A_1}{dx} = \frac{1}{e_2}\frac{dV_2}{dx} + \frac{2}{3}\frac{aT}{e_2}\frac{d\log A_2}{dx} \quad . \quad . \quad (58)$$

Since $e_2 = -e_1$, we might further conclude that

$$\frac{2}{3}aT\frac{d\log(A_1 A_2)}{dx} + \frac{d(V_1 + V_2)}{dx} = 0.$$

which means that

$$\log(A_1 A_2) + \frac{3}{2aT}(V_1 + V_2) = \psi(T)$$

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

$$\varphi_Q - \varphi_P = \frac{1}{e_1}(V_{1P} - V_{1Q}) + \frac{2}{3}\frac{\alpha T}{e_1} \log \left(\frac{A_{1P}}{A_{1Q}}\right) =$$
$$= \frac{1}{e_2}(V_{2P} - V_{2Q}) + \frac{2}{3}\frac{\alpha T}{e_2} \log \left(\frac{A_{2P}}{A_{2Q}}\right), \quad . \quad . \quad (59)$$

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 $E_1 = E_2$,

$$\frac{2}{3}\frac{\alpha T}{e_1}\frac{d \log A_1}{dx} + \frac{4}{3}\frac{\alpha}{e_1}\frac{dT}{dx} = \frac{2}{3}\frac{\alpha T}{e_2}\frac{d \log A_2}{dx} + \frac{4}{3}\frac{\alpha}{e_2}\frac{dT}{dx},$$

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

$$i \int \frac{dx}{\sigma\Sigma} = F. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

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 $\mathrm{E}_1$ and $\mathrm{E}_2$ 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. 1. 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 Fårö, 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 Fårö 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.

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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. tuberculala* Brünn. | *c*—*f* | *I* |
| *C. elegantula* Lov. sp. | *c* | *1* |

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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*I. De Hondsrug in de provincie Groningen.*

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*I. De Hondsrug in de provincie Groningen.*
*2. Bovensilurische zwerfsteenen.*
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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 $10\,\mu$ 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

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ERNST DE VRIES: "Note on the Ganglion vomeronasale."

Fig. 1

Fig. 2

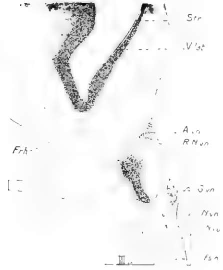

Fig. 3

Fig. 4.

Fig. 5

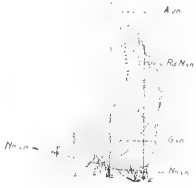

Fig. 6.

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.

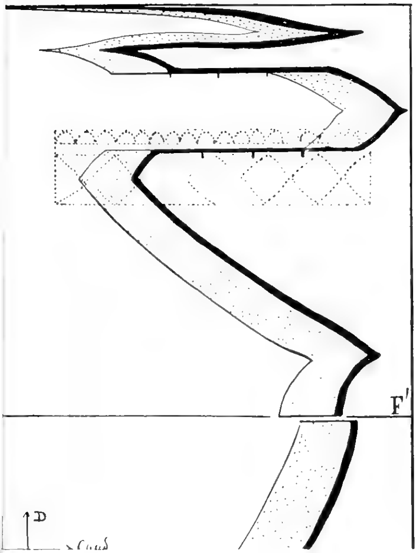
Before the two ascending rootfilaments join, they each give off a small branch, which also unite to form a small nerve, the first external branch of the posterior divisions (fig. VI) entering the septum at 2*D* fig. IV and leaving the septum to pass over in the skin at the corresponding place of fig. V.

Both descending rootfilaments before joining each givē 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



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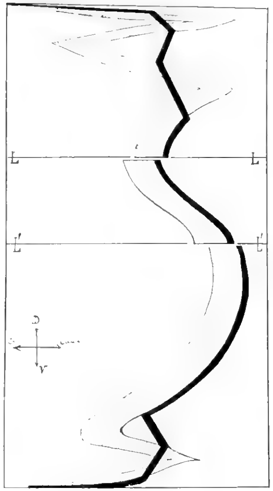

Fig I. External surface of the myotome extended in a plane
The blackline indicates the transition of the intermyotomal septum in the skin. Nat. Size

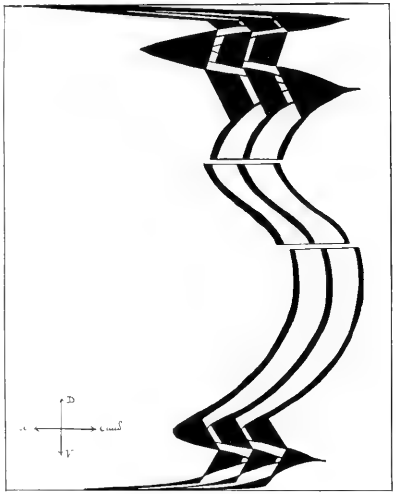

Fig. II. Form of the intermyotomal tissue adjacent to the corium. Nat. size

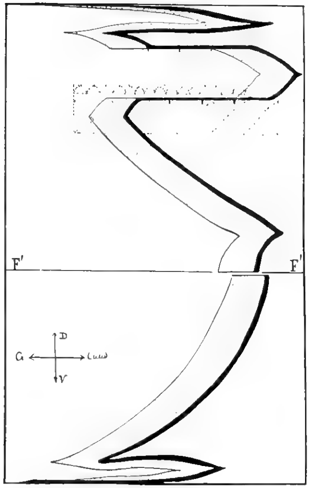

Fig III. Mesial surface of the myotome, with the line of transition of the intermyotomal septum. Nat. Size

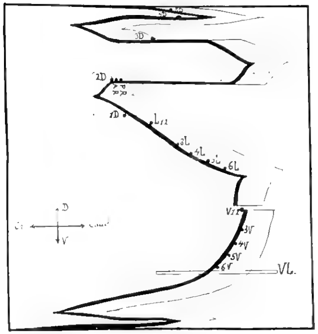

Fig. IV. Mesial surface of the myotome, projected on a sagittal plane, with the places where the nervebranches enter the intermyotomal septum Nat. size

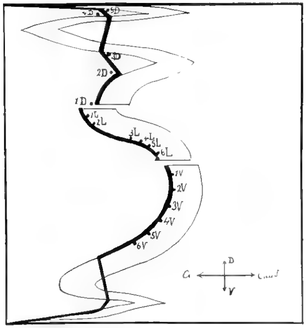

Fig. V. External surface of the myotome, with the places where the nervefilaments leave the septum Nat. size

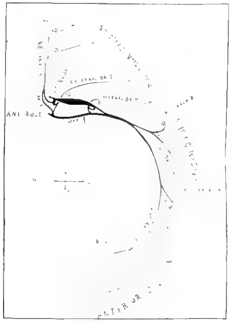

Fig VI. Spinal nerve of Acanthias with omission of the rami sympathici. Nat. size which one is recurrent (recurrent br. fig. VI) and leaves the septum to go over into the skin at 1 *V* and 2 *V*. fig. V.

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 differentation 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 $\infty^k$ 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 $\tfrac{1}{2}(k+1)(2n-k)$, on which $O$ is a $\tfrac{1}{2}k(k+1)$-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 $\tfrac{1}{2}k(k+1)$-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 $I^{n-1}$) 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 $\alpha$. The curve $\alpha^n$ along which $\alpha$ cuts the surface $\Phi^n$ is evidently nodal curve of **A**. The tangents in the $3n(n-2)$ inflectional points of $\alpha^n$ being principal tangents of $\Phi^n$, the scroll **A** has $3n(n-2)$ right lines and the curve $\alpha^n$ to be counted twice in common with $\Phi^n$, so it is a scroll of order $n(3n-4)$.

The two principal tangents $a$ and $a'$ in a point of $\alpha^n$ have each three points in common with $\Phi^n$; consequently $\alpha^n$ belongs six times to the section of **A** and $\Phi^n$. 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 $\Phi^n$ is cut by the principal tangents $a$ situated in $\alpha$. In each of the remaining $n(11n-24)$ points of intersection of this curve with $\alpha$ the surface $\Phi^n$ has *four* coinciding points of intersection in common with $a$. From this ensues:

*The locus of the points in which* $\Phi^n$ *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 $\Phi^n$ in points $B$ of the plane $\beta$.

Out of each point $B$ of the section $\beta^n$ 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 $\beta^n$. The inflectional tangents lying in $\beta^n$ 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 $\alpha^n$ and one of their points of intersection $B$ on $\beta^n$. So this number indicates the order of the curve along which $\Phi^n$ is osculated by **B**. Beside this curve of contact and the manyfold curve $\beta^n$ the surfaces $\Phi^n$ and **B** have still in common the locus of the points $B'$ which determine the principal tangents $AB$ moreover on $\Phi^n$. 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 $\Phi^n$ in a point $B$ of $\beta^n$.

*The points of intersection of* $\Phi^n$ *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 $\Phi^n$, 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* $\Phi^n$ *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 $\beta$. Each point of intersection of $\beta^n$ with an inflectional tangent lying in $\beta$ 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 $\beta^n$ on the inflectional tangents of $\beta^n$. In each of the remaining points of intersection of $(B')$ with $\beta$ we find that $\Phi^n$ is touched by a right line having elsewhere three coinciding points in common with $\Phi^n$. 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 $\gamma^n$ according to which $\Phi^n$ is cut by the plane $\gamma$ I shall regard the $(n-3)\,(n+2)$ tangents $c$ which touch $\Phi^n$ moreover in a point $C''$. On the scroll **C** of the double tangents $c$ the curve $\gamma^n$ is a manyfold curve in which $(n-3)\,(n+2)$ sheets meet. Each double tangent situated in $\gamma$ 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 $\Phi^n$ and **C** touch each other along the locus $(C'')$ of the two points of contact. Of this curve the plane $\gamma$ contains the points of contact of the right lines $c$ lying in $\gamma$ 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 $\gamma^n$ to be counted $2(n-3)\,(n+2)$-times **C** and $\Phi^n$ have moreover in common the locus of the points $S$ determined by the double tangents $c$ on $\Phi^n$. 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 $\gamma$ belong the points of intersection of $\gamma^n$ 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 $\gamma$ are apparently points of osculation of the tangents $t_{2,3}$. So from this ensues:

*The points of osculation of the principal tangents touching $\Phi^n$ 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* $\Phi^n$ *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 $\Phi^n$ in points $D$ of the plane $\delta$ form a scroll **D**, on which the section $\delta^n$ of $\Phi^n$ with $\delta$ is a manyfold curve bearing $\frac{1}{2}(n-3)(n-4)(n^2+n+12)$ [1] sheets. As moreover every double tangent of $\delta^n$ belongs to $(n-4)$ different points $D$ the order of **D** is equal to

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

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 $\gamma$ and at the same time one of their points of contact $D$ in the plane $\delta$. So this number indicates the order of the curve along which **D** and $\Phi^n$ touch each other. If we take the manyfold curve $\delta^n$ into consideration, it is evident that the points $D'$ which the right lines of **D** have in common with $\Phi^n$ besides the points of contact $C$ and the points of intersection $D$ lying in $\delta$, 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 $\delta$ $(n-4)(n-5)$-times on each double tangent of $\delta^n$. In each of its remaining points of intersection with $\delta$ the surface $\Phi^n$ 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* $\Phi^n$ *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 $\lambda'$, $\lambda''$, 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 $\lambda$ evidently representing $(n-5)(n-6)$ coincidences $\lambda' \equiv \lambda''$. The remaining coincidences of the system $(\lambda)$ 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 $\Phi^n$ 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 $\Phi^n$ on the curve $\sigma^n$ is but the third part of the number of the indicated coincidences of $(\lambda)$, 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 $\Phi^n$.

Now we can also find the order $x$ of the scroll $(d)$. This scroll being touched by $\Phi^n$ 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 $\Phi^n$ form a scroll the order of which is* $\tfrac{1}{3}\, n\,(n-3)\,(n-4)\,(n-5)\,(n^2+3n-2)$ [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 $\alpha$. If two rays $s$ and $s'$ of a pencil $(S, \sigma)$ are conjugate to each other, when they rest on two right lines $a$ and $a'$, then in $(S, \sigma)$ 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 $\alpha^n$; 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 $n^2+3n+2$ instead of $n^2+3n-2$.

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 $\lambda$ 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:

$$\left.\begin{aligned}
&(a_{11}A_1+a_{12}A_2+a_{13}A_3)\mu^2+(a_{11}B_1+a_{12}B_2+a_{13}B_3+b_{11}A_1+b_{12}A_2+b_{13}A_3)\lambda\mu+\\
&\quad+(b_{11}B_1+b_{12}B_2+b_{13}B_3)\lambda^2+A_1\mu k+A_1\lambda k=0 .\\
&(a_{12}A_1+a_{22}A_2+a_{23}A_3)\mu^2+(a_{12}B_1+a_{22}B_2+a_{23}B_3+b_{12}A_1+b_{22}A_2+b_{23}A_3)\lambda\mu+\\
&\quad+b_{12}B_1+b_{22}B_2+b_{23}B_3)\lambda^2+A_2\mu k+B_2\lambda k=0 ,\\
&(a_{13}A_1+a_{23}A_2+a_{33}A_3)\mu^2+(a_{13}B_1+a_{23}B_3+a_{33}B_3+b_{13}A_1+b_{23}A_2+b_{33}A_3)\lambda\mu+\\
&\quad+(b_{13}B_1+b_{23}B_2+b_{33}B_3)\lambda^2+A_3\mu k+B_3\lambda k=0 .
\end{aligned}\right\}(a)$$

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:

$$\left.\begin{array}{l} P_1\mu^2 + Q_1\lambda\mu + R_1\lambda^2 + A_1\mu k + B_1\lambda k = 0 \,, \\ P_2\mu^2 + Q_2\lambda\mu + R_2\lambda^2 + A_2\mu k + B_2\lambda k = 0 \,, \\ P_3\mu^2 + Q_3\lambda\mu + R_3\lambda^2 + A_3\mu k + B_3\lambda k = 0 \,, \end{array}\right\} \quad . \; . \; . \quad (b).$$

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

$$\left|\begin{array}{ccccccccc} P_1 & & & P_2 & & & P_3 & & \\ Q_1 & P_1 & & Q_2 & P_2 & & Q_3 & P_3 & \\ R_1 & & P_1 & R_2 & & P_2 & R_3 & & P_3 \\ A_1 & Q_1 & & A_2 & Q_2 & & A_3 & Q_3 & \\ B_1 & R_1 & Q_1 & B_2 & R_2 & Q_2 & B_3 & R_3 & Q_3 \\ & & R_1 & & & R_2 & & & R_3 \\ & A_1 & & & A_2 & & & A_3 & \\ & B_1 & A_1 & & B_2 & A_2 & & B_3 & A_3 \\ & & B_1 & & & B_2 & & & B_3 \end{array}\right| = 0 \,,$$

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

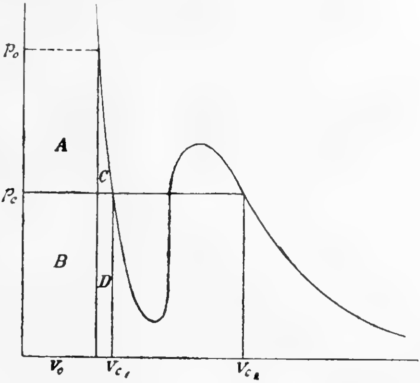
$$M_1 \mu_1 = \psi - v \left(\frac{\partial \psi}{\partial v}\right)_x - x \left(\frac{\partial \psi}{\partial x}\right)_v =$$

$$= \int_v^\gamma p dv + p\, v + MRT\, l\, (1 - x) - x \int_v^\gamma \left(\frac{\partial p}{\partial x}\right)_{vT} dv + F(T)$$

in which the integrations must be extended from a volume $\gamma$ 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 $\int\limits_{v_0}^{7} pdv$ may be split into three parts:

$$\int\limits_{v_o}^{v_{c_1}} pdv + \int\limits_{v_{c_1}}^{v_{c_2}} pdv + \int\limits_{v_{c_2}}^{7} pdv$$

For the middle quantity we may write:

$$\int\limits_{v_{c_1}}^{v_{c_2}} pdv = p_c\,(v_{c_2} - v_{c_1})$$

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:

$$\int_{v_o}^{\gamma} pdv + p_o v_o = \int_{v_o}^{v_{c_1}} pdv + p_o v_o - p_c v_{c_1} + MRT + MRT\, l\, p_c/p_\gamma .$$

§ 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 $C = \int_{v_o}^{v_{c_1}} pdv - D$. 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 $\int_{v_0}^{v_{c_1}} + \int_{v_{c_1}}^{v_{c_2}} + \int_{v_{c_2}}^{\gamma}$. The last integral is now zero according to the law of AVOGRADO. The middle one we find from the equation already used above:

$$\int_{v_{c_1}}^{v_{c_2}} p dv = p_c (v_{c_2} - v_{c_1})$$

by differentiating, taking into consideration that the limits of the integral are functions of $x$. We get:

$$\int_{v_{c_1}}^{v_{c_2}} \left(\frac{\partial p}{\partial x}\right)_{vT} dv + \left[p \frac{\partial v_c}{\partial x}\right]_1^2 = \frac{\partial p_c}{\partial x} (v_{c_2} - v_{c_1}) + p_c \frac{\partial v_{c_2}}{\partial x} - p_c \frac{\partial v_{c_1}}{\partial x} .$$

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 $\int_{v_0}^{v_{c_1}} \left(\frac{\partial p}{\partial x}\right) dv$. As we were allowed to neglect $\int_{v_0}^{v_{c_1}} pdv$, we might be inclined to think that this term too might be omitted. But as follows form the equation of state:

$$\frac{\partial p}{\partial x} = \frac{MRT}{(v-b)^2} \frac{db}{dx} - \frac{{}^{da}/_{dx}}{v^2},$$

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:

$$- \left[ \frac{MRT}{v-b} \frac{db}{dx} - \frac{{}^{da}/_{dx}}{v} \right]_{v_0}^{v_{c_1}} .$$

Here we may substitute $p + a/v^2$, for $MRT/v - b$, so that our expression for the thermodynamic potential becomes:

$$M_1\mu_1 = MRTl(1-x) + p_0v_0 - p_cv_0 + MRT + MRT\, lp_c/p_\gamma - x \frac{\partial p_c}{\partial x} (v_{c_2} - v_{c_1}) +$$

$$+ x \frac{db}{dx} (p_c - p_0) + x \frac{db}{dx} \left\{ \frac{a}{{v_{c_1}}^2} - \frac{a}{{v_0}^2} \right\} - x \frac{da}{dx} \left\{ \frac{1}{v_{c_1}} - \frac{1}{v_0} \right\} + F(T).$$

§ 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:

$$p_o - p_c = -\frac{MRT}{v_o - x\dfrac{db}{dx}}\left\{log\frac{p_c(1-x)}{p_{coex.}} - x\frac{dlog p_c}{dx}\right\}$$

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 $p_o = p_{coex.}$ and if we take $v_{coex.}$ instead of $v_o$, 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 $v_o$) 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 $v_o = v_{c_1}$ 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 $p - \Delta p$, where $\Delta p$ 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 [2]), 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 $\frac{a_x}{v_o^2}$ which works towards the solution, is in first approximation neutralized by the force $\frac{a}{v_g^2}$ 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 $^1/_2\ \sigma$ ($\sigma$ 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 $\sigma$) 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 $^1/_2\ \sigma$. 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

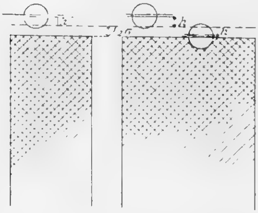

Fig. 1.

$$\frac{S\left(1-\frac{b}{v}\right)}{v-2b}$$

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 permissible 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 $\infty$ 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 $\zeta$-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 $\zeta$-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 $\zeta$-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:

$$M\mu = F(N) + C. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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: <br> $M\mu = pv + \int_{v_0}^{v} pdv + MRTl(1-x) + F(T) + \int_{v_0}^{v} \left(\frac{\partial p}{\partial x}\right)_{vT} dv$ <br> $pv$ 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 <br> $\int_{v_0}^{v} \left(\frac{\partial p}{\partial x}\right) dv = 0$ 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: <br> $\underline{pV}$ <br> (when we neglect $v$ by the side of $V$). | 3. <br> $\int_{v_{c_1}}^{v_{c_2}} pdv = \underline{p_c (v_{c_2}} - v_{c_1})$ |

| | |
|---|---|
| 4. Let the vapour expand to infinite volume, the work done is: $\int_{V}^{\infty} pdv = \underline{MRT\,l\,\frac{V_\infty}{V}}$ | 4. $\int_{v_{c_2}}^{\gamma} pdv = \underline{MRT\,l\,\frac{\gamma}{v_{c_2}}}.$ |
| 5. Now press the vapour again into the solution, then a work is done by the substance: $-\int_{V}^{\infty} pdv = -\underline{MRT\,l\,\frac{V_\infty}{V}}$ | 5. The thermodynamic potential of pure water is: $M\mu = pv + \int_{v_g}^{\gamma} pdv + F(T)$ <br> $\int_{v_g}^{\gamma} pdv = \underline{MRT\,l\,\frac{\gamma}{v_{c_2}}}\ ;\ pv = \underline{p_c\ v_{c_2}}$ |
| 6. The total quantity of work must be zero, so: $Pv = pV$ . | 6. The two potentials are the same, so: $(p_0 - p_c)\,v_{c_1} = -MRT\,l\,(1-x)$ |

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 $p_0$ $\left(\text{in the term} \int \frac{\partial p}{\partial x}\, dv\right)$ 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 $t$; $\tau$ 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 $n = \dfrac{x_1y - y_1x}{x_1y_3 - y_1x_3} = \dfrac{\text{triangle } P_1ZP}{\text{triangle } P_1ZP_3}$ 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 $\ddot{n}$ | $0$ | $-\dfrac{n_3}{r_2^{\,3}}$ | $-\dfrac{1}{r_3^{\,3}}$ |

Consequently in the development of $n$ in a series of ascending powers of $\tau$ 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 $\tau$, we require only 3 indefinite coefficients which may be eliminated from the following 4 relations:

$$\begin{aligned} n_3 &= K_1\tau_3 + K_3\tau_3^{\,3} + K_4\tau_3^{\,4} + f_4 \\ 1 &= K_1\tau_2 + K_3\tau_2^{\,3} + K_4\tau_2^{\,4} + F_4 \\ -\frac{n_3}{r_2^{\,3}} &= \quad + 6K_3\tau_3 + 12K_4\tau_3^{\,2} + f_2 \\ -\frac{1}{r_3^{\,3}} &= \quad + 6K_3\tau_2 + 12K_4\tau_2^{\,2} + F_2\,. \end{aligned}$$

The remaining relation yields an expression for $n_3$ in $\tau_2, \tau_3, r_2, r_3$ 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 $\tau$; $F_4$, for instance, which begins with $K_5\tau_2^{\,5}$ is of the 4th order of $\tau$, 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 $\dot{n}_0$. For clearness I shall here give this development:

$$\frac{d^3 n}{d\boldsymbol{\tau}^3} = - n\dot{z} - z\dot{n}\ , \quad \text{where } z \text{ is put for } \frac{1}{r^3}$$

$$\frac{d^4 n}{d\boldsymbol{\tau}^4} = (z^2 - \ddot{z})\, n - 2\dot{z}\dot{n}$$

$$\frac{d^5 n}{d\boldsymbol{\tau}^5} = (4z\dot{z} - \dddot{z})\, n + (z^2 - 3\ddot{z})\, \dot{n}\ .$$

From the differential equation $\frac{d}{d\boldsymbol{\tau}}(r^3\ddot{r} + r) = 0$, 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.

$$\frac{d^5 n}{d\boldsymbol{\tau}^5} = 5\left(z - \frac{\ddot{z}}{z} + \frac{8}{9}\,\frac{\dot{z}^2}{z^2}\right)\dot{z}n + (z^2 - 3\ddot{z})\,\dot{n}\ .$$

For $\boldsymbol{\tau} = 0$, $n$ is equal to zero and $\dot{n} = K_1$, hence

$$K_3 = -\frac{1}{6}\,z_1 K_1 \quad , \quad K_4 = -\frac{1}{12}\,\dot{z}_1 K_1 \quad , \quad K_5 = \frac{z_1^{\,2} - 3\ddot{z}_1}{120}\,K_1 .$$

If we substitute the expressions for the coefficients $K$ in the second of the 4 relations, this becomes:

$$1 = K_1\boldsymbol{\tau}_2 \left\{1 - \frac{1}{6}\,z_1\boldsymbol{\tau}_2^{\,2} - \frac{1}{12}\,\dot{z}_1\boldsymbol{\tau}_2^{\,3} + \frac{z_1^{\,2} - 3\ddot{z}_1}{120}\,\boldsymbol{\tau}_2^{\,4} \ldots\right\}$$

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 $\frac{1}{\boldsymbol{\tau}_2}$.

From the 4 relations with the indefinite coefficients $K_1$, $K_3$, $K_4$ we find by eliminating the latter:

$$\left\{n_3 - f_4 - \frac{\boldsymbol{\tau}_2^{\,2} + \boldsymbol{\tau}_2\boldsymbol{\tau}_3 - \boldsymbol{\tau}_3^{\,2}}{12}\left(\frac{n_3}{r_2^{\,3}} + f_2\right)\right\}\boldsymbol{\tau}_2 = \left\{1 - F_4 - \frac{\boldsymbol{\tau}_3^{\,2} + \boldsymbol{\tau}_3\boldsymbol{\tau}_2 - \boldsymbol{\tau}_2^{\,2}}{12}\left(\frac{1}{r_3^{\,3}} + F_2\right)\right\}\boldsymbol{\tau}_3 .$$

From this equation I solve:

$$n_3 = \frac{\boldsymbol{\tau}_3}{\boldsymbol{\tau}_2}\,\frac{1 - \dfrac{\boldsymbol{\tau}_3^{\,2} + \boldsymbol{\tau}_3\boldsymbol{\tau}_2 - \boldsymbol{\tau}_2^{\,2}}{12 r_3^{\,3}}}{1 - \dfrac{\boldsymbol{\tau}_2^{\,2} + \boldsymbol{\tau}_2\boldsymbol{\tau}_3 - \boldsymbol{\tau}_3^{\,2}}{12 r_2^{\,3}}} + R_4$$

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 $\tau_1$ 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 $\tau_1$ and $\tau_3$; this correction takes the following form, which is symmetrical with respect to $\tau_1$ and $\tau_3$:

$$\frac{1}{3} K_5\tau_1\tau_3 (2\tau_1 + \tau_3)(\tau_1 + 2\tau_3)(\tau_1 - \tau_3) .$$

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:

$$\frac{\tau_1}{\tau_2}\left(1 - \frac{\tau_1{}^2+\tau_1\tau_2-\tau_2{}^2}{12r_1{}^3}\right)ZP_1 + \frac{\tau_3}{\tau_2}\left(1 - \frac{\tau_3{}^2+r_3\tau_2-\tau_2{}^2}{12r_3{}^3}\right)ZP_3 =$$
$$= \left(1 - \frac{\tau_2{}^2+\tau_2\tau_3-\tau_3{}^2}{12r_2{}^3}\right)\overline{ZP_2}.$$

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

$$\frac{\tau_1}{\tau_2}\Delta\,\overline{ZP_1} + \frac{\tau_3}{\tau_2}\Delta\,\overline{ZP_3} = \Delta\,\overline{ZP_2}$$

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 $n_3$.

$$\begin{aligned}
n_3 &= K_1\,\tau_3 + K_3\,\tau_3{}^3 + K_4\,\tau_3{}^4 + K_5\,\tau_2{}^5 + f_5\\
1 &= K_1\,\tau_2 + K_3\,\tau_2{}^3 + K_4\,\tau_2{}^4 + K_5\,\tau_2{}^5 + F_5\\
-z_2\,n_3 &= \quad + 6K_3\,\tau_3 + 12K_4\,\tau_3{}^2 + 20K_5\,\tau_3{}^3 + f_3\\
-z_3 \quad &= \quad + 6K_3\,\tau_2 + 12K_4\,\tau_2{}^2 + 20K_5\,\tau_2{}^3 + F_3\\
0 &= K_1\,z_1 + 6K_3
\end{aligned}$$

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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:

$$R_5 = \tfrac{1}{2}\, K_6\, (\tau_2^{\,4} - \tau_2^{\,3}\, \tau_3 - \tau_2^{\,2}\, \tau_3^{\,2} - \tau_2\, \tau_3^{\,3} + \tau_3^{\,4})\, \tau_3\, (\tau_2 - r_3).$$

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:

$$\tfrac{1}{2} L_6 (\tau_2^4 - \tau_2^3\tau_1 - \tau_2^2\tau_1^2 - \tau_2\tau_1^3 + \tau_1^4)\, v_1 (\tau_2 - \tau_1)$$

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 $\tau_6$ 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 $\tau^6$ in the development of $\dfrac{\text{triangle } P_1ZP}{\text{triangle } P_1ZP_3}$, where the variable $\tau$ 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 $\tau_2$ 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 $\tau_1$, $\tau_2$, and $\tau_3$, I remark that it may be performed quickly if we modify these forms in the following way:

$$A_{12} = -\frac{\tau_3}{10}\left(\frac{1}{2}\frac{\tau_1^{\,2}}{\tau_3} + \frac{1}{3}\frac{\tau_1^{\,2}}{\tau_2}\right) \quad B_{1.2} = +\frac{\tau_1}{10}\left\{\frac{1}{2}\frac{\tau_2^{\,2}}{\tau_1} - \frac{1}{3}\left(\tau_1 + \tau_2 + \frac{\tau_1^{\,2}}{\tau_2}\right)\right\}$$

$$A_{2.1} = -\frac{\tau_3}{10}\left(\frac{1}{2}\frac{\tau_2^{\,2}}{\tau_3} - \frac{1}{3}\frac{\tau_2^{\,2}}{\tau_1}\right) \quad B_{2.1} = +\frac{\tau_2}{10}\left\{\frac{1}{2}\frac{\tau_1^{\,2}}{\tau_2} - \frac{1}{3}\left(\tau_1 + \tau_2 + \frac{\tau_3^{\,2}}{\tau_1}\right)\right\}$$

$$A_{32} = -\frac{\tau_1}{10}\left(\frac{1}{2}\frac{\tau_3^{\,2}}{\tau_1} + \frac{1}{3}\frac{\tau_3^{\,2}}{\tau_2}\right) \quad B_{3.2} = +\frac{\tau_3}{10}\left\{\frac{1}{2}\frac{\tau_2^{\,2}}{\tau_3} - \frac{1}{3}\left(\tau_2 + \tau_3 + \frac{\tau_3^{\,2}}{\tau_2}\right)\right\}$$

$$A_{2.3} = -\frac{\tau_1}{10}\left(\frac{1}{2}\frac{\tau_2^{\,2}}{\tau_1} - \frac{1}{3}\frac{\tau_2^{\,2}}{\tau_3}\right) \quad B_{2.3} = +\frac{\tau_2}{10}\left\{\frac{1}{2}\frac{\tau_3^{\,2}}{\tau_2} - \frac{1}{3}\left(\tau_2 + \tau_3 + \frac{\tau_2^{\,2}}{\tau_3}\right)\right\}$$

$$A_{3.1} = -\frac{\tau_2}{10}\left(\frac{1}{2}\frac{\tau_3^{\,2}}{\tau_2} - \frac{1}{3}\frac{\tau_3^{\,2}}{\tau_1}\right) \quad B_{3.1} = +\frac{\tau_3}{10}\left\{\frac{1}{2}\frac{\tau_1^{\,2}}{\tau_3} + \frac{1}{3}\left(\tau_1 - \tau_3 + \frac{\tau_3^{\,2}}{\tau_1}\right)\right\}$$

$$A_{1.3} = -\frac{\tau_2}{10}\left(\frac{1}{2}\frac{\tau_1^{\,2}}{\tau_2} + \frac{1}{3}\frac{\tau_1^{\,2}}{\tau_3}\right) \quad B_{1.3} = +\frac{\tau_1}{10}\left\{\frac{1}{2}\frac{\tau_3^{\,2}}{\tau_1} + \frac{1}{3}\left(\tau_3 - \tau_1 + \frac{\tau_1^{\,2}}{\tau_3}\right)\right\}.$$

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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 :

$$\frac{dx}{dt}=\{k_1+\Sigma\, k f(x)\}(A-x)(B-x)\;\ldots\;,$$

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.

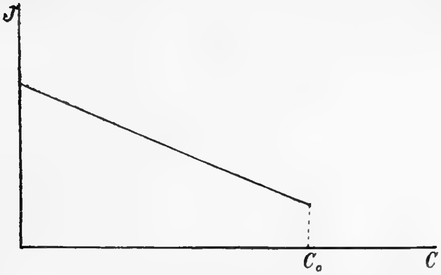

Fig. 1.

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:

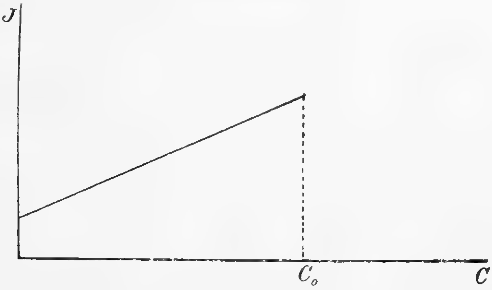

Fig. 2.

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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 $\gamma$-hydroxy-acids into their lactones. The acid is split up into ions and according to Paul Henry[2]), who studied the transformation of $\gamma$-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:

$$\gamma\text{-hydroxy-acid} \rightleftarrows \text{positive ions} + \text{negative ions} \qquad \text{I}$$

$$\text{positive ions} + \text{negative ions} = \text{lactone} + \text{water} \qquad \text{II}$$

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 $\gamma$-hydroxy-acids must be considered. In constructing reaction-equations it must be borne in mind that the transformations of $\gamma$-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 $\gamma$-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)

$$\frac{p^2 C}{1-p} = k.$$

$k$ is the dissociation-constant of the hydroxy-acid.

Suppose the concentration of the ions after a time $t = y$, then is:

$$y = pC = \tfrac{1}{2}\left\{\sqrt{4kC + k^2} - k\right\}$$

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:

$y_0 = \frac{1}{2}\{\sqrt{4kC_0 + k^2} - k\}$ the initial concentration of the ions,

$y = \frac{1}{2}\{\sqrt{4kC + k^2} - k\}$ the concentration of the ions after a time $t$,

$\beta = y_\infty = \frac{1}{2}\{\sqrt{4kC_\infty + k^2} - k\}$ 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 $C_\infty$ has not been determined and this is necessary in order to calculate $\beta$ and $\alpha$. The question therefore arises how these may be determined. In the condition of equilibrium $-\frac{dy}{dt}=0$ therefore:

$$k_1\, y^2_\infty = k_2\,(C_0 - C_\infty)$$

$$y_\infty = \tfrac{1}{2}\,\{\sqrt{4kC_\infty + k^2} - k\},\ \text{so}$$

$$2 \times \frac{k_2}{k_1} = \frac{2kC_\infty + k^2 - k\sqrt{4kC_\infty + k^2}}{C_0 - C_\infty}.$$

$C_0$, 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,

$C_\infty$ 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 $\gamma$-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 hydroxy-butyric-acid was converted to the extent of about 65 %, the hydroxy-valeric-acid had been converted to the extent of 93 %.

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 $\gamma$-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.

$C_0 = 0.17166$

$\beta = 0.000741$

$\alpha = -0.000703$

| $t$ in hours. | $y$ | $\kappa$. |
|---|---|---|
| 0 | 0.001810 | — |
| 25 | 0.001742 | 0.00067 |
| 66 | 0.001634 | 71 |
| 120 | 0.001520 | 71 |
| 148½ | 0.001476 | 68 |
| 172 | 0.001448 | 66 |
| 219 | 0.001377 | 66 |
| ∞ | 0.000741 | — |

Tab. 94 and 95 PAUL HENRY p. 128

$C_0 = 0.3390$

$\beta = 0.001313$

$\alpha = -0.001318$

| $t$ in hours. | $y$ | $\kappa$. |
|---|---|---|
| 0 | 0.002549 | — |
| 24 | 0.002476 | 0.00085 |
| 48 | 0.002372 | 97 |
| 72 | 0.002274 | 107 |
| 123 | 0.002118 | 110 |
| 151½ | 0.002049 | 109 |
| 174½ | 0.002006 | 106 |
| 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.

$C_0 = 0.3580$

$\beta = y_\infty = 0.000701$

$\alpha = -0.000703$

| | | |
|---|---|---|
| 0 | 0.002690 | — |
| 240 | 0.002607 | 0.000032 |
| 450 | 0.002541 | 29 |
| 1170 | 0.002350 | 30 |
| 1500 | 0.002266 | 31 |
| 1890 | 0.002188 | 30 |
| 2840 | 0.002053 | 28 |
| 3530 | 0.001942 | 28 |
| 4310 | 0.001895 | 27 |
| 4940 | 0.001773 | 27 |
| 6170 | 0.001580 | 26 |
| 7740 | 0.001557 | 25 |
| ∞ | 0.000701 | — |

Tab. 72 and 73. PAUL HENRY. p. 121.

$C_0 = 0.1769$

$\beta = 0.000501$

$\alpha = -0.000502$

| | | |
|---|---|---|
| 0 | 0.001885 | — |
| 390 | 0.001830 | 0.0000193 |
| 1170 | 0.001705 | 226 |
| 1860 | 0.001615 | 226 |
| 2640 | 0.001520 | 230 |
| 3300 | 0.001460 | 225 |
| 4080 | 0.001385 | 227 |
| 4710 | 0.001335 | 225 |
| 5550 | 0.001275 | 224 |
| 6900 | 0.001185 | 225 |
| ∞ | 0.000501 | — |

$$y = pC$$

$$\frac{dC}{dy} = \frac{1}{p}$$

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:

$$C = \frac{y}{2k}\{(y + k) + \sqrt{(y + k)^2 + 4k\,C'}\}.$$

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 $\frac{2k}{k\,k_1+k_2}=N$

$$-\frac{1}{N}\cdot\frac{dt}{dz}=\frac{z^2+4k\,C'}{z\,\{(z^2-\,2k\,z-4\kappa\,C')\,(z-Nk\,k_1)-2Nk_2\,C_0\,z\}}=$$

$$=\frac{z^2+4\,k\,C'}{z^3-(Nk\,k_1+2k)\,z^2+2\,(Nk^2\,k_1-2k\,C'-Nk_2\,C_0)\,z+4Nk^2\,k_1\,C'}=$$

$$=\frac{p}{z}+\frac{q}{z-\alpha}-\frac{r}{z-\beta}+\frac{s}{z-\gamma}.$$

Therefore:

$$\alpha+\beta+\gamma=Nkk_1+2k\ \ (a);\ \ \alpha\beta+\alpha\gamma+\beta\gamma=2(Nk^2k_1-2kC'-Nk_2C_0)\ \ (b);$$

$$-\alpha\beta\gamma=4\,Nk^2k_1C'\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ (c)$$

From $(b)$ and $(c)$ follows:

$$\alpha+\gamma=\frac{2\beta\,(Nk^2k_1-2kC'-Nk^2C_0)+4Nk^2k_1C'}{\beta^2}\ \ .\ \ .\ \ .\ \ (d)$$

$$\alpha\gamma=-\frac{4Nk^2k_1C'}{\beta}\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ (e)$$

From $(a)$ and $(d)$ follows:

$$\beta^3-(Nkk_1+2k)\beta^2-2\beta(Nk^2k_1-2kC'-Nk^2C_0)-4Nk^2k_1C'\ \ .\ \ (f)$$

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 $\beta$, 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:

$$\beta^3=\left\{\frac{2k^2}{k+\frac{k_2}{k_1}}+2k\right\}\beta^2-\left\{\frac{2k^3}{k+\frac{k_2}{k_1}}-2kC'-\frac{2k\,.\,\frac{k_2}{k_1}\,.\,C_0}{k+\frac{k_2}{k_1}}\right\}2\beta-\frac{8k^3C'}{k+\frac{k_2}{k_1}}\,.\ (g)$$

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) $\beta$ may be calculated from equation ($g$) $\alpha$ and $\gamma$ may then be calculated from ($d$) and ($e$).

For this transformation the reaction-equation becomes,

$$\frac{k\,k_1 + k_2}{2k} \times t = p\,l\frac{z_0}{z} + q\,l\frac{z_0-\alpha}{z-\alpha} - r\,l\frac{z_0-\beta}{z-\beta} + s\,l\frac{z_0-\gamma}{z-\gamma}.$$

Tab. 74 and 75. PAUL HENRY. p. 123.

$C_0 = 0.1708$  $p = 26976,89$

$C' = 0.2058$  $q = -232,46$

$\beta = 0.0041945$  $r = -233,84$

$\alpha = -0.004153$  $s = -27005,45$

$\gamma = 0.000035$

| $t$ in hours | $z$ | $\frac{k\,k_1+k_2}{2k}$ |
|---|---|---|
| 0 | 0.005495 | — |
| 210 | 0.005439 | 0.014 |
| 390 | 0.005349 | 21 |
| 1170 | 0.005226 | 21 |
| 1860 | 0.004953 | 21 |
| 2640 | 0.004806 | 21 |
| 3300 | 0.004692 | 22 |
| 4080 | 0.004591 | 23 |
| 4710 | 0.004529 | 23 |
| 5550 | 0.004435 | 25 |

Tab 76 and 77. PAUL HENRY. p. 123.

$C_0 = 0.1795$  $p = 25905,42$

$C' = 0.01977$  $q = -497,543$

$\beta = 0.001653$  $r = -499,052$

$\alpha = -0.001597$  $s = -25906,92$

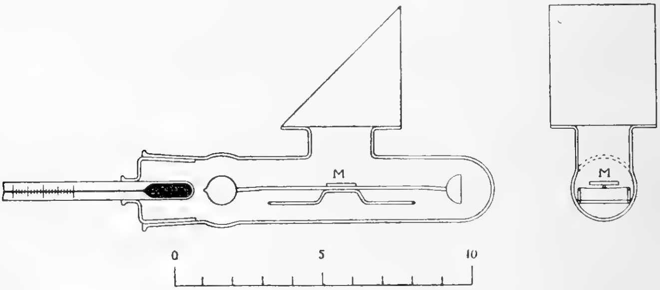
$\gamma = 0.000024$

| $t$ in hours | $z$ | $\frac{k\,k_1+k_2}{2k}$ |
|---|---|---|
| 0 | 0.004083 | — |
| 390 | 0.003947 | 0.0126 |
| 1170 | 0.003706 | 128 |
| 1860 | 0.003521 | 128 |
| 2640 | 0.003330 | 127 |
| 3300 | 0.003206 | 128 |
| 4080 | 0.003082 | 126 |
| 4710 | 0.002987 | 125 |
| 5550 | 0.002859 | 127 |

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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