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KONINKLIJKE AKADEMIE
VAN WETENSCHAPPEN
-:- TE AMSTERDAM -:-

PROCEEDINGS OF THE SECTION OF SCIENCES

VOLUME IX

JOHANNES MÜLLER :—: AMSTERDAM
JULY 1907

(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling van 26 Mei 1906 tot 24 November 1906. Dl. XV.)

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday May 26, 1906.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 26 Mei 1906, Dl. XV).

CONTENTS.

Chemistry. — "*On the introduction of the conception of the solubility of metal ions with electromotive equilibrium.*" By Dr. A. Smits. (Communicated by Prof. H. W. Bakhuis Roozeboom).

(Communicated in the meeting of April 27, 1906.)

If a bar of NaCl is placed in pure water or in a dilute solution, the NaCl-molecules will pass into the surrounding liquid, till an equilibrium has been established; then the molecular thermodynamic potential of the Na Cl in the bar has become equal to that of the Na Cl in the solution.

As known, this equilibrium of saturation, represented by the equation:

$$\mu_{\mathrm{NaCl}} = \mu'_{\mathrm{NaCl}}$$

is characterized by the fact that per second an equal number of molecules pass from the bar into the solution, as from the solution into the bar.

We shall call this equilibrium a purely chemical equilibrium. It is true that in solution the Na Cl-molecules split up partially into particles charged either with positive or negative electricity, which are in equilibrium with the unsplit molecules, but for the heterogeneous equilibrium solid-liquid under consideration this is not of *direct* importance.

If, however, we immerge a metal e. g. Zn into a solution of a salt of this metal, e. g. $ZnSO_4$, we observe a phenomenon strongly deviating from the one just discussed, which according to our present ideas may be accounted for by the fact that a metal does not send out into the solution *electrically neutral* molecules as a salt, but exclusively *ions with a positive charge.*

If the particles emitted by the bar of zinc were *electrically neutral,* then the zinc would continue to be dissolved till the molecular thermodynamic potential of the zinc in the bar of zinc had become equal to that of the zinc in the solution, in which case the equation:

$$\mu_{zn} = \mu'_{zn}$$

would hold.

This, however, not being the case, and the emitted Zn-particles being electro-positive, an equilibrium is reached *long* before the thermodynamic potential of the zinc-particles with the positive electric charge in the solution has become equal to that of the zinc in the bar of zinc with the negative electric charge. That in spite of this an equilibrium is possible, is due to the fact that an electrical phenomenon acts in conjunction with the chemical phenomenon.

The zinc emitting positive *Zn*-ions, the surrounding solution becomes electro-positive, and the zinc itself electro-negative. As known, this gives rise to the formation of a so-called electric double-layer in the bounding-layer between the metal and the electrolyte, consisting of positive *Zn*-ions on the side of the electrolyte and an equivalent amount of negative electricity or electrons in the metal.

By the formation of this electric double-layer an electric potential difference between metal and electrolyte is brought about, which at first increases, but very soon becomes constant. This takes place when the potential difference has become great enough to prevent the further solution of the *Zn*-ions.

In order to compute the potential difference between the metal and the solution, we shall apply the principle of the virtual displacement, as has been done before by Mr. VAN LAAR.[1])

If we have to do with a purely chemical equilibrium then with virtual displacement of this equilibrium the sum of the changes of molecular potential will be = 0, which is expressed by the equation of equilibrium:

$$\Sigma(\mu_1 \, dn_1) = 0.$$

If the equilibrium is a purely electrical equilibrium then with a virtual displacement of this equilibrium the sum of the changes of electric energy will be = 0.

If however we have an equilibrium that is neither purely chemical, nor purely electrical, but a combination of the two, as is the case with electromotive equilibrium, then with virtual displacement of this equilibrium, the sum of the changes of the molecular-potential + the sum of the changes of the electric energy will have to be = 0.

If we represent the mol. potential of the *Zn*-ions by $\overset{+}{\mu}_{zn}$ in case of electromotive equilibrium, we know that $\overset{+}{\mu}_{zn}$ is *much* smaller than μ_{zn} or the mol. potential of the zinc in the bar of zinc.

If we now suppose that a *Zn*-ion emitted by the zinc virtually carries a quantity of electricity de from the metal towards the solution, then this quantity of electricity being carried by a ponderable quantity $\frac{de}{\nu\varepsilon}$ when ν = valency of the metal and ε = the charge of a univalent ion, the increase of the thermodynamic potential during this process will be equal to

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[1]) Chem. Weekbl. N°. 41, 1905.

$$\frac{\overset{+}{\mu}_{zn} - \mu_{zn}}{\nu \varepsilon} de$$

which increase is negative, because $\mu_{zn} > \overset{+}{\mu}_{zn}$.

In the virtual displacement of the quantity of electricity *de* from the metal towards the solution the change of the thermodynamic potential is not the only one that has taken place during this process.

If we call the electric potential of the solution V_e and that of the zinc V_m, we know that in the above case $V_e > V_m$ and $V_e - V_m = \Delta$ indicates the potential difference of the electrolyte and the metal. With the virtual displacement of the quantity of electricity *de* from the metal to the electrolyte this quantity has undergone an electrical potential increase Δ, and so the electric energy has increased with $\Delta\, de$.

From the principle of virtual displacement follows that with electromotive equilibrium

$$\frac{\overset{+}{\mu}_{zn} - \mu_{zn}}{\nu \varepsilon} de + \Delta\, de = 0, \quad \ldots \ldots \ldots \quad (1)$$

or

$$\Delta = - \frac{\overset{+}{\mu}_{zn} - \mu_{zn}}{\nu \varepsilon} \quad \ldots \ldots \ldots \quad (2)$$

Now we know that the mol. thermodyn. potential of a substance may be split up as follows:

$$\mu = \mu' + R\, T \ln C$$

where in diluted states of matter μ' may be called a function of the temperature alone.

In non-diluted states however, μ' depends also somewhat on the concentration.

If we now apply this splitting up also to equation (2), we get:

$$\Delta = - \frac{(\overset{+}{\mu}'_{zn} - \mu_{zn}) + R\, T \ln C}{\nu \varepsilon} \quad \ldots \ldots \quad (3)$$

where C represents the concentration of the *Zn*-ions in the electrolyte.

If we now put:

$$\frac{\mu_{zn} - \overset{+}{\mu}'_{zn}}{R\, T} = \ln K \quad \ldots \ldots \ldots \quad (4)$$

we may say of this K that for diluted states of matter it will only depend on the temperature, and will therefore be a constant at constant temperature.

From equation (3), (4) follows

$$\Delta = \frac{RT}{\nu \varepsilon} \, ln \, \frac{K}{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

Mr. van Laar already pointed out that this equation, already derived by him in the same way is identical with that derived by Nernst $\Delta = \frac{R\,T}{\nu\,\varepsilon} \, ln \, \frac{P}{p}$, in which therefore $\frac{P}{p}$ stands instead of $\frac{K}{C}$. P represents the "elektrolytische Lösungstension" of the metal, and p the "osmotic pressure" of the metal-ions in the solution.

Rejecting the osmotic phenomenon as basis for the derivation of the different physico-chemical laws, we must, as an inevitable consequence of this, also abandon the osmotic idea "elektrolytische Lösungstension" introduced by Nernst.

The principal purpose of this paper is to prove that there is not any reason to look upon this as a disadvantage, for, when we seek the physical meaning of the quantity K in equation (5), it can be so simply and sharply defined, that when we take the theory of the thermodynamic potential as foundation, we do not lose anything, but gain in every respect.

In order to arrive at the physical meaning of the quantity K, we put for a moment

$$C = K$$

from which follows

$$\Delta = 0.$$

From this follows that there is a theoretical possibility to give such a concentration to the metal-ions in a solution that when we immerge the corresponding metal in it, *neither the metalnor the solution gets electrically charged.*

How we must imagine this condition is shown by equation (2). Let us put there $\Delta = 0$, then follows from this for an arbitrary metal

$$\mu_m = \overset{+}{\mu}_m$$

or in words the molecular potential of the metal in the bar is equal to that of the metal-ions in the solution.

So it appears that we have here to do with an equilibrium which is perfectly comparable with that between the Na Cl in the bar Na Cl, and the salt in the solution.

The only difference is this that the molecules of a salt in solution are neutrally electric, whereas the metal particles in solution are charged with positive electricity, hence the physical meaning of the equation $\mu_m = \overset{+}{\mu}_m$ is simply this that in *absence* of a potential difference, per second an equal number of metal particles are dissolved as there are deposited.

If we express this in the most current terms, we may say, that when $C = K$ the metal-ions have reached their *concentration of saturation,* and that K therefore represents the *solubility of the metal-ions.*

To prevent confusion, it will be necessary to point out that the fact that the dissolved metal-particles in equilibrium with the solid metal have an electric charge, is attended by peculiarities which are met with in no other department.

Thus it will appear presently that in every solution of copper-sulphate which is not extremely diluted, the concentration of the copper-ions is supersaturated with respect to copper. Yet such a copper-sulphate-solution is in a perfectly stable condition, because the copper-ions constitute a part of the following homogeneous equilibrium,

$$CuSO_4 \rightleftarrows Cu^{\cdot\cdot} + SO_4''$$

which is perfectly stable as long as the solution is unsaturate or is just saturate with $CuSO_4$-molecules.

If we now, however, insert a copper bar into the solution, the condition changes, because the Cu-ions which were at first only in equilibrium with the $CuSO_4$-mols and with the SO_4''-ions, must now also get into equilibrium with the copper bar, and, the concentration of the Cu-ions with respect to copper being strongly supersaturate, the Cu-ions will immediately deposit on the copper, till the further depositing is prevented in consequence of the appearance of a double layer.

We shall further see that in the most concentrated solution of a zinc-salt the concentration of the zinc-ions always remains below the concentration of saturation, which appears immediately when we immerge a zinc-bar into such a solution; the zinc emits zinc particles with a positive charge into the solution, till the appearance of the electric double layer puts a stop to the phenomenon of solution.

In order to find the values of K for different metals we make use of the observed potential difference with a definite value of C.

We know the potential difference at 18° and with normal concentration of the ions, i. e. when solutions of 1 gr. aeq. per liter of water are used. These potential differences are called electrode potentials, and will be denoted here by Δ_0.

If we express the concentration in the most rational measure, viz. in the number of gr. molecules dissolved substance divided by the total number of gr. molecules, we may write for the concentration of 1 gr. eq. per liter

$$\frac{1}{55{,}5\,v+1}$$

in which v represents the valency of the metal. In this it has been further assumed, that the dissociation is total, and the association of the water molecules has not been taken into account.

If we now write the equation for the electrode potential of an arbitrary metal, we get:

$$\Delta_0 = \frac{RT}{v\varepsilon}\,ln\,\frac{K}{\dfrac{1}{55{,}5\,v+1}}$$

or

$$\Delta_0 = \frac{RT}{v\varepsilon}\,ln\,K(55{,}5\,v+1)$$

If we use ordinary logarithms for the calculation, we get:

$$\Delta_0 = \frac{RT}{v\varepsilon \times 0{,}4343}\,log\,K(55{,}5\,v+1)$$

If we now express R in electrical measure, then

$$\Delta_0 = \frac{0{,}000198}{v}\,T\,log\,K(55{,}5\,v+1)$$

and for $t=18$ or $T=291°$

$$\Delta_0 = \frac{0{,}0578}{v}\,log\,K(55{,}5\,v+1)$$

If we now calculate the quantity $log\,K$ by means of this equation from the observed values of Δ_0, we get the following. (See table p. 8).

In the succession in which the metals are written down here, the value of Δ_0 decreases and with it the value of $log\,K$.

For the metals down to *Fe* (*Fe* included) $log\,K$ is greater than zero, so K greater than 1.

Now we know that C for a solution is always smaller than 1; hence K will always be larger than C for the metals mentioned, and as K denotes the concentration of saturation of the metal-ions, Values of *log K* at 18°.

metal ion	Δ_0	*log K*	metal ion	Δ_0	*log K*
$K^{\cdot}$	(+ 2,92) 1)	(+48,77)	$Co^{\cdot\cdot}$	— 0,045	— 1,805 2
$Na^{\cdot}$	(» 2,54)	(42,19)	$Ni^{\cdot\cdot}$	» 0,049	— 1,872 × 2
$Ba^{\cdot\cdot}$	(» 2,54)	(42.92 × 2)	$Sn^{\cdot\cdot}$	< » 0,085	<— 2,49 × 2
$Sr^{\cdot\cdot}$	(» 2,49)	(42,06 × 2)	$Pb^{\cdot}$	» 0,13	— 3 27 × 2
$Ca^{\cdot}$	(» 2,28)	(38,42 × 2)	$H^{\cdot}$	» 0,28	— 6,6
$Mg^{\cdot}$	» 2,26	38,07 × 2	$Cu^{\cdot\cdot}$	» 0,61	— 11,58 × 2
$Al^{\cdot\cdot\cdot}$	» 1,00	16,56 × 3	$Bi^{\cdot\cdot\cdot}$	< » 0,67	<— 12 33 × 3
$Mn^{\cdot\cdot}$	» 0,80	12,81 × 2	$Hg_2^{\cdot\cdot}$	» 1,03	— 18,84 × 2
$Zn^{\cdot\cdot}$	» 0,49	7,45 × 2	$Ag^{\cdot}$	» 1,05	— 19,92
$Cd^{\cdot\cdot}$	» 0,14	1,39 × 2	$Pd^{\cdot\cdot}$	» 1,07	— 19,03 × 2
$Fe^{\cdot\cdot}$	» 0,063	0,065 × 2	$Pt^{\cdot\cdot\cdot\cdot}$	» 1,14	— 20,62 × 4
$Tl^{\cdot\cdot}$	» 0,045	— 0,245 × 2	$Au^{\cdot\cdot}$	» 1,36	— 26,27 × 3

the metal-ions will not yet have reached their concentration of saturation even in the most concentrated solutions of the corresponding metal-salts. Hence, when the corresponding metal is immerged, metal ions will be dissolved, in consequence of which the solution will be charged with positive and the metal with negative electricity.

Theoretically the case, in which K would always be smaller than C, can of course not occur. If *log* K is smaller than zero, so K smaller than 1, then the theoretical possibility is given to make the potential difference between the metal and the corresponding salt solution reverse its sign, which reversal of sign of course takes place through zero. Whether it will be possible to realize this, depends on the solubility of the salt.

If we now take the metal copper as an example, we see that for this metal K has the very small value of 10^{-23}. On account of this very small value of K, C is greater than K in nearly all copper-salt-solutions, or in other words the concentration of the *Cu*-ions is greater than the concentration of saturation. Hence copper-ions are deposited on a copper bar, when it is immerged, in consequence which the bar gets charged with positive, and the solution with negative electricity.

But however small K may be, it will nearly always be possible to

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1) The values of Δ_0 between parentheses have been calculated from the quantity of heat.

make C smaller than K. In a copper-salt-solution e.g. this can very easily be done, as is known, by addition of KCN, which in consequence of the formation of the complex-ions $[Cu_2(CN)_4]''$, causes copper-ions to be extracted from the solution. The solution, which at first had a negative charge compared with the metal copper, loses this charge completely by the addition of KCN, and receives then a positive charge.

In the above I think I have demonstrated the expediency of replacing the vague idea "elektrolytische Lösungs-tension" by the sharply defined idea solubility of metal ions.

Amsterdam, April 1906. *Anorg. Chem. Lab. of the University.*

Physics. — "*On the course of the P, T-curves for constant concentration for the equilibrium solid-fluid.*" By Dr. A. Smits. (Communicated by Prof. J. D. van der Waals.)

(Communicated in the meeting of April 27, 1906).

In connection with my recent investigations it seemed desirable to me to examine the hidden connection between the sublimation and melting-point curves for constant concentration, more particularly when the solid substance is a dissociable compound of two components. This investigation offered some difficulties, which I, however, succeeded in solving by means of data furnished by a recent course of lectures giving by Prof. van der Waals. Though his results will be published afterwards, Prof. van der Waals allowed me, with a view to the investigations which are in progress, to use that part that was required for my purpose.

In his papers published in 1903 in connection with the investigation on the system ether-anthraquinone [1]) van der Waals also discussed the P, T-lines for constant x for the equilibrium between solid-fluid [2]), and more particularly those for concentrations in the immediate neighbourhood of the points p and q, where saturated solutions reach their critical condition.

Then it appeared that the particularity of the case involved also particularities for the P, T-line, so that the course of the P, T-line as it would be in the usual case, was not discussed.

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[1]) These Proc. VI p. 171 and p, 484 Zeitschr. f. phys. Chem. **51**, 193 and **52**, 587 (1905).

[2]) These Proc. VI p. 230 and p. 357.

If we start from the differential equation in p,x and T derived by VAN DER WAALS (Cont. II, 112).

$$V_{sf}\,dp = (x_s - x_f)\left(\frac{\partial^2\zeta}{\partial x^2_f}\right)_{PT} dx_f + \frac{W_{sf}}{T}\,dT \quad . \quad . \quad . \quad (1)$$

we get from this for constant x that

$$V_{sf}\,dp = \frac{T}{W_{sf}}\,dT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$T\left(\frac{dp}{dT}\right)_{xf} = \frac{W_{sf}}{V_{sf}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we now multiply numerator and denominator by $\frac{\partial^2\psi}{\partial v_f^2}$ as will prove necessary for simplifying the discussion, we get:

$$T\left(\frac{dp}{dT}\right)_{xf} = \frac{\frac{\partial^2\psi}{\partial v_f^2} \cdot W_{sf}}{\frac{\partial^2\psi}{\partial v_f^2} \cdot V_{sf}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In order to derive the course of the P, T-lines from this equation, the loci must be indicated of the points for which the numerator, resp. the denominator = zero, and at the same time the sign of these quantities within and outside these loci must be ascertained.

In the v, x-fig. **1** the lines ab and cd denote the two connodal lines at a definite temperature. The line $P_S Q_S$ whose $x = x_s$ the concentration of the solid compound AB cuts these connodal lines and separates the v,x-figure into two parts, which call for a separate discussion.

If P_S denotes the concentration and the volume of the solid compound at a definite temperature, then the isobar $MQRDD'R'Q'N$ of the pressure of P_S will cut the connodal lines in two points Q and Q', which points indicate the fluid phases coexisting with the solid substance AB, and therefore will represent a pair of nodes.

The points for which $\frac{\partial^2\psi}{\partial v^2} = 0$ or $-\frac{dp}{dv} = 0$ are situated where the isobar has a vertical tangent, so in the points D and D' as VAN DER WAALS [1]) showed already before. In D the isobar passes through the minimum pressure of the mixture whose $x = x_D$, and so it has there an element in common with the isotherm of this concentration. In D' however, the isobar passes through the maxi-

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[1]) These Proc. IV p. 455.

mum pressure of the mixture whose $x = x_{D'}$, and will therefore have an element in common with the isotherm of the concentration $x_{D'}$.

As for the sign of $\frac{\partial^2 \psi}{\partial v^2}$ we may remark that it is positive outside the points D and D' and negative inside them.

The ordinary case being supposed in the diagram, viz. $V_s < V_f$, we may draw two tangents to the above mentioned isobar from the point P_s with the points of contact R and R'. These points of contact now, indicate the points where the quantity $V_{sf} = 0$, as VAN DER WAALS [1]) showed.

This quantity is represented by the equation:

$$V_{sf} = (V_s - V_f) - (x_s - x_f) \left(\frac{dv_f}{dx_f} \right)_{PT} \quad . \quad . \quad . \quad . \quad (5)$$

and denotes the decrease of volume per molecular quantity when an infinitely small quantity of the solid phase passes into the coexisting fluid phase at constant pressure and temperature.

For the case that the coexisting phase is a vapour phase, V_{sf} is negative, but this quantity can also be positive, and when the pressure is made to pass through all values, there is certainly once reversal of sign, for the case $V_f > V_s$ even twice.

To elucidate this Prof. VAN DER WAALS called attention to the geometrical meaning of V_{sf}.

Let us call the coordinates of the fluid phases Q' coexisting with P_s, V_f and X_f and let us draw a tangent to the isobar in Q'. Then $P_s\ P'$ will be equal to V_{sf} if P' is the point where this tangent cuts the line drawn parallel to the axis of v through P_s.

If the point P' lies above P_s, V_{sf} is negative, and if P' lies under P_s, then V_{sf} is positive. For the case that the tangent to the isobar passes through P_s, which is the case for the points R and R', $V_{sf} = 0$.

In this way it is very easy to see that for the points outside those for which $V_{sf} = 0$, the value of V_{sf} is negative, and for the points within them, V_{sf} is positive, but this latter holds only till the points D and D' have been reached, where $V_{sf} = \infty$. Between D and D', V_{sf} is again negative. The transition from positive to negative takes therefore place through ∞.

As each of the lines of equal pressure furnishes points where

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[1]) These Proc. VI, p. 234.

$\frac{\partial^2\psi}{\partial v^2}=0$ and $V_{sf}=0$, when connecting the corresponding points we obtain loci of these points, indicated by lines.

As, however, we simplify the discussion, as VAN DER WAALS has shown, when we consider the quantity $\frac{\partial^2\psi}{\partial v_f^2}\,.\,V_{sf}$ instead of the quantity V_{sf}, because this product can never become infinitely great and is yet zero when $V_{sf}=0$, the locus of the points where $\frac{\partial^2\psi}{\partial v_f^2}\,.\,V_{sf}=0$ is given in fig. 1.

We know then too that this quantity on the left of the line ot the compound is negative outside this locus, and positive within it.

Further the locus of $\frac{\partial^2\psi}{\partial v^2}=0$ is indicated, and we see that these two lines intersect at the point where they pass through the line of the compound.

In his lectures VAN DER WAALS has lately proved in the following way that this must necessarily be so: If we write for $\frac{\partial^2\psi}{\partial v_f^2}\,.\,V_{sf}$

$$(V_s - V_f)\frac{\partial^2\psi}{\partial v_f^2} + (x_s - x_f)\frac{\partial^2\psi}{\partial v_f \partial x_f} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

we see that when this quantity $=0$, and when at the same time $x_s=x_f$:

$$(V_s - V_f)\frac{\partial^2\psi}{\partial v_f^2}=0$$

or

$$\frac{\partial^2\psi}{\partial v_f^2}=0.$$

I, too, had already arrived at the conclusion that in the left half of our diagram the two loci mentioned had interchanged places, by assuming that there existed a three-phase equilibrium also on the right, and by drawing the corresponding isobar $M_1Q_1D_1R_1R_1'D_1'Q_1'N'$. It appears then that here the points R_1 and R_1' lie within the points D_1 and D_1', which points to a reversed situation (compared with the left half) of the loci $\frac{\partial^2\psi}{\partial v_f^2}\,.\,V_{sf}=0$ and $\frac{\partial^2\psi}{\partial v_f^2}=0$. VAN DER WAALS has also given this graphical proof.

As for the sign of the quantity $\frac{\partial^2\psi}{\partial v_f^2}$ on the right of the line of the compound also there it is negative outside, positive inside the first mentioned locus.

Before proceeding to my real subject, I shall, for the sake of completeness, first call attention to the fact that the spinodal curve, for which the equation:

$$\frac{\partial^2\psi}{\partial x^2}-\frac{\left(\frac{\partial^2\psi}{\partial x\partial v}\right)}{\frac{\partial^2\psi}{\partial v^2}}=0 \quad \text{or} \quad \frac{\partial^2\zeta}{\partial x^2_p}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

holds, lies entirely ontside the locus $\frac{\partial^2\psi}{\partial v^2}=0$. VAN DER WAALS [1]) proved this in the following way:

On the spinodel curve $\frac{\partial^2\psi}{\partial x^2}$ and $\frac{\partial^2\psi}{\partial v^2}$ must both be positive, and so also $\left(\frac{\partial^2\psi}{\partial x\partial v}\right)^2$. As $\frac{\partial^2\psi}{\partial v^2}=-\frac{\partial p}{\partial v}$ is positive outside the line for which $\frac{\partial^2\psi}{\partial v^2}=0$, the spinodal line will always have to lie outside the curve $\frac{\partial^2\psi}{\partial v^2}=0$.

That the spinodal curve which coming from the left, runs between the lines $\frac{\partial^2\psi}{\partial v^2_f}\cdot V_{sf}=0$ and $\frac{\partial^2\psi}{\partial v^2_f}=0$, cuts the line for $\frac{\partial^2\psi}{\partial v_f^2}\cdot V_{sf}=0$ on the left of the line of the compound in two points q_1 and q_2 which will be discussed afterwards, follows from this, that *on* the line of the compound $\frac{\partial^2\psi}{\partial v_f^2}\cdot V_{sf}=0$ coincides with $\frac{\partial^2\psi}{\partial v_f^2}=0$ and that the line $\frac{\partial^2\psi}{\partial v_f^2}$ always lies within the spinodal line, whereas on the right of the line of the compound $\frac{\partial^2\psi}{\partial v_f^2}\cdot V_{sf}=0$ lies within the line $\frac{\partial^2\psi}{\partial v_f^2}=0$.

When we start from the maximum temperature of sublimation, we get now v,x-lines which have been indicated by T_1, T_2, T_3 and T_4 in fig. 1 for the equilibria between solid-fluid according to the equation [2])

$$\frac{dv_f}{dx_f}=-\frac{\left[(v_s-v_f)\frac{\partial^2\psi}{\partial v_f\,.\,\partial x_f}+(x_s-x_f)\frac{\partial^2\psi}{\partial x^2_f}\right]}{\frac{\partial^2\psi}{\partial v^2_f}\cdot v_{sf}} \quad . \quad . \quad . \quad . \quad (8)$$

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[1]) loc cit.

[2]) These Proc. VI, p. 489.

The v,x-curve denoted by T_1, relating to the *maximum temperature of sublimation,* consists of two branches, which pass continuously into each other. The points of intersection with the connodal line $a\,b$ indicate the vapour phases and those with the connodal line $c\,d$ the liquid phases. In this way we get two pairs of fluid phases which can coexist with the solid compound at the same temperature.

At the place where the two branches of the v,x-line cut the locus $\frac{\partial^2\psi}{\partial v^2{}_f} V_{sf}$, $\frac{\partial v}{\partial x} = \infty$.

With increase of temperature these branches draw nearer to each other, and when they would *touch,* intersection takes place; this is here supposed to take place for the v,x-line denoted by T_2. This point of intersection is the point q_1, it lies therefore both on the spinodal curve and on the curve $\frac{\partial^2\psi}{\partial v^2{}_f} \cdot V_{sf} = 0$.

If we now proceed to higher temperatures, detachment takes place, and the v,x-figure consists of two separate branches, one of which, viz. the vapour branch is closed. This case is represented by the v,x-line T_3, for which it is also assumed, that this temperature is the *minimum-melting point* of the compound, which follows from the fact that the liquid branch of the v,x-line T_3, simultaneously cuts the connodal line $c\,d$ and the line of the compound.

With rise of temperature the closed v,x-line contracts, and the corresponding liquid branch descends. The points of intersection of the closed vapour branch and the liquid branch with the connodal curves draw nearer and nearer to each other, and at a certain temperature the two branches will show contact. The closed vapour branch touches the connodal curve $a\,b$ and the liquid branch the connodal curve $c\,d$. This is represented by the v,x-figure T_4, which represents the condition at the *maximum-threephase-temperature,* at which the points of contact on the connodal curves and the point for the solid substance must lie in one line.

At higher temperature no three phase equilibrium is possible any longer, and both the closed vapour branch and the liquid branch have got detached from the connodal curves. The liquid branch descends lower and lower, and the closed branch contracts more and more, and vanishes as a point in q_2, where the upper branch of the spinodal curve and the curve $\frac{\partial^2\psi}{\partial v^2{}_f} V_{sf} = 0$ intersect.

If we now also indicate the locus of the points where $\frac{\partial^2\psi}{\partial v_f{}^2} \cdot W_{sf} = 0$

the peculiarities of the course of the PT-lines may easily be derived by means of the foregoing.

For the determination of the last mentioned locus, we start from the equation:

$$W_{sf} = \left[p + \left(\frac{\partial \varepsilon_f}{\partial v_f}\right)_{T,x}\right] V_{sf} + (\varepsilon_{sf})_v \quad . \quad . \quad . \quad . \quad (9)$$

The factor of V_{sf} being naturally positive and $(\varepsilon_{sf})_v$ being always negative, W_{sf} can only be equal to zero in a point x where V_{sf} is positive, so between the loci where $V_{sf} = 0$ and $\frac{\partial^2 \psi}{\partial v_f^2} = 0$.

Further it is now easy to understand that at the same time with V_{sf} the quantity W_{sf} will become infinitely great, there where $\frac{\partial^2 \psi}{\partial v_f^2} = 0$. In order to avoid this complication VAN DER WAALS has multiplied the quantity W_{sf} by $\frac{\partial^2 \psi}{\partial v_f^2}$ as equation (4) shows; the obtained product never becomes infinitely great now.

If we multiply equation (9) by $\frac{\partial^2 \psi}{\partial v_f^2}$, we get:

$$\frac{\partial^2 \psi}{\partial v_f^2} \,.\, W_{sf} = \left[p + \left(\frac{\partial \varepsilon_f}{\partial v_f}\right)_{T,x}\right] \frac{\partial^2 \psi}{\partial v_f^2} \,.\, V_{sf} + \frac{\partial^2 \psi}{\partial v_f^2} (\varepsilon_{sf})_v \quad . \quad . \quad (10)$$

Now we know that the locus for $\frac{\partial^2 \psi}{\partial v_f^2} \,.\, W_{sf} = 0$ will have to lie between that for $\frac{\partial^2 \psi}{\partial v_f^2} \,.\, V_{sf} = 0$ and for $\frac{\partial^2 \psi}{\partial v_f^2} = 0$, as drawn in fig. 1, which compels us to make $\frac{\partial^2 \psi}{\partial v_f^2} \,.\, W_{sf} = 0$ and $\frac{\partial^2 \psi}{\partial v_f^2} \,.\, V_{sf} = 0$ intersect on the line of the compound.

That this must really be so, is easily seen, when we bear in mind, that on the line of the compound the locus where $\frac{\partial^2 \psi}{\partial v_f^2} = 0$ coincides with that where $\frac{\partial^2 \psi}{\partial v_f^2} \,.\, V_{sf} = 0$, from which in connection with equation (10) it follows immediately that at the same point also $\frac{\partial^2 \psi}{\partial v_f^2} \,.\, W_{sf} = 0$. In this way we arrive at the conclusion, that the three loci $\frac{\partial^2 \psi}{\partial v_f^2} = 0$, $\frac{\partial^2 \psi}{\partial v_f^2} \,.\, V_{sf} = 0$ and $\frac{\partial^2 \psi}{\partial v_f^2} \,.\, W_{sf} = 0$ will intersect on the line of the compound, and that therefore the loci $\frac{\partial^2\psi}{\partial v_f^2} \,.\, V_{sf} = 0$ and $\frac{\partial^2\psi}{\partial v_f^2} \,.\, W_{sf} = 0$ will interchange places on the left and the right of the line of the compound.

By means of equation (10) we understand now easily that the sign of the quantity $\frac{\partial^2\psi}{\partial v_f^2} \,.\, W_{sf}$ must be negative outside the locus $\frac{\partial^2\psi}{\partial v_f^2} \,.\, W_{sf} = 0$, and positive within it.

As connecting link for the transition to the P,T-lines we might discuss the V,T-lines; for this purpose we should then have to make use of the following equation (Cont. II, 106)

$$\left[(V_s - V_f)\frac{\partial^2\psi}{\partial v_f^2} + (x_s - x_f)\frac{\partial^2\psi}{\partial v_f \,.\, \partial x_f}\right] dv_f + \left[(v_s - v_f)\frac{\partial^2\psi}{\partial v_f \,.\, \partial x_f} + \right.$$
$$\left. + (x_s - x_f)\frac{\partial^2\psi}{\partial x_f^2}\right] dx_f = -(\varepsilon_{sf})_v \frac{dT}{T} \,.$$

By taking x constant we derive from this

$$T\left(\frac{dv_f}{dT}\right)_{x_f} = \frac{-(\varepsilon_{sf})_v}{(v_s - v_f)\frac{\partial^2\psi}{dv_f^2} + (x_s - x_f)\frac{\partial^2\psi}{\partial x_f \partial v_f}} \,.$$

or

$$T\left(\frac{dv}{dT}\right)_{x_f} = \frac{-(\varepsilon_{sf})_v}{\frac{\partial^2\psi}{\partial v_f^2} \,.\, V_{sf}} \,.$$

I shall, however, not enter into a discussion of the VT-lines because it is to be seen even without this connecting link, what the course of the P,T-lines must be.

If now for simplication we call $\frac{\partial^2\psi}{\partial v_f^2} V_{sf} = X_1$ and $\frac{\partial^2\psi}{\partial v_f^2} \,.\, W_{sf} = X_2$ and if we indicate what the signs are of these quantities in the different regions on the left and the right of the line of the compound, and where these quantities become $= 0$, we get the following:

left		*right*	
$X_1 - X_2 -$		$X_1 - X_2 -$	
	$X_1 = 0$		$X_2 = 0$
$X_1 + X_2 -$		$X_1 - X_2 +$	
	$X_2 = 0$		$X_1 = 0$
$X_1 + X_2 +$		$X_1 + X_2 +$	
	$X_2 = 0$		$X_1 = 0$
$X_1 + X_2 -$		$X_1 - X_2 +$	
	$X_1 = 0$		$X_2 = 0$
$X_1 - X_2 -$		$X_1 - X_2 -$	

If now led by equation

$$T\left(\frac{dp}{dT}\right)_{x_f} = \frac{X_2}{X_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4a)$$

we draw the P, T-line for a concentration on the *left* of the curve of the compound, we obtain a curve as given by $GF'FD$ in fig. 2.

As we have assumed in our diagram, that the vapour-tension of A is the greatest and of B the smallest, whereas that of AB is intermediate, we cut now that branch of the three phase line of the compound, which has a maximum.

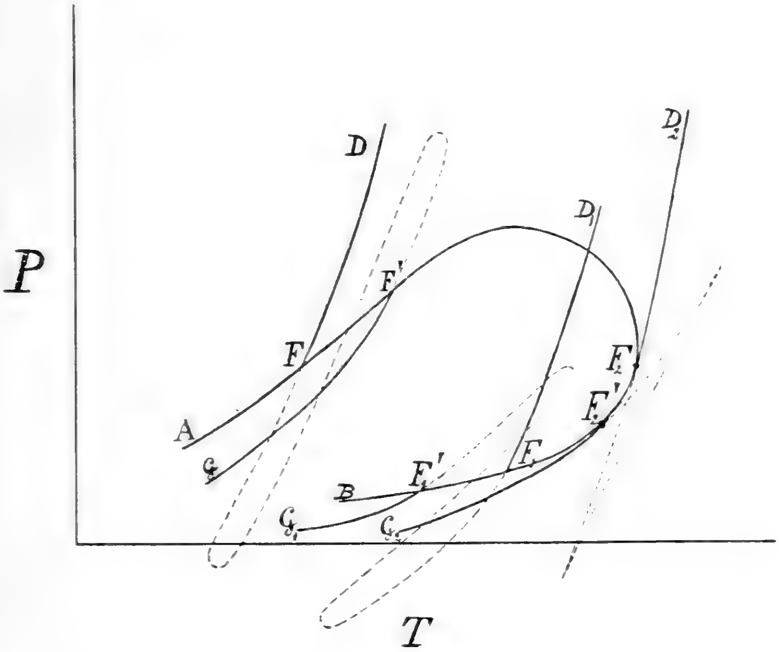

Fig. 2.

This intersection takes place in the points F' and F, about which it may be observed, that F' lies at a higher temperature than F. This situation can, however, also be reversed, and as appears from the diagram, the transition takes place at a concentration somewhat to the left of that of the compound. We see further, that the intermediate piece, which continuously joins the line of sublimation GF' to the melting-point curve FD, has a maximum and a minimum (points where $X_2 = 0$), about which the isotherm teaches us, that, when we are not in the immediate neighbourhood of the critical state, they are very far apart and that the minimum lies at a negative pressure.

It is also noteworthy about this figure, that when following the P, T-line, starting with the point G resp. with the point D, we first meet with a point, where the tangent is vertical, and (place where $X_1 = 0$) *after that* with a point where it is horizontal.

If we now consider a concentration on the *right* of the line of the compound, the P, T-line corresponding with this will cut the other continually ascending branch of the three phase line of the compound, and by means of equation (4a) and the scheme for the reversal of sign of X_1 and X_2 preceding it, we obtain a curve as indicated by $G_1 F_1' F_1 D_1$. The situation of the loci $X_1 = 0$ and $X_2 = 0$ being different on the right from that on the left, this P, T-line differs from that just discussed. When now, starting from the point G_1 resp. D_1, we follow the P, T-line, we meet *first* with a point, where it is vertical, so we have just the reverse of the preceding case. About the situation of the points F_1' and F_1 we may point out, that F_1' *always* lies at lower temperature than F_1.

The loci $X_1 = 0$ and $X_2 = 0$ intersecting on the line of the compound, the P, T-line for the concentration of the compound will have to give to a certain extent the transition-case between the two lines discussed.

What happens when we approach the curve of the compound, we see immediately from fig. 1. The distance between the loci $X_1 = 0$ and $X_2 = 0$ becoming smaller and smaller, the points of contact of the vertical and horizontal tangents will draw nearer and nearer, which prepares us for what happens when we have arrived at the line of the compound. We see from the scheme for the signs of X_1 and X_2 that when the loci $X_1 = 0$ and $X_2 = 0$ have coincided, the signs of X_1 and X_2 reverse simultaneously, on account of which $T\left(\frac{dp}{dT}\right)_{x_f}$ retains the same sign, viz. remains positive. Combining this with what we know about the course of the P, T-lines somewhat to the right and the left of the curve of the compound we are led to the conclusion, that the P, T-line for the concentration of the compound will have two *cusps*, each formed by two branches with a common tangent. I have not been able to decide whether these points will be cusps of the first or the second kind. The former has been assumed in the diagram.

It is further noteworthy for this P, T-line that, as VAN DER WAALS [1]) already demonstrated before, both the line of sublimation and the melting-point line must touch the three-phase line, so that the P, T-line

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[1]) Verslag 21 April 1897, 482.

for the concentration of the compound assumes a shape, as given by the line $G_2\,F_2'\,F_2\,D_2$ in fig. 2.

If it were possible to make the degree of association of the compound smaller and smaller, the points F_2' and F_2 would move to lower pressure and higher temperature. Moreover these two points and the neighbouring point of intersection of the melting-point and sublimation branches would draw nearer and nearer to each other, till with perfect absence of dissociation these *three* points would have coincided.

Another peculiarity will present itself for the case that we have a three-phase-line as described by me before, viz. with two maxima and one minimum[1]), for then there is a point where $x_d = x_l$[2]) on

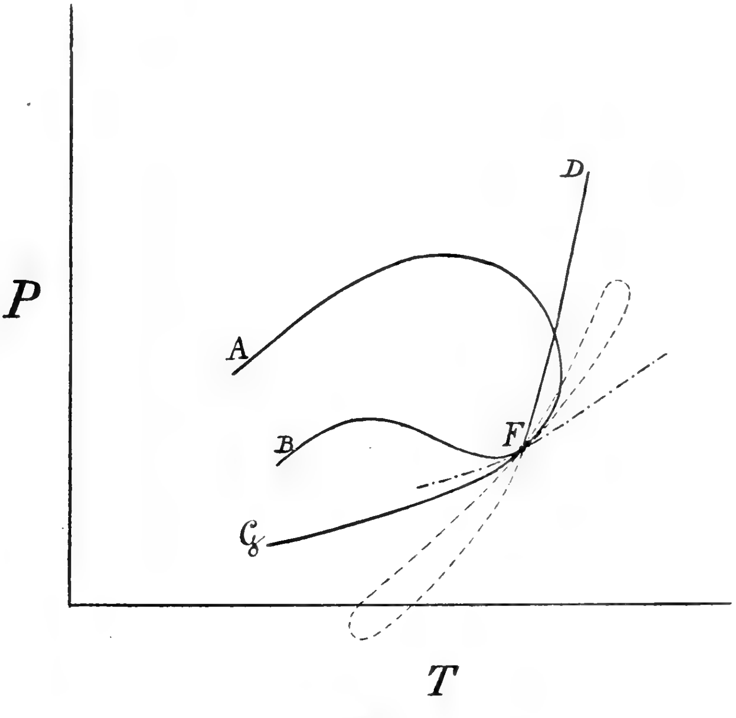

Fig. 3.

this line, and then it is immediately to be seen that in consequence of the coinciding of the points F' and F, we get for this concentration a P,T-line, as represented in fig. 3, which curve has the form of a *loop*.

Amsterdam, April 1906. *Anorg. Chem. Lab. of the University.*

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[1]) These Proc. VIII, p. 200.

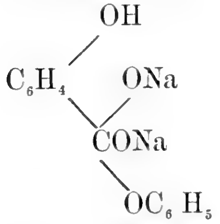
[2]) In this point the direction of the three-phase line is given by $T\frac{dp}{dT}=\frac{r}{v_d-v_l}$.

Chemistry. — *"The formation of salicylic acid from sodium phenolate."* By Dr. J. Moll van Charante. (Communicated by Prof. A. P. N. Franchimont).

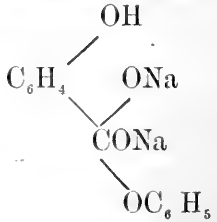
(Communicated in the meeting of April 27, 1906).

The communication from Lobry de Bruyn and Tijmstra read at the meeting of 28 May 1904 and their subsequent article in the Recueil **23** 385 induced me to make this research. Their theory, and particularly the proofs given in support do not satisfy me and as, in consequence of other work, I had formed an idea of the reaction I made some experiments in that direction.

According to my idea, an additive product of sodium phenolate with sodium phenylcarbonate, or what amounts to the same an additive product of two mols of sodium phenolate with one mol. of carbondioxide $C_6H_5OC(ONa)_2OC_6H_5$ might be the substance which undergoes the intramolecular transformation to the salicylic acid derivative and then forms, dependent on the temperature, sodium salicylate and sodium phenolate or else phenol and basic sodium salicylate. This view is supported by previous observations of various chemists and has been partially accepted also by Claisen [1]).



As Lobry de Bruyn and Tijmstra give no analytical figures in their paper it did not seem to me impossible that the phenolsodium-*o*-carboxylic acid obtained by them might be the substance formed by intramolecular transformation of my supposed additive product. I, therefore, took up their method of working, prepared sodium phenylcarbonate in the usual manner, from sodium phenolate and carbon dioxide, and heated this to 100° in a sealed tube for 100 hours. On opening the tube considerable pressure was observed. This pressure was always found when the experiments were repeated. The gas liberated proved to consist entirely of carbondioxide and amounted to $^1/_4$—$^1/_3$ of that present in the sodium phenylcarbonate. If we argue that the sodium phenylcarbonate under these circumstances is partially resolved into carbon dioxide and sodium phenolate the latter compound ought to be present or else the splitting up might give carbon dioxide and my supposed



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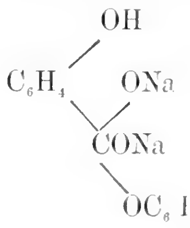
[1]) B. B. (1905) 38 p. 714.

intermediary product $(C_6H_5O)_2\,C(ONa)_2$. In the first case it is strange that during the cooling of the tube, which often was left for a few days, the carbon dioxide is not greatly reabsorbed. Those substances had now to be searched for in the product of the reaction. On treatment with ether a fair amount of phenol was extracted although moisture was as much as possible excluded. It was then brought into contact with cold, dry acetone, by which it was partially dissolved, but with evolution of gas and elevation of temperature. From the clear solution, petroleum ether precipitated a substance which, after having been redissolved and reprecipitated a few times in the same manner, formed small white needles containing acetone which effloresced on exposure to the air. On analysis, this compound proved to be sodium salicylate with one mol. of acetone. As an ebullioscopic determination in acetone, according to LANDSBERGER, did not give the expected molecular weight, sodium salicylate was dissolved in acetone and precipitated with petroleum ether and a quite identical product was obtained as proved both by analysis and determination of the molecular weight. Both products, after being dried at 100°, yielded no appreciable amount of salicylic ester when heated with methyl iodide.

The amount of sodium salicylate obtained by heating sodium phenylcarbonate in the manner indicated was, however, very trifling.

I suspected that the evolution of gas noticed in the treatment with acetone, and which was identified as pure carbondioxide without any admixture, was caused by the presence of unchanged sodium phenylcarbonate, so that, therefore, the reaction was not completed, and that the tube after being heated must still contain a mixture of unchanged sodium phenylcarbonate, sodium phenolate, sodium salicylate and free phenol, besides the said additive product $(C_6H_5O)_2$ $C(ONa)_2$ and the salicylic acid derivative possibly formed from this. I now thought it of great importance to first study the behaviour of acetone with these substances as far as they are known.



$C_6H_4(OH)\,C(ONa)_2\,OC_6H_5$

Sodium phenolate dissolves in boiling acetone, from which it crystallises on cooling in soft, almost white needles, several c.m. long, which contain one mol. of acetone. They lose this acetone, in vacuo, over sulphuric acid. At the ordinary temperature acetone dissolves only 0,1 °/₀.

Sodium phenylcarbonate placed in carefully dried acetone gives off carbon dioxide with a slight elevation of temperature. The quantity amounts to about $^1/_3$ of the carbon dioxide actually present, at least if account is taken of the comparatively large solubility of that gas in acetone. The acetone, or if the mixture is extracted with ether, also the ether, contains a quantity of phenol corresponding with the total amount obtainable from the sodium phenylcarbonate. The undissolved mass consists of a mixture of neutral and acid sodium carbonate, nearly, or exactly in equivalent proportions. The decomposition of $3\,C_6H_5OCOONa$ to $3\,C_6H_5OH + CO_2 + NaHCO_3 + Na_2CO_3$ requires 2 mols. of water. As the experiments however, have been made in a specially constructed apparatus into which no moisture or moist air could enter, with extremely carefully dried acetone, we are bound to admit that this water has been generated by the acetone, and we may, therefore, expect a condensation product of the acetone which, however, could not be isolated, owing to the small quantities of materials used in the experiments. It seems strange that in this reaction the evolution of carbon dioxide is so extraordinarily violent.

Sodium salicylate dissolves in acetone from which it crystallises, with or without addition of petroleum ether, in small needles, which may contain one mol. of acetone of crystallisation. In different determinations the acetone content was found to vary from one-half to a full molecule. At 16° it dissolves in about 21 parts of acetone.

Disodium salicylate was prepared by adding an (95 %) alcoholic solution of salicylic acid to a concentrated solution of sodium ethoxide in alcohol of the same strength. After a few moments it crystallises in delicate, white needles. By boiling with acetone in which it is entirely insoluble it may be freed from admixed monosodium salicylate.

The behaviour of acetone with these substances now being known, the experiment of heating the sodium phenylcarbonate for 100 hours was once more repeated, without giving, however any further results. A portion was treated with acetone in the same apparatus which had been used for the sodium phenylcarbonate. A quantity of carbon dioxide was collected corresponding with an amount of unchanged sodium phenylcarbonate representing 50—60 % of the reaction-product. Another portion was extracted with ether and yielded about 20 % of phenol whilst, finally, a small amount of sodium salicylate was also found. The residue which had been extracted with ether and acetone contained sodium carbonate but no disodium-salicylate. It, however, contained phenol, probably from sodium phenolate.

It seems strange there is such a large quantity of free phenol in the heated sodium phenylcarbonate, and as no disodium-salicylate has been found it cannot have been caused by the formation of that compound.

I have not been able to find the looked for additive product; perhaps it has been decomposed by acetone in the same manner as sodium phenylcarbonate. The results obtained show in my opinion that the formation of salicylic acid from sodium phenylcarbonate is not so simple as is generally imagined.

A more detailed account of research will appear in the "Recueil".

Chemistry. — *"On the crystal-forms of the* 2,4-*Dinitroaniline-derivatives, substituted in the* NH_2*-group"*. By Dr. F. M. Jaeger. (Communicated by Prof. P. van Romburgh).

(Communicated in the meeting of April 27, 1906).

More than a year ago I made an investigation as to the form-relation of a series of position-isomeric *Dinitroaniline*-derivatives [1]). On that occasion it was shown how these substances exhibit, from a crystallonomic point of view, a remarkable analogy which reveals clearly the morphotropous influence of the hydrocarbon-residues, substituted in the NH_2-group.

Among the compounds then investigated, there were already a few 1-2-4-*Dinitroaniline*-derivatives kindly presented to me by Messrs. van Romburgh and Franchimont. Through the agency of Prof. van Romburgh and Dr. A. Mulder, I have now received a series of other derivatives of 2,4-*Dinitroaniline* which in the happiest manner complete my former publications. I wish to thank these gentlemen once more for their kindness. I will describe and illustrate all these derivatives in a more detailed article in the Zeits. f. Kryst.

For the present I will merely give a survey of the results obtained, which have been collected in the annexed table.

I have chosen such a form-symbolic, that the morphotropous relation of the great majority of these substances is clearly shown. They all possess the same family-character which is shown in the values of the axial relations and the topic parameters. Only a few of these substances show no simple relationship with the other ones.

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[1]) Jaeger, Ueber morphotropische Beziehungen bei den in der Amino-Gruppe substituierten Nitro-Anilinen; Zeits. f. Kryst. (1905). **40.** 113—146.

No.	Name of the compound	Survey of			
		M.p.	Mol. weight.	Equiv. Vole. (in the solid state.)	Sy
1	1-2-Nitro-Aniline.	72°	138	95.70	Rho
2	1-4-Nitro-Aniline.	146°	138	96.03	Mo
3	1-2-4-Dinitro-Aniline.	182°	183	113.30	Mo
4	1-2-4-6-Trinitro-Aniline.	190°	228	129.39	Mo
5	1-4-Nitro-Diethyl-A.*)	78°	194	162.07	Mo
6	1-2-4-Dinitro-Methyl-A.	178°	197	125.24	Mo
7	1-2-4-Dinitro-Ethyl-A.	114°	211	145.41	Tri
8	1-2-4-Dinitro-Dimethyl-A.	87°	211	142 95	Rho
9	1-2-4-6-Trinitro-Dimethyl-A.	154°	256	165.05	Rho
10	1-2-4-Dinitro-Methyl-Ethyl-A.	59°	225	157.45	Tri
11	1-2-4-Dinitro-Diethyl-A.	80°	239	173.94	Rho
12	1-2-4-, + 1-3-4-Dinitro-Diethyl-A. (Double compound.)	59°	478	½(361.02)	Mo
13	1-2-4-6-Trinitro-Diethyl-A.	164°	284	192.41	M
14	1-2-4-Dinitro-Ethyl-n-Propyl-A.	55°	253	189.13	Rh
15	1-2-4-6-Trinitro-Ethyl-Isopropyl-A.	109°	298	211.80	Tr
16	1-2-4-Dinitro-Isopropyl-A.	95°	225	153.79	Tr
17	1-2-4-Dinitro Dipropyl-A.	40°	267	202.50	Rh
18	1-2-4-6-Trinitro-Dipropyl-A.	138°	312	227.23	T
19	1-2-4-Dinitro-Isobutyl-A.	80°	239	172.70	M
20	1-2-4-6-Trinitro-Isobutyl-A	95°	284	196.53	Rh
21	1-2-4-Dinitro-Diïsobutyl-A.	112°	295	250.21	M
22	1-2-4-Dinitro-Allyl-A.	76°	223	157.93	T
23	1-2-4-Dinitro-Methyl-Phenyl-A.	166°	273	194.16	M
24	1-2-4-Dinitro Ethyl-Phenyl-A.	95°	287	210.48	M
25	1-2-4-Dinitro-Benzyl-A.	116°	273	187.50	T
26	1-2-4-Dinitro-Methyl-Benzyl-A.	144°	287	204.41	M
27	1-2-4-Dinitro-Ethyl-Benzyl-A.	73°	301	219 87	M
28	1-2-4-Dinitro-Phenyl-Benzyl-A.	168°	349	250.00	
29	1-2-4-6-Trinitro-Ethyl-Nitraniline.	96°	301	183.09	
30	1-2-4-6-Trinitro-Isopropyl-Nitraniline.	108°	315	201.53	
31	1-2-3-4-6-Tetranitro-Methyl-Nitraniline.	146°	332	189.71	

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*) On the isomorphism and the complete miscibility of this compound with p-Nitrosodiethylanil

stallographically-investigated derivatives of 1—2—4—Dinitro-Aniline.

	Axial-Elements:	Topic Parameters:	No.
r.	$a : b : c = 1.3667 : 1 : 1.1585.$	$\chi : \psi : \omega = 5.3635 : 3.9245 : 4.5465$	1
.	$a : b : c = 2.0350 : 1 : 1.4220; \quad \beta = 88^\circ 10'$	$\chi : \psi : \omega = 6.5406 : 3.2141 : 4.5704$	2
.	$a : b : c = 1.9826 : 1 : 1.4088; \quad \beta = 85^\circ 1\frac{1}{2}'$	$\chi : \psi : \omega = 6.8206 : 3.4403 : 4.8467$	3
.	$a : b : c = 1.6560 : 1 : 1.5208; \quad \beta = 80^\circ 47\frac{1}{2}'$	$\chi : \psi : \omega = 5.9313 : 3.8119 : 5.7975$	4
.	$a : b : c = 1.0342 : 1 : 0.9894; \quad \beta = 80^\circ 34'$	$\chi : \psi : \omega = 5.6210 : 5.4354 : 5.3775$	5
.	$a : b : c = 1.2286 : 1 : 0.9707; \quad \beta = 83^\circ 28'$	$\chi : \psi : \omega = 5.8090 : 4.7281 : 4.5897$	6
.	$a : b : c = 1.2251 : 1 ; 0.9745$ $\alpha = 33^\circ 25\frac{1}{2}' \quad \beta = 83^\circ 22' \quad \gamma = 75^\circ 41'.$	$\chi : \psi : \omega = 6.2321 : 5.0871 : 4.9880$	7
r.	$a : b : c = 1.2154 : 1 : 1.0803.$	$\chi : \psi : \omega = 5.8035 : 4.7750 : 5.1583$	8
n.	$a : b : c = 1.2936 : 1 : 1.3831.$	$\chi : \psi : \omega = 5.8455 : 4.5184 : 6.2493$	9
.	$a : b : c = 1.1497 : 1 : 1.6639.$ $\alpha = 75^\circ 46' \quad \beta = 92^\circ 33' \quad \gamma = 68^\circ 57'$	$\chi : \psi : \omega = 5.1900 : 4.5140 : 7.5106$	10
r.	$a : b : c = 1.2045 : 1 : 1.1513.$	$\chi : \psi : \omega = 6.0294 : 5.0058 : 5.7631$	11
.	$a : b : e = 1.3435 : 1 : 1.3013; \quad \beta = 86^\circ 39'$	$\chi : \psi : \omega = 6.3064 : 4.6940 : 6.1083$	12
.	$a : b : c = 1.1750 : 1 : 0.9462; \quad \beta = 86^\circ 28'$	$\chi : \psi : \omega = 6.5523 : 5.5762 : 5.2763$	13
r.	$a : b : c = 1.0535 : 1 : 0.9227.$	$\chi : \psi : \omega = 6.1045 : 5.7946 : 5.3466$	14
c.	$a : b : c = 2.0162 : 1 .$ $\alpha = 75^\circ 0' \quad \beta = 99^\circ 17' \quad \gamma = 111^\circ 16\frac{1}{2}'$	———	15
c.	$a : b : c = 1.1527 : 1 : 1.5790.$ $\alpha = 118^\circ 43' \quad \beta = 104^\circ 33' \quad \gamma = 85^\circ 12\frac{1}{2}'$	$\chi : \psi : \omega = 5.3440 : 4.6360 : 7.3201$	16
r.	$a : b : c = 1.0191 : 1 : 0.9246.$	$\chi : \psi : \omega = 6.4042 : 5.9890 : 6.5382$	17
c.	$a : b : c = 1.3327 : 1 : 0.9055$ $\alpha = 119^\circ 46' \quad \beta = 111^\circ 0' \quad \gamma = 102^\circ 35'$	$\chi : \psi : \omega = 8.1556 : 6.1197 : 5.5414$	18
.	$a : b : c = 0.7104 : 1 : 0.3591; \quad \beta = 85^\circ 34\frac{1}{2}'$	$\chi : \psi : \omega = 6.1870 : 8.7092 : 3.2145$	19
yr.	$a : b : c = 0.7325 : 1 : 0.3470.$	$\chi : \psi : \omega = 6.7231 : 9.1782 : 3.1849$	20
.	$a : b : c = 1.0717 : 1 : 0.9124; \quad \beta = 63^\circ 5\frac{1}{2}'$	$\chi : \psi : \omega = 7.0686 : 6.5960 : 6.0181$	21
c.	$a : b : c = 1.0251 : 1 : 0.9632$ $\alpha = 71^\circ 16\frac{1}{2}' \quad \beta = 111^\circ 0' \quad \gamma = 116^\circ 40'$	$\chi : \psi : \omega = 5.9480 : 5.8024 : 5.5890$	22
.	$a : b : c = 1.1518 : 1 : 1.6968; \quad \beta = 86^\circ 1'$	$\chi : \psi : \omega = 5.3389 : 4.6341 : 7.8650$	23
.	$a : b : c = 0.4933 : 1 : 0.6586; \quad \beta = 78^\circ 6\frac{1}{4}'$	$\chi : \psi : \omega = 4.2994 : 8.7156 : 5.7401$	24
c.	$a : b : c = 1.0385 : 1 : 0.8586$ $\alpha = 107^\circ 57' \quad \beta = 139^\circ 47' \quad \gamma = 78^\circ 23'$	$\chi : \psi : \omega = 7.2441 : 6.9757 : 5.9891$	25
.	$a : b : c = 1.5086 : 1 : 1.3276; \quad \beta = 71^\circ 40'$	$\chi : \psi : \omega = 7.1735 : 4.7551 : 6.3129$	26
.	$a : b : c = 1.7258 : 1 : 1.3087; \quad \beta = 84^\circ 5'$	$\chi : \psi : \omega = 6.9531 : 4.6084 : 6.0310$	27
.	$a : b : c = 1.1373 : 1 : 1.3645; \quad \beta = 64^\circ 21\frac{1}{2}'$	$\chi : \psi : \omega = 6.4059 : 5.7640 : 7.6856$	28
.	$a : b = 1.4187 : 1. \quad \beta = 86^\circ 23\frac{1}{4}'$	———	29
.	$a : b : c = 1.3924 : 1 : 0.9368; \quad \beta = 78^\circ 33'$	$\chi : \psi : \omega = 7.3676 : 5.2913 : 5.2743$	30
.	$a : b : c = 1.6686 : 1 : 1.4712; \quad \beta = 76^\circ 37'$	$\chi : \psi : \omega = 7.1730 : 4.2987 : 6.3243$	31

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ese Proceedings (1905) p. 658.

Crystallography. — "*On a new case of form-analogy and miscibility of position-isomeric benzene-derivatives, and on the crystal-forms of the six Nitrodibromobenzenes.*" By Dr. F. M. JAEGER. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of April 27, 1906).

§ 1. The following contains the investigation of the crystal-forms exhibited by the six position-isomeric *Nitrodibromobenzenes,* which may be expected from the usual structure-representations of benzene. It has been shown that, in this fully investigated series, there again exists a miscibility and a form-analogy between two of the six terms.

The above compounds were kindly presented to me by Prof. HOLLEMAN, to whom I again express my thanks.

This investigation is connected with that on the isomeric *Dichloronitrobenzenes,* which has also appeared in these proceedings (1905, p. 668).

A. Nitro-2-3-Dibromobenzene.

Structure: $C_6H_3 . (NO_2)_{(1)} . Br_{(2)} . Br_{(3)}$; meltingpoint: 53° C.

The compound, which is very soluble in most organic solvents, crystallises best from ligroïn + ether in small, flat, pale sherry-coloured needles which generally possess very rudimentary terminating planes.

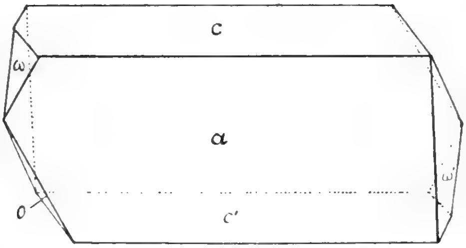

Fig. 1.

Triclino-pinacoidal.

$$a : b : c = 1,4778 : 1 : 1,9513.$$

$A = 90°30'$ $\qquad \alpha = 90°45^2/_3{}'$

$B = 110°37'$ $\qquad \beta = 110°36^3/_4{}'$

$C = 90°16^1/_2{}'$ $\qquad \gamma = 89°59^1/_4{}'$

The crystals, therefore, show a decided approach to the monoclinic system; on account, however, of their optical orientation, they can only be credited with a triclinic symmetry.

The forms observed are: $a = \{100\}$, strongly predominant and very lustrous; $b = \{010\}$, smaller but yielding good reflexes; $c = \{001\}$, narrower than a, but very lustrous; $o = \{1\bar{1}\bar{1}\}$, well developed and very lustrous; $\omega = \{1\bar{1}1\}$, smaller but very distinct; $s = \{\bar{1}\bar{1}\bar{1}\}$, very narrow but readily measurable.

The habit is elongated towards the b-axis with flattening towards $\{100\}$.

	Measured:	*Calculated.*
$a : b = (100) : (0\bar{1}0) =^{*}$	$90^\circ 16\frac{1}{2}'$	—
$a : c = (100) : (001) =^{*}$	69 23	—
$a : o = (100) : (1\bar{1}\bar{1}) =^{*}$	65 11	
$c : o = (00\bar{1}) : (1\bar{1}\bar{1}) =^{*}$	$75\ 47\frac{1}{3}$	—
$b : o = (0\bar{1}0) : (1\bar{1}\bar{1}) =^{*}$	36 6	—
$a : \omega = (100) : (1\bar{1}1) =$	50 52	$50^\circ 49'$
$c : \omega = (001) : (1\bar{1}1) =$	56 52	56 43
$b : \omega = (0\bar{1}0) : (1\bar{1}1) =$	46 28	46 35
$o : \omega = (1\bar{1}\bar{1}) : (1\bar{1}1) =$	47 13	$47\ 29\frac{2}{3}$
$a : s = (\bar{1}00) : (\bar{1}\bar{1}\bar{1}) =$	49 59	$50\ 49\frac{1}{3}$
$b : s = (0\bar{1}0) : (\bar{1}\bar{1}\bar{1}) =$	45 48	$45\ 52\frac{1}{2}$
$c : s = (00\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	—	56 4
$o : s = (1\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	63 39	$63\ 59\frac{2}{3}$

Readily cleavable, parallel $\{100\}$.

The extinction on $\{100\}$ amounts to about $26\frac{1}{2}$ in regard to the b-axis; in convergent light a hyperbole is visible occupying an eccentric position.

The sp. gr. of the crystals is 2,305 at 8°; the equivalent volume 121.47.

B. Nitro-2-5-Dibromo-Benzene.

Structure: $C_6H_3 \cdot (NO_2)_{(1)} \cdot Br_{(2)} \cdot Br_{(5)}$; m.p.: 84°,5.

This compound has been previously studied crystallographically by G. Fels, (Zeits. f. Kryst. **32**, 377). This paper, however, contains several errors, which render a renewed investigation desirable; moreover, another choice of axial (coordinate) planes is required, which makes the crystals show more analogy with the other triclinic terms of this series.

The crystals deposited from acetone + ligroïn have the form of small plates flattened towards $\{001\}$ (figs. 2 and 3). They are pale yellow and very lustrous.

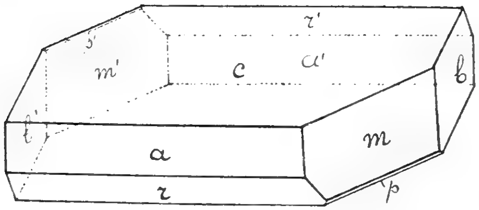

Fig. 2.

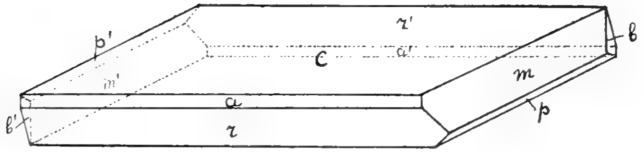

Fig. 3.

Triclino-pinacoïdal.

$$a : b : c = 1{,}4909 : 1 : 2{,}0214.$$

$$A = 91^\circ\ 3^1/_2{}' \qquad \alpha = 90^\circ 57^1/_2{}'$$
$$B = 113^\circ 21^1/_2{}' \qquad \beta = 113^\circ 21^1/_3{}'$$
$$C = 90^\circ 27' \qquad \gamma = 90^\circ\ 2'.$$

Forms observed: $c = \{001\}$, strongly predominant and reflecting ideally; $a = \{100\}$, and $r = \{\bar{1}01\}$, usually developed equally broad and also yielding sharp reflexes; $b = \{010\}$, smaller, readily measurable; $m = \{110\}$, large and lustrous; $p = \{11\bar{3}\}$, mostly narrow but very lustrous; sometimes as broad as m.

Broad flattened towards $\{001\}$. The approach to monoclinic symmetry is also plain in this case.

	Measured:	*Calculated:*
$a : b = (100) : (010) =$	*89°33'	—
$b : c = (010) : (001) =$	*88 $56^1/_2$	—
$c : a = (001) : (100) =$	*66 $38^1/_2$	—
$b : m = (010) : (110) =$	*35 $59^1/_2$	—
$a : r = (100) : (10\bar{1}) =$	*43 45	—
$c : m = (001) : (110) =$	75 46	75°$38^2/_3$'
$a : m = (100) : (110) =$	53 33	53 $33^1/_2$
$c : r = (00\bar{1}) : (10\bar{1}) =$	69 37	69 $36^1/_2$
$r : m = (10\bar{1}) : (110) =$	65 20	65 11
$p : m = (11\bar{3}) : (110) =$	60 59	60 $44^1/_2$
$r : b = (10\bar{1}) : (010) =$	89 55	89 22
$r : p = (10\bar{1}) : (11\bar{3}) =$	50 53	—

Readily cleavable, parallel *m*.

The optical orientation is that of Fels, in which his forms {010}, {001} and {$11\bar{1}$} assume, respectively, in my project the symbols {001}, {110} and {010}. It may be remarked that Fels has incorrectly stated the structure and also the melting point. Moreover, his angles ($11\bar{1}$) : (100) and ($11\bar{1}$) : (010) appear to be > 90°. Perhaps it is owing to this, that the agreement between the calculated and found values is with him so much more unfavourable than with me. I have never observed forms {$\bar{5}52$} and {$\overline{15}$. 15 . 4}

The sp. gr. at 8° is 2,368; the equiv. volume: 118,66.

Topical axes: $\chi : \psi : \omega = 5{,}2190 : 3{,}5005 : 7{,}0758$.

On comparing the said position-isomeric derivatives, one notices at once not the great similarity between the two compounds, which, although constituting a case of direct-isomorphism, still very closely resembles it.

Nitro-2-3-Dibromobenzene.	*Nitro-2-5-Dibromobenzene.*
Triclino-pinacoidal.	Triclino-pinacoidal.
$a : b : c = 1{,}4778 : 1 : 1{,}9513$	$a : b : c = 1{,}4909 : 1 : 2{,}0214.$
$A = 90°30'$ $B = 110°37'$ $C = 90°16^1/_2{}'$	$A = 91°3^1/_2{}'$ $B = 113°21^1/_2{}'$ $C = 90°27'$
$\alpha = 90°45^2/_3{}'$ $\beta = 110°36^3/_4{}'$ $\gamma = 89°59^1/_4{}'$	$\alpha = 90°57^1/_2{}'$ $\beta = 113°21^1/_3{}'$ $\gamma = 90°2'$
$\chi : \psi : \omega = 5{,}2565 : 3{,}5571 : 6{,}9409.$	$\chi : \psi : \omega = 5{,}2190 : 3{,}5005 : 7{,}0758.$
However:	However:
Forms: {100}, {010}, {001}, {$1\bar{1}\bar{1}$}, {$\bar{1}\bar{1}1$} and {$\bar{1}\bar{1}\bar{1}$}	Forms: {100}, {010}, {001}, {$\bar{1}01$}, {110}, {$11\bar{3}$}.
Cleavable parallel {100}.	Cleavable parallel {110}.
Habit tabular towards {100}.	Habit tabular towards {001}.

We, therefore, still notice such a difference in habit and cleavability that a direct isomorphism, in the ordinary meaning of the word, cannot be supposed to be present. There occurs here a case of isomorphotropism bordering on isomorphism.

Notwithstanding that difference, both substances can form an interrupted series of mixed crystals, as has been proved by the determination of the binary melting point curve and also crystallographically ¹).

The melting point of the 1-2-3-derivative (53°) is depressed by addition of the 1-2-5-derivative. The melting point line has also

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¹) The binary melting-curve possesses, — as proved by means of more a exact determination, — a *eutectic point* of 52° C. at 2% of the higher melting component; therefore here the already published melting-diagram is eliminated. There is a *hiatus* in the series of mixed-crystals, from ± ½% to circa 48% of the 1-2-3-derivative. I shall, however point out, that the possibility of such a hiatus thermodynamically can be proved, — even in the case of directly-isomorphous substances.

(Added in the English translation).

not, as in the previously detected case of the two tribromotoluenes (Dissertation, Leyden 1903) a *continuous* form; the difference is caused by the lesser degree of form-analogy which these substances possess in proportion to that of the two said *tribromotoluenes.*

The third example of miscibility, — although partially —, and of form-analogy of position-isomeric benzene-derivatives¹) is particularly interesting.

Mixed crystals were obtained by me from solutions of both components in acetone + ether.

They possess the form of fig. 1 and often exhibit the structure of a sand time-glass or they are formed of layers. With a larger quantity of the lower-melting derivative, long delicate needles were obtained which are not readily measurable. The melting points lie between ± 75° and $84\frac{1}{2}°$; I will determine again more exactly the mixing limits.

C. Nitro-2-4-Dibromobenzene.

Structure: $C_6H_3 . (NO_2)_{(1)} . Br_{(2)} . Br_{(4)}$; m. p. 61°.6.

Recrystallised from alcohol, the compound forms large crystals flattened towards *a* and elongated towards the *c*-axis. They are of a sulphur colour.

Triclino-pinacoidal.

$$a : b : c = 1{,}1307 : 1 : 1{,}1698.$$

$A = 97°13^1/_2{}'$ $\alpha = 97°36'$

$B = 113°30^1/_2{}'$ $\beta = 113°37'$

$C = 90°38^1/_2{}'$ $\gamma = 87°33'$

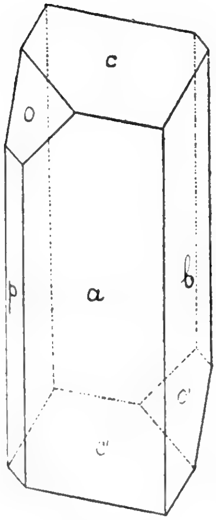

Fig. 4.

Forms observed: $a = \{100\}$ predominant and very lustrous; $b = \{010\}$ and $c = \{001\}$, equally broad, both strongly lustrous; $p = \{1\bar{1}0\}$, narrow but readily measurable; $o = \{1\bar{1}1\}$, large and yielding good reflexes.

The compound has been measured previously, by GROTH and BODEWIG (Berl. Berichte, **7**, 1563). My results agree in the main with theirs; in the symbols adopted here, their *a*- and *b*-axes have changed places and the agreement with the other derivatives of the series is more conspicuous.

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[1] The examples now known are 1-2-3-5-, and 1-2-4-6-*Tribromobenzene;* 1-2-3-5-*Tribromo*-4-6-*Dinitro*- and 1-2-4-6-*Tribromo*-3-5-*Dinitrotoluene*; and 1-2-5-, and 1-2-3-*Nitrodibromobenzene,* partially miscible.

	Measured:	*Calculated:*
$a : b = (100) : (010) =$	* 89°21½′	—
$a : c = (100) : (001) =$	* 66 29½′	—
$b : c = (010) : (001) =$	* 82 46½′	—
$p : a = (1\bar{1}0) : (100) =$	* 46 36	—
$c : o = (001) : (1\bar{1}1) =$	* 48 42	—
$o : p = (1\bar{1}1) : (110) =$	51 43 (circa)	52° 1′
$c : p = (001) : (\bar{1}10) =$	100 29 (circa)	100 43′

Cleavable towards {010}; Groth and Bodewig did not find a distinct plane of cleavage.

Spec. Gr. of the crystals = 2,356, at 8° C., the equiv. vol. = 119,27.

Topic Axes: $\chi : \psi : \omega = 5,2365 : 4,6304 : 5,4166$.

Although the analogy of this isomer with the two other triclino-isomers is plainly visible, the value of $a : b$ is here quite different. In accordance with this, the derivative melting at 84½° *lowers* the melting point of this substance. A mixture of 87% 1-2-4- and 13% 1-2-5-*Nitrodibromobenzene* melted at 56°. There seems, however, to be no question of an isomorphotropous mixing.

D. Nitro-2-6-Dibromobenzene.

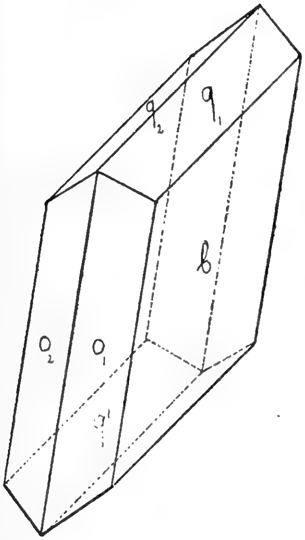

Fig._5.

Structure: $C_6H_3\ (NO_2)_{(1)}\ .\ Br_{(2)}\ .\ Br_{(6)}$; m.p. 82°.

Recrystallised from alcohol the compound generally forms elongated, brittle needles which are often flattened towards two parallel planes.

Monoclino-prismatic.

$$a : b : c = 0,5678 : 1 : 0,6257.$$

$$\beta = 83°24'.$$

Forms observed: $b = \{010\}$, strongly predominant; $q = \{011\}$ and $o = \{111\}$ about equally strongly developed. The crystals are mostly flattened towards b with inclination towards the a-axis.

	Measured:	*Calculated:*
$q : q = (011) : (0\bar{1}1) =$	* 63°43½'	—
$o : o = (111) : (11\bar{1}) =$	* 47 52	—
$o : q = (111) : (0\bar{1}1) =$	* 74 20½	—
$o : q = (111) : (011) =$	45 42½	45°42'
$q : b = (011) : (010) =$	58 8¼	58 8¼
$b : o = (010) : (111) =$	66 6	66 4

No distinct plane of cleavage is present. An optical investigation was quite impossible owing to the opaqueness of the crystals.

Sp. Gr. = 2,211 at 8° C.; the equiv. vol.: 127,09.

Topic parameters: $\chi : \psi : \omega = 4{,}0397 : 7{,}1147 : 4{,}4516$.

E. Nitro-3-5-Dibromobenzene.

Structure: $C_6H_3\,(NO_2)_{(1)} \,.\, Br_{(3)} \,.\, Br_{(5)}$; m.p.: 104°,5. The compound has already been measured by Bodewig (Zeitschr. f. Kryst. **1**. 590); my measurements quite agree with his.

Monoclino-prismatic.

Bodewig finds $a : b : c = 0{,}5795 : 1 : 0{,}2839$, with $\beta = 56°12'$. Forms: {110}, {100}, {001} and {011}.

I take $\beta = 85°26'$ and after exchanging the *a*-, and *c*-axis

$$a : b : c = 0{,}5678 : 1 : 0{,}4831,$$

with the forms {011}, {001}, {201} and {211}. Completely cleavable towards {201}. Strong, negative double refraction.

Sp. Gr. = 2,363 at 8° C.; equiv. vol. = 118,91.

Topic axes: $\chi : \psi : \omega = 4{,}3018 : 7{,}5761 : 3{,}6601$.

The great analogy in the relation $a : b$ of this and of the previous substance is remarkable; also that of the value of angle β.

F. Nitro-3-4-Dibromo-Benzene.

Structure $C_6H_3\,(NO_2)_{(1)} \,.\, Br_{(3)} \,.\, Br_{(4)}$; m.p. 58° C. Has been measured by Groth and Bodewig (Berl. Ber. **7**.1563). *Monoclino-prismatic.*

$a : b = 0{,}5773 : 1$ with $\beta = 78°31'$. Forms {001}, {110} and {100}, tabular crystals. Completely cleavable towards {100}, distinctly so towards {010}. The optical axial plane is {010}; on *a* both optical axes (80°) are visible. I found the sp. gr. at 8° C. to be 2,354. The equivalent volume is therefore 119,34.

I have tried to find a meltingpoint-line of the already described type in the monoclinic derivatives in which some degree of form-analogy is noticeable. However, in none of the three binary mixtures this was the case; the lower melting point was *lowered* on addition of the component melting at the higher temperature, without formation of mixed crystals. For instance:

A mixture of 82,3 °/₀ 1-2-3- and 17,7 °/₀ 1-3-5-*Nitrodibromo-benzene* melted at $48^{1}/_{2}$° C.

A mixture of 76,5 °/₀ 1-2-6- and 23,5 °/₀ 1-3-5-*Nitrodibromo-benzene* at $68^{1}/_{2}$° C.

A mixture of 90,5 °/₀ 1-3-4- and 9,5 °/₀ 1-2-6-*Nitrodibromo-benzene* at 54° C.

Moreover, no mixed crystals could be obtained from mixed solutions.

The slight form-analogy with the *Nitro-dichloro-benzenes* [1]) investigated by me some time ago is rather remarkable.

Nitro-2-3-*Dichloro-Benzene* (62° C. rhombic) and *Nitro*-2-6-*Dichloro-Benzene* (71° C. monoclinic) exhibit practically no form-analogy with the two *Dibromo*-compounds. There is also nothing in the *Dichloro*-derivatives corresponding with the isomorphotropous mixture of the 2-3- and 2-5-*Dibromo*-product. The sole derivatives of both series which might lead to the idea of a direct isomorphous substitution of two *Cl*- by two *Br*-atoms are the *Nitro*-3-5-*Dihalogen-Benzenes* (65° C. and 104°,5 C.); the melting point of the *Dichloro*-derivative is indeed *elevated* by an addition of the *Dibromo*-derivative.

As a rule, the differences in the crystal-forms of the compounds of the brominated series are much less than those between the forms of the chlorinated derivatives — a fact closely connected with the much greater value which the molecular weight possesses in the *Nitro-Dibromo-Benzenes* than in the corresponding *Chloro*-derivatives.

Zaandam, April 1906.

Physiology. — "*On the nature of precipitin-reaction.*" By Prof. H. J. Hamburger and Prof. Svante Arrhenius (Stockholm).

(Communicated in the meeting of April 27, 1906).

One of the most remarkable facts discovered during the last years in the biological department, is most certainly the phenomenon that when alien substance is brought into the bloodvessels the individual reacts upon it with the forming of an antibody. By injecting a

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[1]) These Proc. VII, p. 668.

toxin into the bloodvessels, the result is, that this is bound and free antitoxin proceeds. **Ehrlich** explains this as follows. When a toxin is injected, there are most probably cells which contain a group of atoms able to bind that alien substance. Now **Weigert** has stated the biological law, that when anywhere in the body tissue is destroyed, the gap usually is filled up with overcompensation. So, it may be assumed, that when the cell looses free groups of atoms, so many of these new ones are formed, that they can have no more place on this cell and now come in free state in circulation. This group of atoms is the antitoxin corresponding to the toxin.

As a special case of this general phenomenon the forming of precipitin is to be considered.

When a calf is repeatedly injected with horseserum, which can be regarded as a toxic liquid for the calf, then after some time it appears that in the bloodserum of that calf an antitoxin is present. In taking some bloodserum from this calf and by adding this to the horseserum a sediment proceeds. This sediment is nothing else than the compound of the toxin of the horseserum with the anti-toxin that had its origin in the body of the calf. We are accustomed to call this antitoxin *precipitin,* and the toxin here present in the horseserum, and which gave cause to the proceeding of precipitin, *precipitinogen* substance. The compound of both is called *precipitum.*

It is very remarkable that such a precipitate proceeds only, when the precipitin is brought in contact with its *own* precipitinogen substance. Indeed by adding the designed calfserum containing precipitin, not to the horseserum but to the serum of another animal, no precipitate proceeds. In this we have also an expedient to state if in a liquid (e.g. an extract of blood stain) horseserum is present or not (**Uhlenhuth**, **Wassermann** inter alia). Meanwhile such a calfserum gives notwithstanding also a precipitum with serum of the ass related to the horse.

To the same phenomenon the fact is to be brought, that when a rabbit has been injected with oxenserum, the serum taken from the rabbit does not only give a precipitate with oxenserum but also with that of the sheep and the goat, which are both related to the ox.

Some time ago an expedient was given to distinguish also [1]) serum proteid from *related* species of animals by a quantitative way, and in connection with this a method [2]) was proposed to determine accu-

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[1]) H. J. **Hamburger**, Eine Methode zur Differenzirung von Eiweiss biologisch verwandter Thierspecies. Deutsche Med. Wochenschr. 1905, S. 212.

[2]) H. J. **Hamburger**, Zur Untersuchung der quantitativen Verhältnisse bei der Präcipitinreaction. Folia haematologica. II Jahrg. N⁰. 8.

rately the quantity of precipitate which is formed by the precipitin reaction. This method also permitted to investigate quite generally the conditions which rule the formation of precipitate from the two components.

Immediately two facts had pushed themselves forward by a preliminary study which were also stated in another way by EISENBERG [1]) and ASCOLI [2]).

1. That when to a fixed quantity of calfserum [3]) (precipitin = antitoxin) increasing quantities of diluted horseserum (precipitinogen substance = toxin) were added, the quantity of precipitate increased, in order to decrease by further admixture of diluted horse serum.

2. that whatever may have been the proportion in which the two components were added to each other, the clear liquid delivered from precipitate always give a new precipitate with each of the components separately. This leads to the conclusion that here is question of an equilibrium reaction in the sense as it has been stated and explained for the first time by ARRHENIUS and MADSEN [4]).

This conclusion has become also the starting point of the now following researches of *which the purpose was to investigate by quantitative way the principal conditions by which precipitin reaction is ruled.*

Methods of investigation.

To a fixed quantity of calfserum [5]) (precipitin = antitoxin) increasing quantities of diluted horse-serum (precipitinogen substance =

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[1]) EISENBERG. Beiträge zur Kenntniss der specifischen Präcipitationsvorgänge Bulletin de l'Acad. d. Sciences de Cracovie. Class. d. Sciences Mathem. et nat. p. 289.

[2]) ASCOLI. Zur Kenntnis der Präcipitinewirkung. Münchener Med. Wochenschr. XLIX Jahrg. S. 398.

[3]) They used sera of other animals.

[4]) ARRHENIUS und MADSEN. Physical chemistry to toxins and antitoxins. Festskrift ved indvielsen of Statens Serum Institut. Kjobenhavn 1902; Zeitschr. f. physik. Chemie **44**, 1903, S. 7.

In many treatises the authors have continued these investigations; compare e.g. still:

ARRHENIUS. Die Anwendung der physikalischen Chemie auf die Serumtherapie. Vortrag gehalten im Kaiserl. Gesundheitsamt zu Berlin am 22 Sept. 1903. Arbeiten aus dem Kaiserl. Gesundheitsamt **20**, 1903.

ARRHENIUS. Die Anwend. der physik. Chemie auf die Serumtherapeutischen Fragen. Festschrift f. BOLTZMANN 1904. Leipzig, J. A. BARTH.

[5]) To make it easy for the reader, we speak here only of calfserum and horseserum. Compare the third note on this page.

toxin) are added. There upon the mixtures are heated for one hour at 37° and then centrifugated in funnelshaped tubes of which the capillary neck was fused at the bottom. The in 100 equal volumes calibrated capillary portion contains 0.02 or 0.04 c.c. The centrifugating is continued till the volume of the precipitate has become constant [1]).

Experiment with calf-horse serum.

As it was of importance, at all events for the first series of proofs, to dispose of a great quantity of serum containing precipitin, a large animal was taken to be injected. Dr. M. H. J. P. THOMASSEN at Utrecht was so kind to inject at the Governement Veterinaryschool there, a large calf several times with fresh horse serum and to prepare the serum out of the blood drawn under asceptic precautions.

The serum used for the following series of experiments was collected Nov. 28, 1905, sent to Groningen and there preserved in ice. On the day of the following experiment January 25, 1906, the liquid was still completely clear and free from lower organisms; there was only on the bottom a thin layer of sediment, which naturally was carefully left behind at the removing of the liquid. [2])

The horseserum used for the proof in question was fresh and 50 times diluted with a sterile NaCl-solution of 1°/₀.

Each time two parallel proofs were taken as a control. The capillary portion of the funnel shaped tubes used for this experiment had a calibrated content of 0.04 cc. Each division of the tubes thus corresponded to 0.0004 cc.

To this series of experiments another was connected in which the quantity of diluted horseserum was constant, but increasing quantities of calfserum were used.

From the first table it appears, that when to 1 cc. calfserum increasing quantities of diluted horseserum are added, the quantity of precipitate rises. When more horseserum is added as is the case in the second table, the quantity of precipitate descends. This appears from the following.

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[1]) Compare Folia haematologica l. c. for further particulars of the method.

[2]) Fuller details of other proofs taken on other days with calf-horseserum, also of experiments with serum obtained by injecting rabbits with pig-, oxen-, sheep- and goat-serum will be communicated elsewhere.

TABLE I.

1 *cc of the mixture of* 1 cc. *calfserum* (precipitin or serum containing antitoxin) + . . . cc. horseserum $^1/_{50}$ (precipitinogen or toxin containing serum.	Volume of the precipitate, after centrifugating for:							The quantity of precipitate found in 1cc. of the mixtures calculated for the *total* quantity of the mixed components according to the last observation.
	½ h.	½ h.	½ h.	½ h.	½ h.	20m.	15m.	
$\frac{0.04}{3}$ cc. horseserum $^1/_{50}$	1	$^1/_2$	not to be measured accurately					
$\frac{0.04}{3}$ » » »	1	$^1/_2$	»	»	»	»	»	
$\frac{0.08}{3}$ » » »	3	3	3	3	3	3	3	3.08
$\frac{0.08}{3}$ » » »	3	3	3	3	3	3	3	3.08
$\frac{0.1}{2}$ » » »	12	11	10	10	10	10	10	10.5
$\frac{0.1}{2}$ » » »	12	11	10	10	10	10	10	10.5
$\frac{0.16}{2}$ » » »	26	23	20	18	17	17	17	18.4
$\frac{0.16}{2}$ » » »	26	23	20	18	17	17	17	18.4
$\frac{0.2}{2}$ » » »	32	26	24	22	21	21	21	23.1
$\frac{0.2}{2}$ » » »	33	26	24	22	21	21	21	23.1
0.13 » » »	48	43	39	34	32	32	32	36.2
0.13 » » »	48	43	39	34	32	32	32	36.2
0.15 » » »	52	45	40	36	34	34	34	39.1
0.15 » » »	50	45	40	36	34	34	34	39.1
0.18 » » »	65	61	54	48	42	43	43	50.7
0.18 » » »	65	61	54	48	42	43	43	50.7
0.2 » » »	65	62	55	49	45	45	45	54
0.2 » » »	65	62	55	49	45	45	45	54
0.25 » » »	78	73	65	58	55	53	53	66.3
0.25 » » »	78	73	65	58	54	53	53	66.3
0.3 » » »	85	80	70	62	58	57	57	74.1
0.3 » » »	84	80	70	62	58	57	57	74.1

So e. g. the quantity of precipitate when 0.3 cc. horse serum is added to 1 cc. calfserum, is 74.1 (table I). But when, as may be read in the second table 0.5 cc. horse serum is added to 0.9 cc. calfserum the precipitate has a volume

TABLE II.

1 cc of the mixture of 0.5 cc horseserum $^1/_{50}$ + ... cc calfserum.	Volume of the precipitate, after centrifugating for ½ h. - ½ h. - ½ h. - ½ h. - ½ h. - 20m. - 15m.	The quantity of precipitate found in 1cc of the mixtures calculated for the total quantity of the mixed components, according to the last observation.
0.1 cc calfserum,	1 — ½ — not to be measured accurately	
0.1 » »	1 — ½ — » » » » »	
0.3 » »	2 — 2 — 2 — 2 — 2 — 2 — **2**	1.6
0.3 » »	2 — 2 — 2 — 2 — 2 — 2 — **2**	1.6
0.5 » »	6 — 5 — 5 — 5 — 5 — 5 — **5**	5
0.5 » »	7 — 5 — 5 — 5 — 5 — 5 — **5**	5
0.7 » »	48 — 36 — 32 — 28 — 25 — 25 — **25**	30
0.7 » »	50 — 38 — 33 — 29 — 25 — 25 — **25**	30
0.9 » »	84 — 65 — 57 — 50 — 43 — 43 — **43**	51.6
0.9 » »	81 — 63 — 55 — 49 — 43 — 43 — **43**	51.6
1.1 » »	95 — 81 — 67 — 58 — 52 — 50 — **50**	80
1.1 » »	94 — 81 — 68 — 56 — 52 — 50 — **50**	80
1.3 » »	62 — 79 — 66 — 59 — 59 — 55 — **55**	99
1.3 » »	97 — 80 — 69 — 60 — 59 — 55 — **55**	99
1.5 » »	96 — 84 — 74 — 65 — 62 — 59 — **59**	118
1.5 » »	95 — 84 — 73 — 64 — 62 — 59 — **59**	118
1.9 » »	90 — 75 — 65 — 55 — 53 — 51 — **51**	122.4
1.9 » »	89 — 75 — 65 — 55 — 53 — 51 — **51**	122.4

of 51.6. If instead of 0.9 calfserum 1 cc. was used the quantity of horseserum would necessarily have amounted to $0,5 \times \frac{1}{0\,9} = 0,55$ cc. So it appears that by the addition of 0.3 cc. horseserum to 1 cc. calfserum the precipitate amounts to 74.1 and by the addition of 0.55 cc. horseserum but to 37.3 [1]).

This decrease must be attributed partly to the solubility of the precipitum in NaCl-solution, a solubility which is felt the more strongly as a greater quantity of diluted horseserum is added. (Compare also Fol. Haematol l. c.).

So we see that the clear liquid above the precipitate contains, besides free precipitin and free precipitinogen substance, as has already been stated, also dissolved precipitate.

These three substances must form a variable equilibrium, which according to the rule of GULDBERG and WAAGE is to be expressed by the following relation.

Concentration of the free precipitinogen subst. × Concentr. of the precipitin $= k_1 \times$ Concentr. of the dissolved precipitate . . . . (I)

in this k_1 is the constant of reaction.

Meanwhile it appears from the experiment, that a greater quantity of precipitate must be dissolved than corresponds with this equation, or to express it more clearly, than corresponds with the conception that the solubility of the precipitate in NaCl solution is the only fact by which the quantity of sediment decreases.

To take away the difficulty, the hypothesis was made *that still another portion of the precipitate forms a dissolvable compound with free precipitinogen substance* (of horseserum) and that we have here a case analogical to the reaction of CaH_2O_2 with CO_2. As is known CaH_2O_2 is precipitated by CO_2, but by addition of more CO_2 the sediment of $CaCO_3$ decreases again, while CO_2 with $CaCO_3$ forms a dissolvable substance.

As will soon be seen, a very satisfactory conformity between calculated and observed quantity of precipitate is obtained through this hypothesis, which could afterwards be experimentally affirmed.

Let us now try, reckoning both with the solubility of the precipitate in NaCl-solution and with the forming of a dissolvable mixture of precipitate with precipitinogen substance, to precise more closely equation I.

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[1]) The hyperbolic form of the precipitate curve with ncreasing quantity of horseserum may still appear from the following series of experiments taken on another day (Table III). This series has not been used for the following calculation.

TABLE III.

1 cc of the mixture of 1 cc calfserum + ... cc horse-serum $^1/_{50}$.	Volume of the precipitate after centrifugating for: ½ h. — ½ h. — ½ h. — ½ h. — 20 m. — 15 m. — 10 m.	The quantity of precipitate found in 1 cc. of the mixtures calculated for the *total* quantity of the mixed components according to the last observation.
0.1 cc horseser. $^1/_{50}$	38 — 38 — 28 — 24 — 23 — 23 — **23**	25.3
0.1 » » »	40 — 32 — 29 — 24 — 23 — 23 — **23**	25.3
0.2 » » »	66 — 54 — 48 — 44 — 42 — 42 — **42**	50.4
0.2 » » »	59 — 50 — 45 — 43 — 41 — 41 — **41**	50.4
0.3 » » »	88 — 69 — 65 — 56 — 55 — 55 — **55**	71.5
0.3 » » »	87 — 68 — 65 — 56 — 55 — 55 — **55**	71.5
0.4 » » »	98 — 76 — 70 — 62 — 58 — 57 — **57**	79.8
0.4 » » »	89 — 73 — 68 — 62 — 58 — 57 — **57**	79.8
0.6 » » »	84 — 62 — 57 — 49 — 44 — 44 — **44**	70.4
0.6 » » »	71 — 57 — 53 — 47 — 43 — 43 — **43**	68.8
0.7 » » »	65 — 49 — 45 — 39 — 37 — 37 — **37**	62.9
0.7 » » »	66 — 49 — 45 — 39 — 37 — 37 — **37**	62.9
0.8 » » »	61 — 45 — 40 — 38 — 33 — 31 — **31**	55.8
0.8 » » »	62 — 45 — 40 — 38 — 33 — 31 — **31**	55.8
0.9 » » »	41 — 30 — 26 — 25 — 22 — 21 — **21**	39.9
0.9 » » »	41 — 30 — 26 — 25 — 22 — 21 — **21**	39.9
1 » » »	24 — 17 — 15 — 15 — 13 — 13 — **13**	26
1 » » »	25 — 10 — 15 — 15 — 13 — 13 — **13**	26
1.2 » » »	2 — 2 — 2 — 2 — 2 — 2 — **2**	4
1.2 » » »	2 — 2 2 — 2 — 2 — 2 — **2**	4
1.4 » » »	not to be measured	
1.4 » » »	» » » »	

Firstly we shall try to find an expression for the three substances occurring in the clear liquid which stands above the precipitate: for the free precipitinogen substance, for the free precipitin which it contains and for the quantity of dissolved precipitate.

Firstly the quantity of *free precipitinogen substance*. Let A be the *total* quantity of that substance used for an experiment. To determine how much of this is still present in the liquid in free state, it is to be determined how much is bound. Bound is:

1. a certain quantum to form the precipitate which is present in solid condition. If we set down as a rule that 1 mol. precipitum proceeds from 1 mol. precipitinogen substance and 1 mol. precipitin, then the wanted precipitinogen substance will be expressed by P, if the molecular quantity precipitate also amounts to P.

2. a quantity pV when p represents the percentage of the quantity of dissolved precipitate and V the total volume of the liquid.

3. a quantity necessary to form the compound of precipitate- and precipitinogen substance. Admitting that 1 mol. of this compound proceeds from 1 mol. precipitate and 1 mol. precipitinogen substance and then that y of this compound is present, then together $2y$ must be charged, while in each of the two components y mol. precipitinogen substance is present, so that the quantity of precipitinogen substance, which is left in free state, amounts to

$$A-P-pV-2y.$$

So when the volume of the liquid is V, the *concentration* of the free precipitinogen substance =

$$\frac{A-P-pV-2y}{V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is possible to calculate in the same way the concentration of the free precipitin.

If B is the *total* quantity of precipitin, which is used for the experiment, then there is to be subtracted from this:

1st. a quantity P for the same reason as is given at the calculation of the free precipitinogen substance (see above).

2nd. a quantity pV, likewise as explained there.

3rd. a quantity necessary to form the compound precipitate-precipitinogen substance. While in this compound but 1 mol. precipitin is present, only $1y$ is to be charged. So that the quantity of precipitin which remains in free state, amounts to $B-P-pV-y$.

While the volume of the liquid amounts to V, the concentration of the free precipitin is =

$$\frac{B-P-pV-y}{V} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

As for the *concentration* of *dissolved precipitate* in the third place, this must be expressed by

$$\frac{pV}{V} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

So the equation (1) becomes:

$$\frac{A-P-pV-2y}{V} \times \frac{B-P-pV-y}{V} = k_1 \frac{pV}{V}$$

or

$$\mathbf{(A-P-pV-2y)\,(B-P-pV-y) = k_1\, pV^2} \; . \quad . \quad . \quad (5)$$

Now one more equation, expressing the reaction according to which precipitate combines with precipitinogen substance. This is to be written down as follows.

Concentration free precipitinogen substance × concentr. dissolved precipitate = k₂ concentr. compound precipitinogen subst. — precipitate.

$$\frac{A-P-pV-2y}{V} \times \frac{pV}{V} = k_2 \frac{y}{V}$$

or

$$\mathbf{(A-P-pV-2y)\,p = k_2\, y} \; . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

By putting shortly $P+pV=P'$ and by substituting the value of y of equation (6) into equation (5) we obtain

$$\left(A-P'-2p\,\frac{A-P'}{k_2+2p}\right)\left(B-P'-p\,\frac{A-P_1}{k_2+2p}\right) = k_1\, pV^2 \quad . \quad . \quad (7)$$

In this equation are known:

1st. A, the total quantity of precipitinogen substance (diluted horseserum added);

2nd. B, the total quantity of precipitin (calfserum) used;

3rd. V, the volume of the liquid resulting from the mixing of the two components;

4th. P, the quantity of solid precipitate directly observed.

Unknown are:

1st. p, the quantity in percentages of precipitate which is *dissolved* (so p represents the solubility of the precipitate);

2nd. k_1, the constant for reaction of the formation of precipitate;

3rd. k_2, the constant for reaction of the formation of the compound precipitate-precipitinogen substance;

4th. P', this is however $P+pV$ and therefore known as soon as p has become known.

As equation (7) contains 3 unknown quantities three observations will be necessary to determine them.

When we introduce then the so found values in the other experiments and calculating the quantity of precipitate, it appears that the calculated quantities correspond in very satisfactory way with those which are observed.

Let us observe that to avoid superfluous zeros 1 cc calfserum (B) is taken $= 100$.

While as appears from the experiments in the case in question 1 cc calfserum is equivalent to nearly $^1/_3$ cc horseserum 1 : 50, 1 cc horseserum 1 : 50, that is A, obtains a value of 300.

So, where in the first experiment $\frac{0,04}{3}$ cc. horse serum was used

A obtains a value of $\frac{0,04}{3} \times 300 = 4$.

In the experiment, where on 1 cc. calfserum 0,3 cc. horseserum was used, with a value $B = 100$, A becomes $0,3 \times 300 = 90$.

Let us now combine the two tables to one by calculating for the second table how much $^1/_{50}$ horseserum is used on 1 *calfserum.*.

We see that the conformity between the determined and calculated precipitate (*col. III and IV*) *is very satisfactory. The average of the discrepancy amounts to* 1.3.

This result deserves our attention not only in view of the knowledge of the precipitin reaction as such, but also from a more general point of view, this reaction belonging to the great group of the toxin-antitoxin reactions.

Till now, in studying the last, we were obliged to deduce the equilibrium conditions from the toxins, that is to say by determining the toxic action which was left by the gradual saturation of the toxin by increasing quantities of antitoxin, but with the precipitin-reaction the equilibrium conditions may be deduced from the quantity of the formed toxin-antitoxin compound.

And not only that, but owing to the fact that the compound forms a precipitum, the quantity of this may be fixed in an accurate and direct way by simple measurement, thus without the aid of red blood corpuscles or of injecting-experiments in animals.

So there is good reason to expect that a further study of the precipitin-reaction will facilitate too the insight in other toxin-antitoxin reactions.

TABLE IV.

1cc. calfserum, $B = 100$.

I	II	III	IV	V
Used quantity of horseserum $^1/_{50}$ (*on 1cc. calfserum*).	Used quantity of horseserum expressed in the just accepted units **A.**	*Determined* volumes of the precipitate in 1 cc. of the mixtures.	*Calculated* volumes of the precipitate in 1 cc. of the mixtures.	Difference between III and IV.
0.013 cc.	4	not to be measured.	**0.2**	
0.027 »	8	**3**	**3.9**	+ 0.9
0.05 »	15	**10**	**10.3**	+ 0.3
0.08 »	24	**17**	**17.8**	+ 0.8
0.1 »	30	**21**	**23.6**	+ 2.6
0.13 »	39	**32**	**29.7**	— 2.3
0.15 »	45	**34**	**34**	0
0.18 »	54	**43**	**40.1**	— 2.9
0.2 »	60	**45**	**43.9**	— 1.1
0.25 »	75 { 53 51	**52**	**52.1**	— 0.1
0.266 »	79	**51**	**53.6**	+ 2.6
0.294 »	88.3	**55**	**57.1**	+ 2.1
0.3 »	90	**57**	**57.5**	+ 0.5
0.33 »	100	**59**	**58.9**	— 0.1
0.385 »	115.4	**55**	**57.4**	+ 2.4
0.457 »	137	**50**	**51.3**	+ 1.3
0 557 »	167	**43**	**41.3**	— 1.7
0.713 »	214	**25**	**26.8**	+ 1.8
1 »	300	**5**	**5.5**	+ 0.5
1.67 »	500	**2**	**0**	— 2

RÉSUMÉ.

We may resume our results as follows.

By mixing precipitin and precipitinogen substance (to compare resp. with antitoxin and toxin) an equilibrium reaction proceeds obeying to the law of GULDBERG and WAAGE. By this equilibrium reaction part of the precipitin molecules combines with the corresponding quantity of molecules precipitinogen substance, while by the side of this compound a certain quantity of each of the two components remains in free state. The compound is partly precipitated and partly remains dissolved. How much remains dissolved depends for the greater part on the salt solution which is present, for the sediment is soluble in Na Cl-solution.

Besides this equilibrium reaction there is still another which consists in this, that part of the precipitate combines with free precipitinogen substance to a soluble compound. This reaction too obeys the law of GULDBERG and WAAGE. The case is to be compared with the precipitation of $Ca(OH)_2$ by CO_2. By excess of CO_2 a part of the resulting $CaCO_3$ is transformed in a soluble bicarbonate. So CaH_2O_2 takes the function of the precipitin and CO_2 that of the precipitinogen substance.

Astronomy. — "*Observations of the total solar eclipse of August 30, 1905 at Tortosa (Spain).*" By J. STEIN S.J. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN.)

At the invitation of Mr. R. CIRERA S. J., director of the new "Observatorio del Ebro" I went to Tortosa towards the end of June 1905 in order to take part in the observation of the total solar eclipse. I was charged with making the measurements of the common chords of the sun and moon at the beginning and at the end of the eclipse and had also to determine the moments of the four contacts. The results might perhaps contribute to the correction of the relative places of the sun and moon.

The determination of the co-ordinates was much facilitated by the circumstance that the signals of the three points Espina, Gordo and Montsià of the Spanish triangulation were visible at this place. The measurements of the angles with a theodolite yielded the following results:

$$\varphi = 40°49'\ 13''.43 \quad ; \quad \lambda = 1^m\ 58^s 18 \text{ east of Greenwich.}$$

In these results the spheroïdal shape of the earth is accurately taken into account. Later measurements made by Mr. J. UBAGH gave the same results. Electric time-signals, directly telegraphed from the Madrid observatory, gave for the longitude: $1^m\,58^s.8$ east of Greenwich. As the most probable value we have adopted $1^m\,58^s.5$, the mean value of the two determinations. As a test 30 other determinations of latitude have been made with an instrument temporarily adjusted for Talcott observations, from which I derived as mean value: $\varphi = 40°49' 14''.8$. The height above the sea-level is 55 meters.

The instrument at my disposal for the eclipse observation was a new equatorial of MAILHAT (Paris), $2^m.40$ focal length and 16 cm. aperture, provided with an eye-piece with a double micrometer. I have determined the screw value of one of the two screws from 18 transits of circumpolar stars near the meridian. I found for it:

$$R_1 = 60''.3534 \quad \pm 0''.0117;$$

the value of the other screw was determined by measuring the intervals by means of the first:

$$R_2 = 1.00010 \,.\, R_1.$$

The observatory possesses a good sidereal clock, the rate of which had been carefully determined during four months by means of star transits. In the night of 29—30 August, Mr. B. BERLOTY, a clever observer had observed 20 clock-stars, so that the accuracy of the determination of the clock-error left nothing to be desired.

During the phase observations the object-glass was reduced to 25 mm. by means of a screen of pasteboard. The eye-piece with a power of 30 was provided with a blue glass. The observations of the chords were continued as long as was allowed by the field of view of the eye-piece, which was more than 20′ in diameter. At my signal "top" the moments of the observations were noted by Mr. BELDA, who was seated in front of a mean time standard clock, which before, during, and after, the observations was compared with the sidereal clock; another assistant recorded the micrometer readings.

During the beginning and the end of the eclipse the sky in the neighbourhood of the sun was perfectly clear, so that I could perform the measurements of the chords undisturbed, although now and then I met with difficulties owing to irregularities in the rate of the driving clock. From some minutes before, until after, totality the sun was covered with light clouds, yet the moments of contact could be recorded with sufficient accuracy.

In the derivation of the results I have taken the solar parallax $= 8''.80$; for the rest I have borrowed the constants from the publication "Observatorio Astronomico de Madrid. Memoria sobre el eclipse total de Sol del dia 30 de Agosto de 1905". They are:

Mean radius of the sun	$R_0 = 15'59''.63$	(AUWERS)
,, ,, ,, ,, moon	$r_0 = 15'32''.83$	(KUESTNER and BATTERMANN)
Parallax of the moon	$\pi_0 = 57'\ 2''.68$	

OBSERVATIONS.

First contact: $11^{h}\ 55^{m}\ 39^{s}.1$ (mean time of Greenwich.)

	Length of the chords (corrected for refraction)
11 56 28 .2	294″.93
57 12 .1	390.24
57 35 .2	437 22
58 20 .0	507.74
59 8 .2	566.98
59 38 .9	608.94
12 0 9 .2	642.58
1 25 .0	721.69
2 49 .9	798.82
4 18 .3	876.43
4 57 .0	906.12
5 44 3	935.04
6 15 .9	959.75
6 53 .2	983.94
7 18 .9	1004.93
8 1 .2	1030 37
8 43 .3	1052.50
9 23 .3	1078.17
9 49 .1	1096.89
10 16 .1	1106.16
10 42 .2	1124.37
11 9 .3	1138.90
11 26 .1	1144.49
11 56 .3	1160.37
12 24 .3	1178 82

Second contact: $1^{h}\ 16^{m}\ 13^{s}.2$

Third contact: 1 19 7 .2

	Length of the chords
$2^{h}\ 15^{m}\ 53^{s}.0$	1297″.92

	Length of the chords
h m s	″
2 17 17 .3	1256 94
18 4 .5	1232.27
18 25 .3	1219.81
18 42 .5	1209.51
19 13 .3	1193.25
19 38 .2	1181.49
20 45 .0	1157.42
21 5 .3	1129.77
21 28 .3	1117.78
22 1 .0	1095.75
22 35 .3	1073.82
23 4 .1	1054.40
23 21 .3	1041.52
23 54 .3	1020.90
24 36 .0	993.28
25 2 .2	973.01
25 35 .3	950.47
26 2 .3	920.28
26 29 .3	903.24
26 52 .3	880 81
27 13 .3	863.90
27 36 .2	845.41
28 7 .6	819 14
28 43 .3	779.01
29 5 .3	762.98
29 38 .6	726.38
30 2 .3	697.40
30 22 .3	677.17
30 52 .3	637.13
31 14 .8	610.37
31 40 .6	573.84
32 4 .5	538.62
32 42 .6	480 78
33 3 .3	437.21
33 13 .3	406.92

Fourth contact: 2h 34m 44s .7.

Right ascension of the sun, Aug. 30, 12^h M.T. Gr. $\alpha_{\odot} = 158°10'44''.24$
Declination ,, ,, ,, ,, ,, ,, $\delta_{\odot} = 9° \ 9'33''.19$
Right ascension of the moon ,, ,, ,, $\alpha_{☾} = 157°42'47''.95$
(Hansen-Newcomb).
Declination ,, ,, ,, ,, ,, ,, $\delta_{☾} = 9°53' \ 3''.48$
(Hansen-Newcomb).

Each observation gives an equation of condition for the determination of the corrections Δ of the elements of the sun and moon. Let these corrections be successively

$$\Delta R,\ \Delta r,\ \Delta\alpha_{\odot},\ \Delta\alpha_{☾},\ \Delta\delta_{\odot},\ \Delta\delta_{☾},\ \Delta\pi,$$

then we obtain by comparing the observed distances and chords with those computed the following equations: (the coefficients have been rounded off to two decimals).

EQUATIONS OF THE CHORDS.

I. Observations after the first contact.

										″	Obs.—Comp. ″
+7.98	ΔR	+7.97	Δr	+7.14	$\Delta\alpha_{☾-\odot}$	−3.20	$\Delta\delta_{☾-\odot}$	+1.67	$\Delta\pi =$	+50.71	−10.36
+5.50	,,	+5.49	,,	+4.88	,,	−2.19	,,	+1.12	,,	+36.23	− 5.57
+4.88	,,	+4.87	,,	+4.30	,,	−1.93	,,	+1.01	,,	+37.59	+ 0.70
+4.10	,,	+4.09	,,	+3.56	,,	−1.60	,,	+0.81	,,	+32.40	+ 1.78
+3.58	,,	+3.57	,,	+3.10	,,	−1.39	,,	+0.69	,,	+22.49	− 2.13
+3.34	,,	+3.32	,,	+2.87	,,	−1.29	,,	+0.64	,,	+24.96	+ 0.27
+3.15	,,	+3.13	,,	+2.69	,,	−1.20	,,	+0.59	,,	+22.45	− 0.67
+2.78	,,	+2.76	,,	+2.34	,,	−1.05	,,	+0.51	,,	+19.66	− 0.49
+2.50	,,	+2.48	,,	+2.06	,,	−0.92	,,	+0.43	,,	+16.66	− 1.12
+2.29	,,	+2.26	,,	+1.85	,,	−0.82	,,	+0.38	,,	+20.03	+ 4.06
+2.21	,,	+2.18	,,	+1.76	,,	−0.79	,,	+0.36	,,	+19.60	+ 4.28
+2.13	,,	+2.10	,,	+1.68	,,	−0.75	,,	+0.34	,,	+13.42	− 1.19
+2.08	,,	+2.05	,,	+1.63	,,	−0.73	,,	+0.33	,,	+15.60	+ 1.43
+2.02	,,	+1.99	,,	+1.57	,,	−0.70	,,	+0.31	,,	+14.57	+ 0.47
+1.99	,,	+1.95	,,	+1.53	,,	−0.69	,,	+0.30	,,	+17.85	+ 4.46
+1.94	,,	+1.90	,,	+1.48	,,	−0.66	,,	+0.29	,,	+15.73	+ 2.82
+1.89	,,	+1.85	,,	+1.43	,,	−0.64	,,	+0.27	,,	+11.49	− 0.97
+1.85	,,	+1.81	,,	+1.38	,,	−0.62	,,	+0.26	,,	+12.97	+ 0.87
+1.82	,,	+1.78	,,	+1.35	,,	−0.60	,,	+0.25	,,	+16.44	+ 4.68
+1.80	,,	+1.76	,,	+1.32	,,	−0.59	,,	+0.25	,,	+10.08	− 1.56
+1.77	,,	+1.73	,,	+1.30	,,	−0 58	,,	+0.24	,,	+13.51	+ 1.19
+1.75	,,	+1.71	,,	+1.27	,,	−0.57	,,	+0.24	,,	+12.97	+ 1.77
+1.74	,,	+1.69	,,	+1.26	,,	−0.56	,,	+0.23	,,	+ 9.37	− 1.70
+1.71	,,	+1.67	,,	+1.23	,,	−0.55	,,	+0.22	,,	+10.37	− 0.50
+1.69	,,	+1.65	,,	+1.21	,,	−0.54	,,	+0.22	,,	+12.71	+ 2.06

II. Observations before the last contact.

						Obs.—Comp.
					″	″
+1.52 ΔR	+1.46 Δr	—0.99 Δα (—☉	+0.49 Δδ (—☉	+0.16 Δπ =	— 5.39	+ 0.51
+1.57 „	+1.51 „	—1.05 „	+0.52 „	+0.18 „	— 5.30	+ 0.97
+1.60 „	+1.55 „	—1.09 „	+0.53 „	+0.19 „	— 5.84	+ 0.67
+1.61 „	+1.56 „	—1.10 „	+0.54 „	+0.19 „	— 7.39	— 0.76
+1.62 „	+1.57 „	—1.12 „	+0.55 „	+0.19 „	— 8.59	— 1.88
+1.64 „	+1.59 „	—1.14 „	+0.56 „	+0.20 „	— 8.19	— 1.31
+1.66 „	+1.62 „	—1.16 „	+0.57 „	+0.20 „	— 6.20	+ 0.81
+1.71 „	+1.67 „	—1.23 „	+0.59 „	+0.22 „	[+ 7.95]	—
+1.74 „	+1.70 „	—1.25 „	+0.61 „	+0.22 „	— 2.58	+ 4.99
+1.75 „	+1.71 „	—1.27 „	+0.62 „	+0.23 „	— 5.97	+ 1.72
+1.78 „	+1.74 „	—1.30 „	+0.64 „	+0.24 „	— 7.71	+ 0.22
+1.82 „	+1.78 „	—1.34 „	+0.66 „	+0.25 „	— 7.88	+ 0.29
+1.85 „	+1.81 „	—1.38 „	+0.67 „	+0.25 „	— 8.47	— 0.07
+1.87 „	+1.83 „	—1.40 „	+0.68 „	+0.26 „	— 9.75	— 1.22
+1.91 „	+1.87 „	—1.44 „	+0.70 „	+0.27 „	— 8.05	+ 0.78
+1.96 „	+1.93 „	—1.50 „	+0.73 „	+0.28 „	— 6.19	+ 3.02
+2.00 „	+1.97 „	—1.54 „	+0.75 „	+0.29 „	— 7.13	+ 2.15
+2.05 „	+2.02 „	—1.60 „	+0.78 „	+0.31 „	— 4.88	+ 4.94
+2.10 „	+2 07 „	—1.64 „	+0.80 „	+0.32 „	—13.04	— 2.92
+2.14 „	+2.12 „	—1.69 „	+0.82 „	+0.33 „	— 9.47	+ 0.96
+2.19 „	+2.16 „	—1.74 „	+0.85 „	+0.34 „	—12.56	— 1.80
+2.24 „	+2.21 „	—1.79 „	+0.87 „	+0.35 „	—11.04	+ 0.04
+2 29 „	+2.26 „	—1.84 „	+0.89 „	+0.36 „	—10.50	+ 0.87
+2.36 „	+2.34 „	—1.91 „	+0.93 „	+0.38 „	— 8.40	+ 3.46
+2.46 „	+2.44 „	—2.01 „	+0.98 „	+0.40 „	—14.81	— 2.31
+2.53 „	+2.51 „	—2.08 „	+1.01 „	+0.42 „	— 9.40	+ 3.53
+2.65 „	+2.63 „	—2.20 „	+1.06 „	+0.44 „	—11.28	+ 2.38
+2.74 „	+2.72 „	—2.29 „	+1.11 „	+0.46 „	—14.62	— 0.37
+2.83 „	+2·81 „	—2.37 „	+1.15 „	+0.48 „	—12.33	+ 2.47
+2.98 „	+2.96 „	—2.52 „	+1.22 „	+0.52 „	—16.88	— 1.15
+3.12 „	+3.10 „	—2.65 „	+1.28 „	+0.55 „	—15.37	+ 1.38
+3.29 „	+3.27 „	—2.81 „	+1.36 „	+0.58 „	—18.89	— 1.29
+3.49 „	+3.48 „	—3.00 „	+1.45 „	+0.63 „	—19.50	— 1.52
+3.90 „	+3.89 „	—3.39 „	+1.64 „	+0.71 „	—18.51	+ 2.74
+4.20 „	+4.19 „	—3.67 „	+1.77 „	+0.78 „	—26.71	— 3.86
+4.37 „	+4.34 „	—3.82 „	+1.85 „	+0.81 „	—38.87	—10.28

Equations of the contacts

$$I \quad \Delta R + \Delta r + 0.903\,\Delta\alpha_{(-\odot} - 0.405\,\Delta\delta_{(-\odot} = +\ 3''.78$$

$$II \quad \Delta R - \Delta r - 0.9668\,\Delta\alpha_{(-\odot} - 0.2007\,\Delta\delta_{(-\odot} + $$
$$+ 0.0004\,\Delta^2\alpha_{(-\odot} - 0.0036\,\Delta\alpha\Delta\delta + 0.0091\,\Delta^2\delta_{(-\odot} = -\ 6''.52$$ ¹)

$$III \quad \Delta R - \Delta r + 0.3085\,\Delta\alpha_{(-\odot} - 0.9489\,\Delta\delta_{(-\odot} +$$
$$+ 0.0104\,\Delta^2\alpha_{(-\odot} + 0.0068\,\Delta\alpha\Delta\delta + 0.0012\,\Delta^2\delta_{(-\odot} = +\ 4''.02$$

$$IV \quad \Delta R + \Delta r - 0.889\,\Delta\alpha_{(-\odot} + 0.435\,\Delta\delta_{(-\odot} = -\ 11''.18.$$

A mere glance at the equations derived from the distances of the chords shows the impossibility to derive from them all the unknown quantities. On account of the proportionality of the coefficients we may use one single equation instead of the first 25 equations after the 1st contact; the same for the 35 others. In order to diminish the weight of the observations immediately after the first and before the last contact — when the chord is less sharply defined and varies rapidly — I have formed the two normal equations not according to the method of least squares but simply by addition.

We obtain the following equations:

$$68.1(\Delta R+\Delta r)+56.2\Delta\alpha-25.2\Delta\delta=+489''.46 - 0.35(\Delta R-\angle r) - 12.9\Delta\pi$$
$$-81.6(\Delta R+\Delta r)+65.1\Delta\alpha-31.6\Delta\delta=+397''.87+0.24(\Delta R-\angle r)+12.8\Delta\pi$$

whence:

$$\Delta R + \Delta r = +\ 1''.05 - 0.015\,\Delta\delta - 0.003\,(\Delta R - \Delta r) - 0.16\,\Delta\pi.$$
$$\Delta\alpha = +\ 7''.428 + 0.465\,\Delta\delta - 0.001\,(\Delta R - \Delta r) - 0.02\,\Delta\pi.$$

Neglecting the last terms, we find for the result from the equations derived from the length of the chords:

$$\Delta R + \Delta r = +\ 1''.05 - 0.015\,\Delta\delta_{(-\odot}$$
$$\Delta\alpha_{(-\odot} = +\ 7''.428 + 0.465\,\Delta\delta_{(-\odot}.$$

From the equations of the 2nd and 3rd contact we derive:

$$\Delta\alpha_{(-\odot} = +\ 7''.793 + 0.464\,\Delta\delta_{(-\odot}.$$
$$\Delta\alpha_{(-\odot} = +\ 7''.13 + 0.667\,(\Delta R - \Delta r)$$
$$\Delta\delta_{(-\odot} = -\ 1''.43 + 1.437\,(\Delta R - \Delta r).$$

And lastly the equations of the 1st and 4th contact yield:

$$\Delta\alpha_{(-\odot} = +\ 8''.35 + 0''.468\,\Delta\delta_{(-\odot}$$
$$[\Delta R + \Delta r = -\ 3''.78]$$

The latter result for $\Delta R + \Delta r$, which differs entirely from that found above is little reliable. We can entirely account for it by assuming that the first contact has been observed too late and the last contact too early. It can hardly be doubted that the 1st contact

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¹) It is not allowed (as it is generally done) to neglect the quadratic terms in the equations of the 2nd and 3rd contact, because the corrections $\Delta\alpha$ and $\Delta\delta$, as compared with the distance between the centre of the sun and that of the moon, (in this case 46″) are too large.

is recorded too late because the eclipse began earlier than was expected and in consequence took me by surprise. As an evidence that the time of last contact was given too late there is an instantaneous photograph of the sun (diameter = 10 cm.) taken at the very moment when I gave the signal "top". This plate shows a small impression on the limb of the sun.

To enable me to compare the obtained results, Messrs. TH. WULF and J. D. LUCAS kindly put at my disposal the results of their highly interesting observations of the 2nd and the 3rd contact, made at Tortosa by means of sensitive selenium elements. (See for this Astron. Nachr. N°. 4071). They found:

beginning of totality $1^h\,16^m\,15^s{,}6$
end ,, ,, $1\;\;19\;\;\;6{,}9$,

which yield the following equations:

$$\left.\begin{aligned}\Delta R - \Delta r - 0.9650\,\Delta\alpha_{(-\odot} - 0.2117\,\Delta\delta_{(-\odot} + 0.0004\,\Delta^2\alpha_{(-\odot} - {}&\\ - 0.0039\,\Delta\alpha\,\Delta\delta + 0.0092\,\Delta^2\delta_{(-\odot} = -\,5''.73&\\ \Delta R - \Delta r + 0.3063\,\Delta\alpha_{(-\odot} - 0.9493\,\Delta\delta_{(-\odot} + 0.0105\,\Delta^2\alpha_{(-\odot} + {}&\\ + 0.0069\,\Delta\alpha\,\Delta\delta + 0.0012\,\Delta^2\delta_{(-\odot} = +\,4''.10&\end{aligned}\right\}\quad (A)$$

whence

$$\Delta\alpha_{(-\odot} = +\,6''.42 + 0.653\,(\Delta R - \Delta r)$$
$$\Delta\delta_{(-\odot} = -\,1''.76 + 1.404\,(\Delta R - \Delta r).$$

When we subtract the two equations A from each other we get:

$$\Delta\alpha_{(-\odot} = +\,7''.238 + 0.465\,\Delta\delta_{(-\odot}\,,$$

which agrees exceedingly well with the result of the chord equations $\Delta\alpha = +\,7''.428 + 0.465\,\Delta\delta$; but it also appears that it is impossible to determine $\Delta\alpha$, $\Delta\delta$ and $\Delta R - \Delta r$ separately from the combination of the contact and chord equations.

In the derivation of the final result we have accorded the same weight = 1 to the results of the chord measurements and to those of the contact determinations made by WULF—LUCAS, and the weight $\frac{1}{2}$ to my observations of the 2nd and 3rd contact. Thus we find, leaving out of account the first and the fourth contact:

$$\Delta R + \Delta r = +\,1''.07 - 0.02\,(\Delta R - \Delta r)$$
$$\Delta\alpha_{(-\odot} = +\,6''.66 + 0.66\,(\Delta R - \Delta r)$$
$$\Delta\delta_{(-\odot} = -\,1''.65 + 1.42\,(\Delta R - \Delta r).$$

The last column of the chord equations contains the deviations in the sense of observation — computation, which remain when we substitute these numerical values. The mean error of the first 25 observations (excluding the first) amounts to ± 2."53; that of the last 35 (excluding the last) is ± 2."21.

Chemistry. — "*On the osmotic pressure of solutions of non-electrolytes, in connection with the deviations from the laws of ideal gases.*" By J. J. van Laar. (Communicated by Prof. H. W. Bakhuis Roozeboom.)

Communicated in the meeting of April 27, 1906).

1. By H. N. Morse and J. C. W. Frazer [1]) very accurate experiments were recently made on the determination of the osmotic pressure of *dilute* sugar solutions in water. The solutions had a concentration up to 1-normal, and as c is then about $^1/_{34}$ [the association factor of the water is viz. at 18° C. about 1,65, so that in 1 L. of water about $55,6 : 1,65 = 34$ Gr.mol. of water (simple and complex molecules) are present], the difference between the exact expression $-log\,(1-x)$ and the approximate value x [formula (2)] is not yet appreciable. It is however not so with the difference between the molecular volume of the *solution* $v = (1-x)\,v_1 + xv_2$ (v supposed to be a linear function of x, about which more presently) and the molecular volume of the *solvent* v_1, when v_2 (the molecular volume of the dissolved sugar) cannot be put equal to v_1. We shall see that this difference for 1-normal solutions amounts to $19\,^0/_0$, so that by means of the experiments we can very well ascertain, if we have to make use of v or of v_1. And these have really taught us, that the osmotic pressures measured agree (and even with very great accuracy) with the calculated values, *only* when v_1 is put in the numerator, and not v. This harmonizes therefore perfectly with what I have repeatedly asserted since 1894 [2]). (What I have called above v_1 for the sake of symmetry, was formerly always indicated by v_0). *Not* the molecular volume therefore of the whole solution, but the *molecular* volume of the *solvent in* the solution. And this deprives those of their last support, who in spite of all evidence (for not the dissolved substance, but the *solvent* brings about that pressure) persist in trying to explain the osmotic pressure by a pressure of the molecules of the dissolved substance comparable with the *gas pressure*. If such a thing could be thought of, v should be taken into consideration and not v_1, for the molecules of the dissolved substance move in the *whole* volume v and not in the volume v_1, which is perfectly fictitious with regard

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[1]) Amer. Chem. Journ. **34**, 1905, p. 1—99. See also the extensive abstract N⁰ 274 in the Phys. Chem. Centralblatt III (1906).

[2]) See inter alia my previous paper on this subject in These Proceedings, May 27, 1905, p. 49. (Some remarks on Dr. Ph. Kohnstamm's last papers).

to the *solution,* which would be equal to v only when v_2 happened to be equal to v_1.

2. In order to compare the results, found by MORSE and FRAZER, more closely with those for the osmotic pressure already given by me in 1894, we shall return to its derivation for a moment, chiefly in order to ascertain on what limiting suppositions this formula holds.

With equilibrium between the pure solvent (concentration 0, pressure p_0) and the *solvent* in the solution (concentration c, pressure p) [the dissolved substance is nowhere in equilibrium, for it is supposed that there is a membrane impenetrable to it] the molecular thermodynamic potentials must have the same value. Hence [1]:

$$\mu_1 (x, p) = \mu_1 (0, p_0) .$$

Now in general:

$$\mu_1 = \frac{\partial Z}{\partial n_1} = C_1 - \theta_1 + RT \log c_1 ,$$

when $C_1 = -k_1 T \ (\log T - 1) + ((e_1)_0 - T(s_1)_0),\ c_1 = \frac{n_1}{\Sigma n_1}$ and $\theta_1 = \frac{\partial \Theta}{\partial n_1}$; Θ being given by

$$\Theta = \int pdv - pv - RT \, \Sigma \, n_1 \, . \log \Sigma \, n_1 \, .$$

For *binary* mixtures of *normal* substances we may now introduce the variable x and we obtain (Σn_1 is now $= 1$, so that the term with $\log \Sigma n_1$ vanishes), as may be supposed as known:

$$\underline{\mu_1 = C_1 - \left(\omega - x \frac{\partial \omega}{\partial x}\right) + p \left(v - x \frac{\partial v}{\partial x}\right) + RT \log (1 - x)} , \quad . \ (1)$$

when ω is written for $\int pdv$ by way of abbreviation.

This expression is *perfectly accurate* for the above mentioned mixtures. For the further calculation we now introduce the idea "*ideal*" mixtures. They are such as for which the *influence* of the two components *inter se* may be neglected. Then $\frac{\partial^2 \omega}{\partial x^2} = 0$, and ω becomes a *linear* function of x. But also $\frac{\partial^2 v}{\partial x^2} = 0$, so that v becomes

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[1] The following derivation is only different in form from the cited one in these Proceedings.

also a linear function of x. We shall further demonstrate this in § 6, and show that in the case of such mixtures:

$$\left\{\begin{array}{ll} a. & \omega \text{ is a linear function of } x \\ b. & v \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \\ c. & \frac{a}{b} \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \\ d. & \text{the heat of mixing is} = 0, \end{array}\right.$$

so that we may say: ideal mixtures are such *for which the heat of mixing is practically* $= 0$, or *with which no appreciable contraction of volume takes place,* when $1-x$ Gr.mol. of one component is mixed with x Gr.mol. of the second.

The conditions a, b, c and d are *simultaneously* fulfilled, when the *critical pressures* of the two components are by approximation of the *same* value.

3. For $\omega - x\frac{\partial\omega}{\partial x}$ we may now write ω_1, as $\omega = (1-x)\,\omega_1 + x\,\omega_2$, when $\frac{\partial^2\omega}{\partial x^2} = 0$. $\left[\text{Otherwise evidently } \omega - x\frac{\partial\omega}{\partial x} = \omega_1 - {}^1\!/_2 x^2\left(\frac{\partial^2\omega}{\partial x^2}\right)_1 - {}^1\!/_3\, x^3\left(\frac{\partial^3\omega}{\partial x^3}\right)_1 - \ldots\right]$ In the same way $v - x\frac{\partial v}{\partial x} = v_1$, and we get:

$$\left.\begin{array}{l} \mu_1(x,p) = C_1 - \omega_1 + pv_1 + RT\,log\,(1-x) \\ \mu_1(o,p_0) = C_1 - \omega_1 + p_0v_1 \end{array}\right\},$$

always when v_1 and ω_1 are supposed to be *independent* of the *pressure.* For else ω_1 and v_1 would have another value at the pressure p than at the pressure p_0. We must therefore also suppose that our liquids are *incompressible.* But there is not the slightest objection to this supposition for ordinary liquids far from the critical temperature (and there is only question of such liquids in discussions on the osmotic pressure). Only when x draws near to 1, and so the osmotic pressure would approach to ∞, v_1 (and so also ω_1) must no longer be supposed to be independent of p.

By equating these two last equations, we get:

$$pv_1 + RT\,log\,(1-x) = p_0v_1,$$

hence

$$\underline{\pi = p - p_0 = \frac{RT}{v_1}\left(-\log\left(1 - x\right)\right)} \quad , \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the expression already derived by me in 1894. 1)

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1) Cf. Z. f. Ph. Ch. **15**, 1894; Arch. Teyler 1898; Lehrbuch der math. Chemie, 1901; Arch. Teyler 1903; Chem. Weekbl. 1905, N⁰. 9; These Proceedings, June 21, 1905.

In the original Dutch paper another note followed, which Mr. VAN LAAR has replaced by the following in the English translation.

A conversation with Dr. KOHNSTAMM suggested the following observations to me. Dr. KOHNSTAMM finds (These Proceedings, May 27, 1905) the quantity $v - x\frac{db}{dx}$ in the denominator of the expression for π. This is quite correct, and harmonizes perfectly with the general expression, which according to equation (1) on p. 54, would also have been found by me for non-linear variability of v.

Then we should viz. have:

$$p\left(v - x\frac{\partial v}{\partial x}\right)_p - p_0\,(v_1)_{p_0} = -RT\log\left(1 - x\right) + \left(\omega - x\frac{\partial \omega}{\partial x}\right)_p - (\omega_1)_{p_0},$$

where, when calculating $\omega - x\frac{\partial \omega}{\partial x}$ by means of VAN DER WAALS' equation of state, also a term $-px\frac{\partial\,(v-b)}{\partial x}$ appears, in consequence of which $p\left(v - x\frac{db}{dx}\right)$ occurs in the first member.

Now it is of no importance whether v is diminished by $x\frac{\partial v}{\partial x}$ or by $x\frac{db}{dx}$, as $p\frac{\partial\,(v-b)}{\partial x}$ approaches to 0 both for small and for very large values of p. I therefore obtained a correction term in the denominator, *in connection with the size of the molecules* of exactly the same value as Dr. KOHNSTAMM. That this did not always clearly appear in my previous papers, is due to the fact that I then always introduced the approximation $v - x\frac{\partial v}{\partial x} = v_1$, which was perfectly justifiable for my purpose.

For as $v - x\frac{\partial v}{\partial x} = v_1 - \frac{1}{2}x^2\left(\frac{\partial^2 v}{\partial x^2}\right)_1$ — etc., this is sufficiently accurate for practical purposes. (for ideal mixtures, where v is a linear function of x, it is of course *quite* accurate).

Yet in a so early paper as the one cited by K. of 1894 (Z. f. Ph. Ch. **15**, p. 464) it is clearly to be seen that the result obtained by me agrees perfectly with his. For it says (line 4 from the top) that $v_{a'}$ (the index a' is there always used for the liquid phase) $= \frac{\partial v}{\partial n_{a'}}$. But this is in the x-notation nothing but $v - x\frac{\partial v}{\partial x}$, the physical meaning of which is: the molecular volume of the water in the solution with the concentration x.

The phrase occurring on page 466: "und niemals etwa $v_{a'} - b$ im Sinne etc." refers there to the well-known attempts of EWAN and others. The same is the case with the phrase in the paper on non-diluted solutions in the Ch. Weekblad of June 7th 1905: "Ook heeft men getracht, etc." (p. 5).

We repeat once more: this expression holds from $x=0$ to $x=$ near 1, when the following conditions are satisfied:

a. the solution is an *ideal binary* mixture of *normal* components;
b. the solution is practically *incompressible.*

Then (2) represents the *additional pressure* on the *solution*, in order to repel the penetrating water (the so-called *"osmotic"* pressure).

As however in all the experiments made up to now *water* was the solvent, hence an *anomalous* substance, (2) must not be applied to solutions in water without reservation. It is, however, easy to show that the influence of the association does not play a part before the term with x^2 (just as the influence of the two components inter se), so that in the above experiments, where x^2 may undoubtedly be neglected (cf. § 1), formula (2) may certainly be used.

Let us, however, first reduce it to a form more practical for use.

4. Let us write (2) for this purpose:

$$\underline{\pi = \frac{RT}{v_1}(x + {}^1/_2\, x^2 + \ldots) = \frac{RT}{v_1}\, x\,(1 + \tfrac{1}{2}\, x)}, \quad . \quad . \quad . \quad (2a)$$

which is more than sufficient for solutions up to 1-normal. Let us further assume that c Gr. mol. are dissolved in 1000 Gr. H_2O (called by Morse and Frazer "weight-normal solutions"), then:

$$x = \frac{c}{34 + c} = \frac{c'}{1 + c'},$$

when we put ${}^1/_{34}\, c = c'$ ($34 = 55{,}6 : 1{,}65$ is the number of Gr. mol. H_2O in 1000 Gr. at 18° C; cf. § 1).

We find then:

$$\pi = \frac{RT}{v_1}\,\frac{c'}{1 + c'}\left(1 + {}^1/_2\,\frac{c'}{1 + c'}\right),$$

or when we restrict ourselves to terms of the second degree with respect to c':

$$\pi = \frac{RT}{v_1}\, c'\,(1 - {}^1/_2\, c') = \frac{RT}{v_1}\,\frac{c}{34}\,(1 - {}^1/_{68}\, c).$$

In this $R = 82{,}13$ (c.c.M., Atm.), and $v_1 = 1001{,}4 : 34$ cM^3 at 18°. For $\dfrac{RT}{34\, v_1}$ we therefore find at 18° C.:

$$\frac{RT}{34 v_1} = \frac{82{,}13 \times 291{,}04}{1001{,}4} = 23{,}87,$$

hence

$$\underline{\pi_{18^\circ} = 23{,}87\, c\,(1 - 0{,}015\, c)\ \text{Atm.}} \quad . \quad . \quad . \quad . \quad (2b)$$

We see from the calculation, as we already observed above, that the influence of the association of the solvent is only appreciable in the term with c^2. If water were a normal liquid, we should have had $^1/_{111}\, c$ instead of $^1/_{68}\, c = 0{,}015\, c$. ($\frac{1}{2}\, c'$ would then be $= {^1/_2} \times {^1/_{55,6}}\, c$).

Let us now consider what the last expression would have become for π_{18°, when not v_1 had occurred in the denominator, but the molecular volume of the solution v.

When c Gr. mol. are dissolved in 1000 Gr. H_2O, then the total volume will be (at 18°) $1001{,}4 + 190\, c$ ccM. [For 1 Gr. mol. $= 342{,}2$ Gr. of melted sugar occupies a volume of 190 ccM. at 18° (density $= 1{,}8$)].

Altogether there are now $34 + c$ Gr. mol., hence the molecular volume of the solution will be:

$$v = \frac{1001{,}4 + 190\, c}{34 + c} = \frac{1001{,}4}{34}\;\frac{1 + 0{,}19\, c}{1 + 0{,}03\, c}.$$

For v_1 we found however above:

$$v_1 = \frac{1001{,}4}{34},$$

so that the value of π_{18° with v in the denominator instead of v_1 would have become:

$$\pi_{18^\circ} = 23{,}87\, c\,(1 - 0{,}015\, c) \times \frac{1 + 0{,}03\, c}{1 + 0{,}19\, c}\ \text{Atm.},$$

i. e.

$$\pi_{18^\circ} = 23{,}87\, c\, \frac{1 + 0{,}015\, c}{1 + 0{,}19\, c}\ \text{Atm.}$$

For (weight)normal solutions ($c = 1$) we should therefore have found instead of $\pi_{18^\circ} = 23{,}87\ (1 - 0{,}015) = \underline{23{,}51}$ Atm., π_{18° $= 23{,}87 \times \dfrac{1{,}015}{1{,}19} = \underline{20{,}36}$ Atm.

Now MORSE and FRAZER found 24,52 Atm., which is considerably nearer the theoretical value 23,51 Atm. (with v_1 in the denominator) than near the inaccurate expression with v in the denominator [1]).

So it is out of the question that the molecules of the dissolved substance should exert a certain pressure comparable with the gas-pressure, for then the volume of the *solution as such*, viz. v, would have to be taken into account, and not the in that solution perfectly fictitious molecular volume of the solvent v_1.

5. But there is more. We shall viz. derive the expression for the pressure which *would* be exerted by the dissolved molecules,

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[1]) With 0,5-normal the two values would have been 11,85 and 10,98 Atm., whereas 12,08 Atm. has been found experimentally.

when they, according to the inaccurate interpretation of the osmotic pressure, could move free and undisturbed throughout the space of the solution.

VAN DER WAALS' equation of state, viz.

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

gives for the rarefied gas-state:

$$p = \frac{RT}{v}\left[\frac{v}{v-b} - \frac{a:RT}{v}\right] = \frac{RT}{v}\left(1 + \frac{b}{v} - \frac{a:RT}{v}\right),$$

when we again content ourselves with terms of the degree $\frac{1}{v^2}$.

Let us now write:

$$\frac{a}{RT} - b = \gamma,$$

then

$$p = \frac{RT}{v}\left(1 - \frac{\gamma}{v}\right),$$

where v now represents the volume, in which 1 Gr. mol. of the *dissolved substance* moves. This volume is however evidently (cf. also § 4):

$$v = \frac{1001{,}4 + 190\,c}{c},$$

or

$$v = \frac{1001{,}4}{c}(1 + 0{,}19\,c),$$

so that we get:

$$p = \frac{RT\,c}{1001{,}4\,(1 + 0{,}19\,c)}\left(1 - \frac{\gamma\,c}{1001{,}4\,(1 + 0{,}19\,c)}\right),$$

or as $\frac{RT}{1001{,}4} = 23{,}87$ is (c.f. § 4), and with $\gamma' = \frac{\gamma}{1001{,}4}$:

$$p = 23{,}87\,c\,\frac{1 - \gamma'\,c}{1 + 0{,}19\,c}\,Atm., \quad \ldots\ldots \quad (3)$$

and this is an altogether different expression from (2^b). Not only is v_1 replaced by v (which gives rise to the factor $1 + 0{,}19\,c$), but we also find $1 - \gamma'\,c$ instead of $1 - 0{,}015\,c$. In this γ' is *different for every dissolved substance*, dependent on the values of a and b, whereas the coefficient 0,015 has *the same value* for all substances dissolved in water, *independent of the nature of the dissolved substance* (c.f. § 4). Also the coefficient 0,19 depends on the dissolved substance on its molecular volume). Moreover γ' depends also on T on account of $a : RT$. Except with H_2, where γ is negative at the ordinary temperature, γ is everywhere *positive*. But at higher temperatures its value is reversed, and becomes negative.

So, when comparing (2^b) and (3), we see clearly, that it is out of the question that the so-called osmotic pressure should follow the gas laws. Only with $c = 0$ this would be the case, but for all other values of c the deviation for the osmotic pressure is *altogether different* from that for the gas pressure. This is still more clearly pronounced, when we compare the original formulae. For the osmotic pressure viz. the equation

$$\pi = \frac{RT}{v_1}(-\log(1-x)) = \frac{RT}{v_1}x\left(1 + {}^1/_2\, x^2 + \ldots\right)$$

holds; for the gas pressure on the other hand:

$$p = \frac{RT}{v}\left(1 - \frac{\gamma}{v}\right),$$

so that the deviations from the gas laws (at the ordinary temperatures) are even in *opposite sense* from the deviations of the osmotic pressure for non-diluted solutions.

In view of these facts it is in my opinion no longer possible to uphold the old conception of the osmotic pressure as arising in consequence of a pressure of the molecules of the *dissolved substance* comparable with the *gas pressure*. The molecules of the dissolved substance have nothing to do with the osmotic pressure except in so far as they reduce the *water* in the solutions to *another state of concentration* (*less concentrated*), which causes the pure water (concentration 1) to move towards the water in the solution (concentration $1-x$) in consequence of the *impulse of diffusion*. On account of this a *current*, of which the *equivalent of pressure* $= \frac{RT}{v_1}(-\log(1-x))$, arises in the transition layer near the semi-permeable membrane, which current can only be checked by a *counterpressure on the solution* of equal value: the so-called *osmotic* pressure.

This is in my opinion the *only correct* interpretation of the osmotic pressure.

As I already observed on former occasions, we might just as well speak of an "osmotic" *temperature*, when the impulse of diffusion is not checked by pressure on the solution, but by *cooling* it. For at different temperatures the temperature functions C_1 (cf § 2) are no longer the same in the two members of

$$\mu_1(x, T) = \mu_1(o, T_0),$$

whereas the terms pv are now the same. In this case T would have to be $< T_0$, because the temperature exerts an opposite influence on the change of μ from the pressure.

In consequence of the term $RT \, log \, (1 - x)$, $\mu_1 (x)$ will be $< \mu_1 (o)$. μ_1 must therefore be increased. Now $\frac{\partial \mu_1}{\partial p} = v_1$, hence *positive*, whereas $\frac{\partial}{\partial T}\left(\frac{\mu_1}{T}\right) = -(e_1 + pv_1)$, so *negative*. So the value of $\mu_1 (x)$, which is too small in consequence of x, can again be made equal to that of $\mu_1 (o)$, either by *increase of pressure* ("osmotic" pressure), or by *lowering of the temperature* ("osmotic" temperature).

It would, however, be advisable to banish the idea "osmotic pressure" altogether from theoretical chemistry, and only speak of it, when such differences of pressure are actually met with in case of semi-permeable walls (cell-walls, and such like).

6. *Appendix. Proof of some properties, mentioned in* § 2.

a. In a previous paper in these Proceedings (April 1905) I derived for $\frac{\partial v}{\partial x}$ the perfectly accurate expression [equation (4), p. 651]:

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

With $\frac{db}{dx} = \beta$ and $\frac{da}{dx} = 2\alpha \sqrt{a}$, in which $\beta = b_2 - b_1$ and $\alpha = \sqrt{a_2} - \sqrt{a_1}$, this becomes:

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

And now we see at once, that this passes into β or $\frac{db}{dx}$, when

$$\underline{\beta \sqrt{a} = \alpha v},$$

For then $\frac{\alpha\sqrt{a}}{\beta}$ in the numerator becomes equal to $^a/_v$ in the denominator. But when $\frac{\partial v}{\partial x} = \frac{db}{dx}$, then also $\frac{\partial^2 v}{\partial x^2} = 0$, as $\frac{d^2 b}{dx^2} = 0$, and v is a *linear* function of x.

[We above derived the condition $\beta\sqrt{a}=av$ from the general expression for $\frac{\partial v}{\partial x}$. If we knew this condition beforehand, $\frac{\partial v}{\partial x}=\frac{db}{dx}$ would immediately follow from this by differentiation, and then it would not be necessary to start from the general expression for $\left.\frac{\partial v}{\partial x}\right]$.

b. On p. 651 [equation (5)] of the paper cited the perfectly general expression:

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

was derived for $\frac{\partial^2\Theta}{\partial x^2}$, which becomes therefore $=0$, when again $\beta\sqrt{a}=av$. Now $\Theta=\int pdv-pv=\omega-pv$. And as $\frac{\partial^2\Theta}{\partial x^2}$ and $\frac{\partial^2 v}{\partial x^2}$ are both $=0$ when $av=\beta\sqrt{a}$, also $\frac{\partial^2\omega}{\partial x^2}$ will be $=0$, in other words ω is a *linear* function of x.

c. The heat of dilution. It is given by the formula

$$L_x=-T^2\frac{\partial}{\partial T}\left[\frac{\mu_1(x)}{T}-\frac{\mu_1(o)}{T}\right].$$

This is viz. the so-called *differential* heat of dilution per Gr. mol. of the solvent when dn Gr. mol. solvent $\left(x=\frac{m}{m+n}\right)$ are added to a solution consisting of m Gr. mol. dissolved substance and n Gr. mol. solvent.

This becomes [see equation (1)]:

$$L_x=-T^2\frac{\partial}{\partial T}\left[\frac{1}{T}\left\{-\left(\omega-x\frac{\partial\omega}{\partial x}\right)+p\left(v-x\frac{\partial v}{\partial x}\right)+\omega_1-pv_1\right\}\right].$$

If $\frac{\partial^2\omega}{\partial x^2}=0$, then $\omega-x\frac{\partial\omega}{\partial x}=\omega_1$; and $v-x\frac{\partial v}{\partial x}$ will be $=v_1$, when $\frac{\partial^2 v}{\partial x^2}=0$. But then $L_x=0$. q. e. d.

And hence also the *total heat of mixing* will be $=0$, when x Gr. mol. of the 2nd component are mixed with $1-x$ Gr. mol. of the 1st component.

d. The peculiarities mentioned in § 2 under *a, b* and *d,* which characterize the so-called *ideal* mixtures, are therefore *all* satisfied when

$$\underline{\beta\sqrt{a} = \alpha v.}$$

This yields:

$$\beta\left[\sqrt{a_1} + x\alpha\right] = \alpha\left[b_1 + x\beta\right],$$

when it is permissible — for liquids far from the critical temperature — to replace v by b. Hence we get:

$$\beta\sqrt{a_1} = \alpha b_1,$$

or

$$(b_2 - b_1)\sqrt{a_1} = (\sqrt{a_2} - \sqrt{a_1})\, b_1,$$

or also

$$b_2\sqrt{a_1} = b_1\sqrt{a_2},$$

hence

$$\frac{\sqrt{a_1}}{b_1} = \frac{\sqrt{a_2}}{b_2},$$

from which we see, that the case of *ideal* mixtures occurs, when the *critical pressures* of the components have the *same* value.

e. Finally

$$\frac{\partial^2}{\partial x^2}\left(\frac{a}{b}\right) = \frac{2\,(b_2\sqrt{a_1} - b_1\sqrt{a_2})^2}{b^3},$$

so we see that also $\frac{a}{b}$ will be a linear function of x, when $b_2\sqrt{a_1} = b_1\sqrt{a_2}$ or $p_1 = p_2$. In this way also c of § 2 has been proved.

(June 21, 1906).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday June 30, 1906.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 30 Juni 1906, Dl. XV).

CONTENTS.

Mathematics. — *"Polydimensional Vectordistributions".* [1]) By L. E. J. Brouwer. (Communicated by Prof. D. J. Korteweg.)

Let us call the plane space in which to operate S_n; we suppose in it a rectangular system of coordinates in which a C_p represents a coordinatespace of p dimensions. Let a ${}^pX$-distribution be given in S_n; i.e. let in each point of S_n a p-dimensional system of vectors be given. By $X_{\alpha_1 \alpha_2 \ldots \alpha_p}$ we understand the vector component parallel to C_p indicated by the indices, whilst as positive sense is assumed the one corresponding to the indicatrix indicated by the sequence of the indices. By interchanging two of the indices the sense of the indicatrix changes, hence the sign of the vectorcomponent.

Theorem 1. The integral of ${}^pX$ in S_n over an arbitrary curved bilateral closed S_p is equal to the integral of ${}^{p+1}Y$ over an arbitrary curved S_{p+1}, enclosed by S_p as a boundary, in which ${}^{p+1}Y$ is determined by

$$Y_{\alpha_1 \alpha_2 \ldots \alpha_p \alpha_{p+1}} = \sum_{\alpha_{q_1}=\alpha_1,\alpha_2,\ldots \alpha_{p+1}} \frac{\partial X_{\alpha_{q_2} \alpha_{q_3} \ldots \alpha_{q_{p+1}}}}{\partial x_{\alpha_{q_1}}},$$

where for each of the terms of the second member the indicatrix $(\alpha_{q_1} \alpha_{q_2} \ldots \alpha_{q_p} \alpha_{q_{p+1}})$ has the same sense as $(\alpha_1 \alpha_2 \ldots \alpha_{p+1})$. We call the vector Y the *first derivative* of ${}^pX$.

Proof. We suppose the limited space S_{p+1} to be provided with curvilinear coordinates $u_1 \ldots u_{p+1}$ determined as intersection of curved C_p's, i. e. curved coordinatespaces of p-dimensions. We suppose the system of curvilinear coordinates to be inside the boundary without singularities and the boundary with respect to those coordinates to be everywhere convex.

The integral element of ${}^{p+1}Y$ becomes when expressed in differential quotients of ${}^pX$:

$$\sum_{Y_{\alpha_1 \ldots \alpha_{p+1}}} \sum_{\alpha_{q_1}=\alpha_1 \ldots \alpha_{p+1}} \frac{\partial X_{\alpha_{q_2} \ldots \alpha_{q_{p+1}}}}{\partial x_{\alpha_{q_1}}} \begin{vmatrix} \frac{\partial x_{\alpha_1}}{\partial u_1} & \cdots\cdots & \frac{\partial x_{\alpha_{p+1}}}{\partial u_1} \\ \vdots & & \vdots \\ \frac{\partial x_{\alpha_1}}{\partial u_{p+1}} & \cdots\cdots & \frac{\partial x_{\alpha_{p+1}}}{\partial u_{p+1}} \end{vmatrix} du_1 \ldots du_{p+1}.$$

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[1]) The Dutch original contains a few errors (see Erratum at the end of Verslagen 31 Juni 1906), which have been rectified in this translation.

We now unite all terms containing one of the components of ${}^pX$, e. g. $X_{123\ldots p}$. We then find:

$$\frac{\partial X_{123\ldots p}}{\partial x_{p+1}} \begin{vmatrix} \frac{\partial x_{p+1}}{\partial u_1} & \frac{\partial x_1}{\partial u_1} & \cdots\cdots & \frac{\partial x_p}{\partial u_1} \\ \vdots & \vdots & & \vdots \\ \frac{\partial x_{p+1}}{\partial u_{p+1}} & \frac{\partial x_1}{\partial u_{p+1}} & \cdots\cdots & \frac{\partial x_p}{\partial u_{p+1}} \end{vmatrix} du_1 \ldots du_{p+1} +$$

$$+ \frac{\partial X_{123\ldots p}}{\partial x_{p+2}} \begin{vmatrix} \frac{\partial x_{p+2}}{\partial u_1} & \frac{\partial x_1}{\partial u_1} & \cdots\cdots & \frac{\partial x_p}{\partial u_1} \\ \vdots & \vdots & & \vdots \\ \frac{\partial x_{p+2}}{\partial u_{p+1}} & \frac{\partial x_1}{\partial u_{p+1}} & \cdots\cdots & \frac{\partial x_p}{\partial u_{p+1}} \end{vmatrix} du_1 \ldots du_{p+1} +$$

$$+ \ldots (n - p \text{ terms}).$$

If we add to these the following terms with the value 0:

$$\frac{\partial X_{123\ldots p}}{\partial x_1} \begin{vmatrix} \frac{\partial x_1}{\partial u_1} & \frac{\partial x_1}{\partial u_1} & \cdots\cdots & \frac{\partial x_p}{\partial u_1} \\ \vdots & \vdots & & \vdots \\ \frac{\partial x_1}{\partial u_{p+1}} & \frac{\partial x_1}{\partial u_{p+1}} & \cdots\cdots & \frac{\partial x_p}{\partial u_{p+1}} \end{vmatrix} du_1 \ldots du_{p+1} +$$

$$+ \frac{\partial X_{123\ldots p}}{\partial x_2} \begin{vmatrix} \frac{\partial x_2}{\partial u_1} & \frac{\partial x_1}{\partial u_1} & \cdots\cdots & \frac{\partial x_p}{\partial u_1} \\ \vdots & \vdots & & \vdots \\ \frac{\partial x_2}{\partial u_{p+1}} & \frac{\partial x_1}{\partial u_{p+1}} & \cdots\cdots & \frac{\partial x_p}{\partial u_{p+1}} \end{vmatrix} du_1 \ldots du_{p+1} +$$

$$+ \ldots (p \text{ terms}),$$

the n-terms can be summed up as:

$$\begin{vmatrix} \frac{\partial X_{123\ldots p}}{\partial u_1} du_1 & \frac{\partial x_1}{\partial u_1} du_1 & \cdots\cdots & \frac{\partial x_p}{\partial u_1} du_1 \\ \vdots & \vdots & & \vdots \\ \frac{\partial X_{123\ldots p}}{\partial u_{p+1}} du_{p+1} & \frac{\partial x_1}{\partial u_{p+1}} du_{p+1} & \cdots\cdots & \frac{\partial x_p}{\partial u_{p+1}} du_{p+1} \end{vmatrix}$$

Let us suppose this determinant to be developed according to the first column, let us then integrate partially each of the terms of the development according to the differential quotient of $X_{123\ldots p}$, appearing in it; there will remain under the $(p+1)$-fold integration sign $p\,(p+1)$ terms neutralizing each other two by two. Thus for instance:

$$du_1 \;.\;.\;.\; du_{p+1} \begin{vmatrix} & \frac{\partial^2 x_1}{\partial u_1 \partial u_{p+1}} & \cdots\cdots & \frac{\partial^2 x_p}{\partial u_1 \partial u_{p+1}} \\ & \frac{\partial x_1}{\partial u_2} & \cdots\cdots & \frac{\partial x_p}{\partial u_2} \\ & \vdots & & \vdots \\ & \frac{\partial x_1}{\partial u_p} & \cdots\cdots & \frac{\partial x_p}{\partial u_p} \\ X_{123\ldots p} & & & \end{vmatrix}$$

$$\text{and } du_1 \;.\;.\;.\; du_{p+1} \begin{vmatrix} X_{123\ldots p} & & & \\ & \frac{\partial x_1}{\partial u_2} & \cdots\cdots & \frac{\partial x_p}{\partial u_2} \\ & \vdots & & \vdots \\ & \frac{\partial x_1}{\partial u_p} & \cdots\cdots & \frac{\partial x_p}{\partial u_p} \\ & \frac{\partial^2 x_1}{\partial u_1 \partial u_{p+1}} & \cdots\cdots & \frac{\partial^2 x_p}{\partial u_1 \partial u_{p+1}} \end{vmatrix},$$

as they transform themselves into one another by interchangement of two rows of the matrix-determinant.

So the p-fold integral remains only, giving under the integration sign

$$X_{123\ldots p} \begin{vmatrix} \pm 1 & \frac{\partial x_1}{\partial u_1} du_1 & \cdots\cdots & \frac{\partial x_p}{\partial u_1} du_1 \\ \vdots & \vdots & & \vdots \\ \pm 1 & \frac{\partial x_1}{\partial u_{p+1}} du_{p+1} & \cdots & \frac{\partial x_p}{\partial u_{p+1}} du_{p+1} \end{vmatrix}$$

to be integrated over the boundary, whilst in a definite point of that boundary the h^{th} term of the first column gets the sign $+$ when for the coordinate u_p the point lies on the positive side of the boundary.

Let us now find the integral of $X_{123\ldots p}$ over the boundary and let us for the moment suppose ourselves on the part of it lying for all

u's on the positive side. The indicatrix is in the sense $u_1\, u_2 \ldots u_{p+1}$ and if we integrate $X_{123\ldots p}$ successively over the components of the elements of boundary according to the curved C_p's we find:

$$\sum \int X_{123\ldots p} \begin{vmatrix} \frac{\partial x_1}{\partial u_{\alpha_1}} du_{\alpha_1} & \cdots\cdots & \frac{\partial x_p}{\partial u_{\alpha_1}} du_{\alpha_1} \\ \vdots & & \vdots \\ \frac{\partial x_1}{\partial u_{\alpha_p}} du_{\alpha_p} & \cdots\cdots & \frac{\partial x_p}{\partial u_{\alpha_p}} du_{\alpha_p} \end{vmatrix} .$$

where $(\alpha_{p+1}\, \alpha_1 \ldots \alpha_p) = (1\, 2\, 3 \ldots p\, (p+1))$; so that we can write as well

$$\sum_{q=1,2\ldots(p+1)} \int X_{123\ldots p} \left| \begin{array}{ccc} \frac{\partial x_1}{\partial u_1} du_1 & \cdots\cdots & \frac{\partial x_p}{\partial u_1} du_1 \\ \vdots & & \vdots \\ \frac{\partial x_1}{\partial u_{q-1}} du_{q-1} & \cdots & \frac{\partial x_p}{\partial u_{q-1}} du_{q-1} \\ \hline \frac{\partial x_1}{\partial u_{q+1}} du_{q+1} & \cdots & \frac{\partial x_p}{\partial u_{q+1}} du_{q+1} \\ \vdots & & \vdots \\ \frac{\partial x_1}{\partial u_{p+1}} du_{p+1} & \cdots & \frac{\partial x_p}{\partial u_{p+1}} du_{p+1} \end{array} \right| .$$

$$\text{or: } \int X_{123\ldots p} \begin{vmatrix} 1 & \frac{\partial x_1}{\partial u_1} du_1 & \cdots\cdots & \frac{\partial x_p}{\partial u_1} du_1 \\ \vdots & \vdots & & \vdots \\ 1 & \frac{\partial x_1}{\partial u_{p+1}} du_{p+1} & \cdots & \frac{\partial x_p}{\partial u_{p+1}} du_{p+1} \end{vmatrix} .$$

If we now move to other parts of the boundary we shall continually see, where we pass a limit of projection with respect to one of the coordinates u, the projection of the indicatrix on the relative curved C_p change in sense.

So in an arbitrary point of the boundary the integral is found in the same way as on the entirely positive side; we shall find only, that for each coordinate u_q for which we are on the negative side, the corresponding term under the sign Σ will have to be taken negatively, by which we shall have shown the equality of the p-fold integral of ${}^{p}X$ over the boundary and the $(p+1)$ fold integral of ${}^{p+1}Y$ over the bounded S_{p+1}.

We can also imagine the scalar values of ${}^{p}X$ set off along the normal-S_{n-p}'s. As such the integral over an arbitrary curved bilateral closed S_{n-p} can be reduced to an $(n-p+1)$-dimensional vector over a curved S_{n-p+1}, bounded by S_{n-p}. If again we set off the scalar values of that vector along its normal-S_{p-1}, the vector ${}^{p-1}Z$ appears, which we shall call the *second derivative* of ${}^{p}X$. For the component vectors of ${}^{p-1}Z$ we find:

$$Z_{\alpha_1 \ldots . \alpha_{p-1}} = \sum_{\alpha_q = \alpha_p, \alpha_{p+1} \ldots . \alpha_n} - \frac{\partial X_{\alpha_q \alpha_1 \ldots . \alpha_{p-1}}}{\partial x_{\alpha_q}} .$$

The particularity may appear that one of the derivatives becomes 0. If the first derivative of an ${}^{m}X$ is zero we shall speak of an ${}^{\;\;\;m}_{m-1}X$, if the second is zero of an ${}^{\;\;\;m}_{m+1}X$.

Theorem 2. The first derivative of a ${}^{p}X$ is a ${}^{p+1}_{\;\;\;p}X$, the second a ${}^{p-1}_{\;\;\;p}X$; in other words the process of the first derivation as well as that of the second applied twice in succession gives zero.

The demonstration is simple analytically, but also geometrically the theorem is proved as follows:

Find the integral of the first derivative of ${}^{p}X$ over a closed S_{p+1}, then we can substitute for the addition given by an S_{p+1} element the integral of ${}^{p}X$ along the bounding S_p of that element. Along the entire S_{p+1} each element of those S_p boundaries is counted twice with opposite indicatrix, so that the integral must vanish.

The analogous property for the second derivative is apparent, when we evaluate the integral of the normalvector over a closed S_{n-p+1}.

By *total derivative* we shall understand the sum of the first and second derivatives and we shall represent the operation of total derivation by ∇.

Theorem 3. $\nabla^2 = -\sum_{h=1}^{h=n} \frac{\partial^2}{\partial x_h^2}$.

Proof. In the first place it is clear from theorem 2 that the vector ∇^2 is again a ${}^{p}X$. Let us find its component $X_{12 \ldots p}$.

The first derivative supplies the following terms

$$T_1 = -\sum_{q=p+1}^{q=n} \frac{\partial Y_{q\,1\ldots p}}{\partial x_q},$$

where

$$Y_{q1\ldots p} = \sum_{u=1}^{u=p} \pm \frac{\partial X_{q12\ldots(u-1)(u+1)\ldots p}}{\partial x_u}$$

$$\Big(+ \text{ sign for } (uq\;12\ldots(u-1)\,(u+1)\ldots p) = (q\;1\ldots p)\Big)$$

$$+\frac{\partial X_{12\ldots p}}{\partial x_q}$$

So

$$T_1 = \sum_{u=1}^{u=p}\sum_{q=p+1}^{q=n} \mp \frac{\partial^2 X_{q12\ldots(u-1)(u+1)\ldots p}}{\partial x_u\,\partial x_q}$$

$$\Big(- \text{ sign for } (uq\;12\ldots(u-1)\,(u+1)\ldots p) = (q\;1\ldots p)\Big)$$

$$-\sum_{q=p+1}^{q=n} \frac{\partial^2 X_{12\ldots p}}{\partial x_q^2}.$$

The second derivative supplies the terms

$$T_2 = \sum_{u=1}^{u=p} \pm \frac{\partial Z_{12\ldots(u-1)(u+1)\ldots p}}{\partial x_u}$$

$$\Big(+ \text{ sign for } (u\;12\ldots(u-1)\,(u+1)\ldots p) = (12\ldots p)$$

$$\text{or for } (qu\;1\ldots(u-1)\,(u+1)\ldots p) = (q\;12\ldots p)\Big),$$

where $$Z_{12\ldots(u-1)(u+1)\ldots p} = \sum_{q=p+1}^{q=n} - \frac{\partial X_{q12\ldots(u-1)(u+1)\ldots p}}{\partial x_q} \mp$$

$$\mp \frac{\partial X_{12\ldots p}}{\partial x_u}\Big(- \text{ sign for } (u\;12\ldots(u-1)\,(u+1)\ldots p) = (12\ldots p)\Big).$$

$$\text{So } T_2 = \sum_{u=1}^{u=p}\;\sum_{q=p+1}^{q=n} \mp \frac{\partial^2 X_{q12\ldots(u-1)(u+1)\ldots p}}{\partial x_u \partial x_q}$$

$$\Big(- \text{ sign for } (qu1\ldots(u-1)(u+1)\ldots p) = (q12\ldots p)\Big)$$

$$-\sum_{u=1}^{u=p} \frac{\partial^2 X_{12\ldots p}}{\partial x_u^2}.$$

The terms under the sign $\Sigma\,\Sigma$ of T_1 are annulled by those of T_2, so that only

$$-\sum_{h=1}^{h=n} \frac{\partial^2 X_{12..p}}{\partial x_h^2}$$

is left.

Corollary. If a vectordistribution ${}^pV$ is given, then the vectordistribution $\int \frac{V dv}{k_n(n-2)r^{n-2}}$, integrated over the entire space, has for second derivative V. (if $k_n r^{n-1}$ expresses the surface of the ${}^{n-1}$-sphere in S_n).

The theorem also holds for a distribution of sums of vectors of various numbers of dimensions, e.g. quaternions.

We shall say that a vectordistribution has the *potential property* when its scalar values satisfy the demands of vanishing at infinity, which must be put to a scalar potential function in S_n.[1]) And in the following we shall suppose that the vectordistribution from which we start possesses the potential property. Then holds good:

Theorem 4. A vectordistribution V is determined by its total derivative of the second order.

For, each of the scalar values of V is uniformly determined by the scalar values of $\nabla^2 V$, from which it is derived by the operation $\int \frac{dv}{k_n(n-2)r^{n-2}}$.

Theorem 5. A vectordistribution is determined uniformly by its total derivative of the first order.

For, from the first total derivative follows the second, from which according to the preceding theorem the vector itself.

We shall say that a vectordistribution has the *field property*, if the scalar values of the total derivative of the first order satisfy the demands which must be put to an agens distribution of a scalar potential function in S_n. And in the following we shall suppose that the vectordistribution under consideration possesses the field property. Then we have:

Theorem 6. Each vectordistribution is to be regarded as a total

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[1]) Generally the condition is put: the function must become infinitesimal of order $n-2$ with respect to the reciprocal value of the distance from the origin. We can, however, prove, that the being infinitesimal only is sufficient.

derivative, in other words each vectordistribution has a potential and that potential is uniformly determined by it.

Proof. Let V be the given distribution, then

$$P = \int \frac{\nabla V . dv}{k_n(n-2)r^{n-2}}$$

is its potential. For $\nabla^2 P = \nabla V$, or $\nabla(\nabla P) = \nabla V$, or $\nabla P = V$. Farther follows out of the field property of V, that P is uniformly determined as ∇^{-2} of ∇V, so as ∇ of V. So P has clearly the potential property; it need, however, not have the field property.

N.B. A distribution not to be regarded here, because it has not the field property, though it has the potential property, is e. g. the fictitious force field of a single agens point in S_2. For, here we have not a potential vanishing at infinity — and as such determined uniformly. The magnetic field in S_2 has field property and also all the fields of a single agens point in S_3 and higher spaces.

Let us call $\overline{\nabla}^{1} V$ the first derivative of ${}^{p}V$ and $\overline{\nabla}^{2} V$ the second; we can then break up ${}^{p}V$ into

$$\nabla \int \frac{\overline{\nabla}^{1} V . dv}{k_n\,(n-2)\,r^{n-2}} = \nabla P_1 = \overline{\nabla}^{2} P_1 = {}^{p}_{p+1}V.$$

and

$$\nabla \int \frac{\overline{\nabla}^{2} V . dv}{k_n\,(n-2)\,r^{n-2}} = \nabla P_2 = \overline{\nabla}^{1} P_2 = {}^{p}_{p-1}V.$$

From the preceding follows immediately:

Theorem 7. Each ${}^{p}_{p-1}V$ has as potential a ${}^{p-1}_{p}V$. Each ${}^{p}_{p+1}V$ has as potential a ${}^{p+1}_{p}V$.

We can indicate of the ${}^{p}_{p+1}V$ the elementary distribution, i. e. that particular ${}^{p}_{p+1}V$ of which the arbitrary S_n integral must be taken to obtain the most general ${}^{p}_{p+1}V$.

For, the general ${}^{p}_{p+1}V$ is $\overline{\nabla}^{2}$ of the general ${}^{p+1}V$, so it is the general S_n integral of the $\overline{\nabla}^{2}$ of an isolated $(p+1)$-dimensional vector, which, as is easily seen geometrically, consists of equal ^{p}vectors in the surface of a ^{p}sphere with infinitesimal radius described round the point of the given isolated vector in the R_{p+1} of the vector.

In like manner the general ${}^{p}_{p-1}V$ is the $\overline{\nabla}^{1}$ of the general ${}^{p-1}V$, so it is the general S_n integral of the $\nabla_{\!1}$ of an isolated ${}^{p-1}$vector, consisting of equal ^{p}vectors normal to the surface of an ${}^{n-p}$sphere with infinitesimal radius described round the point of the given isolated vector in the R_{n-p+1}, normal to that vector.

From this follows:

Theorem 8. The general ${}^{p}V$ is an arbitrary integral of elementary fields E_1 and E_2, where:

$$E_1 = \nabla \cdot \int \frac{{}_{p}^{p-1}Z\,dv}{k_n(n-2)r^{n-2}}\,,$$ where ${}_{p}^{p-1}Z$ consists of the ${}^{p-1}$vectors in the surface of an infinitesimal ${}^{p-1}$sphere Sp_z, ... (1)

$$E_2 = \nabla \cdot \int \frac{{}_{p}^{p+1}Y\,dv}{k_n(n-2)r^{n-2}}\,,$$ where ${}_{p}^{p+1}Y$ consists of the ${}^{p+1}$vectors normal to the surface of an infinitesimal ${}^{n-p-1}$sphere Sp_y. . . . (2)

For the rest the fields E_1 and E_2 must be of a perfectly identical structure at finite distance from their origin; for two fields E_1 and E_2 with the same origin must be able to be summed up to an isolated ^{p}vector in that point.

We can call the spheres Sp_y and Sp_z with their indicatrices the *elementary vortex systems* Vo_y and Vo_z. A field is then uniformly determined by its elementary vortex systems and can be regarded as caused by those vortex systems.

We shall now apply the theory to some examples.

The force field in S_2.

The field E_1. The elementary sphere Sp_z becomes here two points lying quite close to each other, the vortex system Vo_z passes into two equal and opposite scalar values placed in those two points. It furnishes a scalar potential $\frac{\cos\varphi}{r}$ in which φ denotes the angle of the radiusvector with the S_1 of Vo_z, i. e. the line connecting the two points. The elementary field is the (first) derivative of the potential (the gradient); it is the field of an agens double point in two dimensions.

The field E_2. The elementary sphere Sp_y again consists of two points lying in close vicinity, the elementary vortex system Vo_y has in those two points two equal and opposite planivectors. The planivector potential (determined by a scalar value) here again becomes $\frac{\cos\varphi}{r}$; so the field itself is obtained by allowing all the vectors of a field E_1 to rotate 90°. As on the other hand it has to be of an identical structure to E_1 outside the origin we may call the field E_1 resp. E_2 "dual to itself".

In our space the field E_1 can be realized as that of a plane, infinitely long and narrow magnetic band with poles along the edges; the field E_2 as that of two infinitely long parallel straight electric currents, close together and directed oppositely.

The planivector (vortex) field in S_4.

The field E_1. The elementary sphere Sp_z is a circlet, the elementary vortex system Vo_z a current along it. It furnishes a linevector potential $= \frac{\sin\varphi}{r^3}$ directed along the circles which project themselves on the plane of Vo_z as circles concentric to Vo_z, and where φ is the angle of the radiusvector with the normal plane of Vo_z. The field is the first derivative (rotation) of this potential.

The field E_2. The elementary sphere Sp_y is again a circlet, the elementary vortex system Vo_y assumes in the points of that circlet equal ^{3}vectors normal to it. The ${}^3V$-potential consists of the ${}^3V$'s normal to the potential vectors of a field E_1; the field E_2 is thus obtained by taking the normal planes of all planivectors of a field E_1. As on the other hand E_1 and E_2 are of the same identical structure outside the origin, we can say here again, that the field E_1 resp. E_2 is dual to itself.

So we can regard the vortex field in S_4 as caused by elementary circular currents of two kinds; two equal currents of a different kind cause vortex fields of equal structure, but one field is perfectly normal to the other.

So if of a field the two generating systems of currents are identical, it consists of isosceles double-vortices.

The force field in S_3.

The field E_1. Vo_z gives a double point, causing a scalar potential $\frac{\cos\varphi}{r^2}$, where φ is the angle of the radiusvector with the axis of the double point; the derivative (gradient) gives the wellknown field of an elementary magnet.

The field E_2. Vo_y consists of equal planivectors normal to a small circular current. If we represent the planivector potential by the linevector normal to it, we shall find for that linevector $\frac{\sin\varphi}{r^2}$ directed along the circles, which project themselves on the plane of Vo_z as circles concentric to Vo_z, and where φ is the angle of the radius-vector with the normal on the circular current. The field E_2 is the second derivative of the planivector potential, i.e. the rotation of the normal linevector.

According to what was derived before the field E_2 of a small circular current is outside the origin equal to the field E_1 of an elementary magnet normal to the current.

In this way we have deduced the principle that an arbitrary force field can be regarded as generated by elementary magnets and elementary circuits. A finite continuous agglomeration of elementary magnets furnishes a system of finite magnets; a finite continuous agglomeration of elementary circuits furnishes a system of finite closed currents, i.e. of finite dimensions; the linear length of the separate currents may be infinite.

Of course according to theorem 6 we can also construct the scalar potential out of that of single agens points $\left(\frac{1}{4\pi} \times\right.$ the second derivative of the field), and the vector potential out of that of rectilinear elements of current (perpendicular to $\frac{1}{4\pi} \times$ the first derivative of the field), but the fictitious "field of a rectilinear element of current" has everywhere rotation, so it is the real field of a rather complicated distribution of current. A field having as its only current a rectilinear element of current, is not only physically but also mathematically impossible. A field of a single agens point though physically perhaps equally impossible, is mathematically just possible in the Euclidean space in consequence of its infinite dimensions, as the field of a magnet of which one pole is removed at infinite distance.

In hyperbolic space also the field of a single agens point is possible for the same reason, but in elliptic and in spherical space being finite it has become as impossible as the field of a rectilinear element of current. The way in which SCHERING (Göttinger Nachr. 1870, 1873; compare also FRESDORF Diss. Göttingen 1873; OPITZ Diss. Göttingen 1881) and KILLING (Crelle's Journ. 1885) construct the potential of elliptic space, starting from the supposition that as unity of field must be possible the field of a single agens point, leads to absurd consequences, to which KLEIN (Vorlesungen über Nicht-Euklidische Geometrie) has referred, without, however, proposing an improvement. To construct the potential of the elliptic and spherical spaces nothing but the field of a double point must be assumed as unity of field, which would lead us too far in this paper but will be treated more in details in a following communication.

With the force field in S_3 the vortex field in S_3 dual to it has been treated at the same time. It is an integral of vortex fields as they run round the force lines of an elementary magnet and as they run round the induction lines of an elementary circuit.

The force field in S_n .

The field E_1. Vo_z again gives a double point, which furnishes a scalar potential $\frac{\cos\varphi}{r^{n-1}}$, where φ is the angle between radiusvector and axis of the double point; its gradient gives what we might call the field of an elementary magnet in S_n.

The field E_2. Vo_y consists of equal planivectors normal to a small ${}^{n-2}$sphere Sp_y. To find the planivector potential in a point P, we call the perpendicular to the S_{n-1} in which Sp_y is lying OL, and the plane LOP the "meridian plane" of P; we call φ the angle LOP and OQ the perpendicular to OL drawn in the meridian plane. We then see that all planivectors of Vo_y have in common with that meridian plane the direction OL, so they can be decomposed each into two components, one lying in the meridian plane and the other cutting that meridian plane at right angles. The latter components, when divided by the $n-2^{\text{nd}}$ power of their distance to P, and placed in P, neutralize each other two by two; and the former consist of pairs of equal and opposite planivectors directed parallel to the meridian plane and at infinitely small distance from each other according to the direction OQ. These cause in P a planivector potential lying in the meridian plane $= c\frac{\sin\varphi}{r^{n-1}}$. The field E_2 is of this potential the $\bigtriangledown = \overline{\nabla^{2}}$, and outside the origin is identical to the field of an elementary magnet along OL.

The force field in S_n can be regarded as if caused 1st. by magnets, 2nd. by vortex systems consisting of the plane vortices erected normal to a small ${}^{n-2}$sphere. We can also take as the cause the spheres themselves with their indicatrices and say that the field is formed by magnets and vortex spheres of $n-2$ dimensions (as in S_3 the cause is found in the closed electric current instead of in the vortices round about it).

Here also fields of a single plane vortex element are impossible. Yet we can speak of the fictitious "field of a single vortex" although that really has a vortex i. e. a rotation vector everywhere in space. We can say namely:

If of a force field in each point the divergence (a scalar) and the rotation (a planivector) are given, then it is the $\bigtriangledown$ of a potential: $\int \frac{div.\, dv}{k_n(n-2)r^{n-2}} + \int \frac{rot.\, dv}{k_n(n-2)r^{n-2}}$; this formula takes the field as an integral of fictitious fields of agens points and of single vortices.

Crystallography. — *"On the fatty esters of Cholesterol and Phytosterol, and on the anisotropous liquid phases of the Cholesterol-derivatives."* By Dr. F. M. JAEGER. (Communicated by Prof. A. P. N. FRANCHIMONT.)

(Communicated in the meeting of May 26, 1906).

§ 1. Several years ago I observed that phytosterol obtained from rape-seed-oil suffers an *elevation* of the melting point by a small addition of cholesterol. The small quantity of the first named substance at my disposal and other circumstances prevented me from going further into the matter.

My attention was again called to this subject by some very meritorious publications of BÖMER[1]) on the meltingpoint-elevations of *phytoterol* by *cholesterol* and also of *cholesterol-acetate* by *phytosterol-acetate*. Apart from the fact that the crystallographic data from O. MÜGGE led me to the conclusion, that there existed here an uninterrupted miscibility between heterosymmetric components, a further investigation of the binary meltingpoint-line of the two acetates appeared to me very desirable, as the ideas of BÖMER on this point are not always clear; this is all the more important, as we know that BÖMER based on these melting point elevations a method for detecting the adulteration of animal with vegetable fats. My further object was to ascertain in how far the introduction of fatty acid-residues into the molecule of *cholesterol* would modify the behaviour of the esters in regard to the phenomenon of the *optically-anisotropous liquid phases*, first noticed with the *acetate, propionate* and *benzoate*, with an increasing carbon-content of the acids. Finally I wished to ascertain whether there was question of a similar meltingpoint-elevation as with the acetates in the other terms of the series too.

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[1]) BÖMER, Zeit. Nahr. u. Genussm. (1898). 21, 81; (1901). 865, 1070; the last paper (with WINTER) contains a complete literature reference to which I refer.

§ 2. In the first place the esters of cholesterol and phytosterol had to be prepared.

The cholesterol used, after being repeatedly recrystallised from absolute alcohol + ether, melted sharply at 149°.2. The phytosterol was prepared by MERCK, by HESSE's[1]) method from Calabar fat, and also recrystallised. It melted at 137°. A microscopic test did not reveal in either specimen any inhomogeneous parts.

First of all, I undertook the crystallographic investigation of the two substances. The result agrees completely with the data given by MÜGGE, to which I refer. I have not, up to the present, obtained any measurable crystals; on account of the optical properties, cholesterol can possess only triclinic, and phytosterol only monoclinic symmetry.

Although an expert crystallographer will have no difficulty in microscopically distinguishing between the two substances, the crystals deposited from solvents are, however, so much alike that a less experienced analyst may easily make a mistake. I, therefore, thought it of practical importance to find a better way for their identification with the microscope.

This was found to be a very simple matter, if the crystals are allowed to form on the object-glass by fusion and solidification, instead of being deposited from solvents. Figs. 1 and 2 show the way in which the solidification of the two substances takes place.

Fig. 1.
Cholesterol,
fused and then solidified.

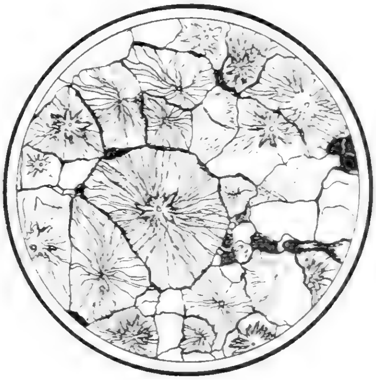

Fig. 2.
Phytosterol,
fused and solidified by cooling.

Phytosterol crystallises in conglomerate spherolites. Between crossed nicols they exhibit a vivid display of colours and each of them is

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[1]) HESSE, Annal. der Chemie, **192.** 175.

traversed by a dark cross, so that the whole conveys the impression of adjacent interference images of monaxial crystals, viewed perpendicularly to the axis and without circular polarisation. The character of the apparently simple crystals is optically negative.

Cholesterol, however, presents a quite different image. When melted on an object-glass, the substance contracts and forms small droplets, which are scattered sporadically and, on solidification, look like little nuggets with scaly edges, which mostly exhibit the white of the higher order.

That the microscopical distinction in this manner is much safer than by Mügge's method, may be seen from fig. 3 where phytosterol and cholesterol are represented as seen under the microscope, after being crystallised from alcohol. *A* is cholesterol, *B* phytosterol.

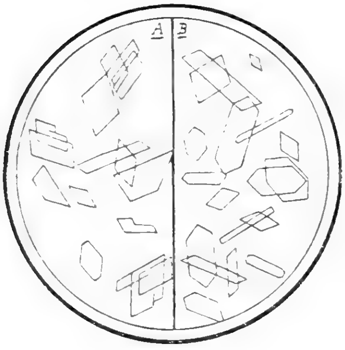

Fig. 3.
Phytosterol and Cholesterol from $95^0/_0$ Alcohol.

§ 3. Of the fatty esters, I have prepared the *acetates, propionates, butyrates* and *isobutyrates* by heating the two alcohols with the pure acid-anhydride in a reflux apparatus. A two or three hours heating with a small flame, and in the case of the cholesterol, preferably in a dark room, gives a very good yield. When cold, the mass was freed from excess of acid by means of sodium hydrocarbonate, and then recrystallised from alcohol + ether, afterwards from ethyl acetate + ligroin, or a mixture of acetone and ligroin, until the meltingpoint was constant. Generally, I used equal parts by weight of the alcohol and the acidanhydride.

The *formiates, valerates, isovalerates, capronates, caprylates* and *caprinates* were prepared by means of the pure anhydrous acids. These (valeric, caprylic and capric acids) were prepared synthetically by Kahlbaum; the isovaleric acid and also the anhydrous formic acid were sold commercially as pure acids "Kahlbaum". Generally, a six hours heating of the alcohol with a little more than its own weight of the acid sufficed to obtain a fairly good yield. Owing, however, to the many recrystallisations required the loss in substance is much greater than with the above described method of preparing.

Both series of esters crystallise well. The phytosterol-esters in soft, flexible, glittering scales; the formiate and the valerates present some difficulties in the crystallisation, as they obstinately retain a trace of an adhesive by-product which it is difficult to remove. The cholesterol-esters give much nicer crystals; the formiate, acetate and benzoate have been measured macroscopically; the other derivatives crystallise in delicate needles or very thin scaly crystals which are not measurable; I hope yet to be able to obtain the butyrate in a measurable form [1]). In the case of the caprylate, the purification was much assisted by the great tendency of the product to crystallise. The purification of the capric ester was, however, much more difficult; at last, this has also been obtained in a pure state even in beautiful, colourless, plate-shaped crystals, from boiling ligroïn [2]).

The phytosterol-esters retain their white colour on exposure to the light; the cholesterol-esters gradually turn yellowish but may be bleached again by recrystallisation.

The determination of the melting points, and in the case of the cholesterol-esters, also that of the transition-temperatures: solid → anisotropous-liquid, was always executed in such manner, that the thermometer was placed in the substance, which entirely surrounded the mercury-reservoir. Not having at my disposal a thermostat, I have not used the graphic construction of the cooling-curve, in the determinations, but simply determined the temperature at which the new phases first occur when the outer bath gets gradually warmer.

As regards the analysis of the esters, nothing or little can be learned from an elementary analysis in this case, where the formulae of cholesterol and phytosterol are still doubtful, and where the molecules contain from 28 to 37 carbon-atoms. I have therefore rested content with saponifying a small quantity of the esters with alcoholic potassium hydroxide, which each time liberated the cholesterol or phytosterol with the known melting points. On acidifying the alkaline solution with hydrochloric acid, the fatty acids could be identified by their characteristic odour.

The esters were called pure, when the melting points, and in the case of cholesterol-esters, *both* temperatures, remained constant on further recrystallisation.

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[1]) I have even succeeded lately in obtaining the formiate in large transparent crystals from a mixture of ligroïn, ethyl acetate and a little alcohol.

[2]) The crystals of the *caprinate* are long, flat needles. They form monoclinic individuals, which are elongated parallel to the *b*-axis, and flattened towards $\{001\}$ The angle β is 88° à 89°; there are also the forms: $\{100\}$ and $\{\bar{1}01\}$; measured: $(\bar{1}00):(\bar{1}01) = \pm 20.°$. The optic axial plane is $\{010\}$; inclined dispersion: $\rho > \nu$ round the first bissectria. Negative double refraction. On $\{001\}$ there is one optical axis visible about the limits of the field. The crystals are curved-plane.

§ 4. I give in the following tables the temperatures observed etc.[1]) Next to my data are placed those of Bömer as far as he has published them. The temperatures in [ ] will be discussed more in detail later on.

I. FATTY ESTERS OF CHOLESTEROL.

	t_1	t_2	t_3	Bömer's data:	
Chol. Formiate	—	[± 90°]	96°.5	—	96°.
» Acetate	—	[80 à 90°]1)	112°.8	—	113°.5
» Propionate	93°.0	107°.2	—	96°	111°
» -*n*-Butyrate	96°.4	107°.3	—	96°	108°
» Isobutyrate	—	—	126°.5	—	—
» -*n*-Valerate	91°.8	99°.2	—	—	—
» Iso-valerate	—	[± 109°]	110°.6	—	—
» Capronate	91°.2	100°.1	—	—	—
» Caprylate	—	[± 101°]	106°.4	—	—
» Caprinte	82°.2	90°.6	—	—	—
» Benzoate	145°.5	178°.5	—	146°	178°.5
» Phtalate 2)	—	—	—	—	182°.5
» Stearinate 3)	—	—	—	65°	

Benzoates and phthalates although not being fatty esters, have nevertheless been included.

1) According to Schönbeck, Diss. Marburg. (1900).

2) According to Bömer loco cit.

3) According to Berthelot. It is as yet undecided, whether liquid crystals are present here; perhaps this case is analogous with that of the caprylate.

The temperatures in [] cannot be determined accurately; see text.

§ 5. Most striking with these remarkable substances are the splen-

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[1]) It should be observed that in these substances *three* temperatures should be considered, namely 1. transition: solid → anisotropous-liquid; 2. transition: anisotropous-liquid → isotropous-liquid; 3. transition: solid → isotropous-liquid.

This distinction has been retained, particularly on account of the cases of labile, liquid crystals discovered here.

did colour-phenomena observed during the cooling of the clear, isotropous, fused mass to its temperature of solidification, and also during the heating in the reverse way. These colour phenomena are caused by interference of the incident light, every time the turbid anisotropous liquid-phase occurs, or passes into the isotropous liquid. During this last transition we notice while stirring with the thermometer, the "oily slides" formerly described by Reinitzer, until the temperature t_2 has been exceeded. These colours also occur when the solid phase deposits from the anisotropous liquid, therefore below t_1. The most brilliant, unrivalled violet and blue colour display is shown by the butyrate and normal valerate, also very well by the capronate and caprinate.

The temperatures in [ ] t_2 answer to anisotropous liquid phases which are *labile* in regard to the isotropous liquid, and *which double-refracting liquids are, therefore, only realisable in undercooled fused material.* Of this case, which is comparable with the monotropism, as distinguished by Lehmann from the case of enantiotropous transformations, the acetate is the only known example up to the present. Now the number of cases is increased by *three,* namely the *formiate,* the *caprylate* and without any doubt also the *isovalerate,* to which I will refer presently. Cholesterol-formiate and caprylate melt therefore, *perfectly sharply* to a clear liquid at, respectively $96^{1}/_{2}$° and 106.°2. If, however, the clear liquid is suddenly cooled in cold water, one notices the appearance of the turbid, anisotropous, more-labile phase, accompanied by the said colour phenomena. The acetate in particular exhibits them with great splendour. It is quite possible that many organic compounds which are described as "melting sharply", belong to this category and on being cooled suddenly possess a double-refracting liquid phase, even although this may last only a moment. The phenomenon of liquid crystals would then be more general than is usually believed.

Prof. Lehmann, to whom I have forwarded a little of the cholesterol-esters, has been able to fully verify my observations. This investigator has, in addition, also found that *cholesterol-caprinate may probably exhibit two anisotropous liquid phases.* Although, personally, I never noticed more than one single phase, and Prof. Lehmann's determinations are only given provisionally, this case would certainly have to be regarded as one of the most remarkable phenomena which may be expected in a homogeneous body, particularly because the perceptibility of those *two* phases implies that they would *not* be miscible in all proportions with each other.

§ 6. The behaviour of *cholesterol-isobutyrate* is a very remarkable one. Microscopic and macroscopic investigation shows absolutely nothing of an anisotropous liquid phase, not even on sudden cooling and this in spite of the fact that the normal butyrate gives the phenomenon with great splendour. This differently-behaving ester has been prepared from the same bulk of cholesterol as was used for preparing the other esters. The cause of the difference can, therefore, be found only *in the structure of the fatty acid-residue,* which contrary to that of the other esters, is branched.

All this induced me, to prepare the analogous ester of isovaleric acid ; perhaps it might be shown also here that the branching of the carbon-chain of the acid destroys the phenomenon of the anisotropous liquid phase. At first I thought this was indeed the case, but a more accurate observation showed that in the rapid cooling there occurs, if only for an indivisible moment, a *labile* anisotropous liquid ; the duration, however, is so short that, for a long time, I was in doubt whether this phase ought to be called stable or labile as in the case of the formiate and caprylate! Even though the carbon-branching does not cause a total abrogation of the phenomenon of liquid crystals, the realisable traject appears to become so much smaller by that branching, that it almost approaches to *zero,* and the expected phase is, moreover, even still labile. From all this I think we may conclude, as has been stated more than once by others, that the occurrence of the liquid phases is indeed a *inherent* property of the matter, which cannot be explained by the presence of foreign admixtures etc. (TAMMANN c. s.).

§ 7. We now give the melting points of the analogous phytosterol-esters which, with one exception, do not exhibit the phenomenon of the double-refracting liquids. As the phytosterols from different vegetable fats seem to differ from each other, and as BÖMER does not mention any phytosterol esters from Calabar-fat in particular, I have indicated in the second column only the *limits* within which the melting points of the various esters prepared by him from diverse oils, vary. (See table following page.)

From a comparison of the two tables it will be seen that the lowering of the melting point of phytosterol by the introduction of fatty acid-residues of increasing carbon-content, takes place *much more rapidly* than with cholesterol. On the other hand, the succession of the melting points of the acetate, propionate, butyrate and *n*-valerate is *more regular* than with the cholesterol-derivates.

All phytosterol-esters share with phytosterol itself the great ten-

II. FATTY ESTERS OF PHYTOSTEROL.

		Limits according to Bömer:
Phytosterol-Formiate	110°	103°—113°
Phytosterol-Acetate	129°.1	123°—135°
Phytosterol-Propionate	105°.5	104°—116°
Phytosterol-Butyrate	91°.2	85°— 90°
Phytosterol-Isobutyrate	117°.	—
Phytosterol-norm.-Valerate	$t_3 = 67°$; $t'_3 = 30°$	—
Phytosterol-Isovalerate	100°.1	—

dency to crystallise from the melted mass in *sphaerolites;* with an increasing carbon-content of the fatty acid-residue, these seem generally to become smaller in circumference.

The formiate crystallises particularly beautifully; this substance possesses, moreover, two solid modifications, as has been also stated by Prof. Lehmann, who is of opinion that these two correspond with the two solid phases of the cholesterol-derivative. In the phytosterol-ester the sphaerolite-form is the *more-labile one.*

On the other hand, when recrystallised from monobromonaphthalene or almond-oil, they form under the microscope well-formed needle-shaped crystals which, however, are always minute. Probably, we are dealing in all these cases with polymorphism. I have also often observed whimsical groroths and dendritics.

A difficulty occurred in the determination of the melting point of the normal valerate. It melts, over a range of temperature at about 67°.1, but if the mass is allowed to cool until solidified, the ester fuses to a clear liquid when heated to 30°. This behaviour is quite analogous to that observed with a few glycerides of the higher fatty acids, for instance with *Trilaurin* and *Trimyristin* by Schey. 1)

After half an hour the melting point had risen again to $53^1/_2$° and after 24 hours to 67°. After 24 hours, small white *sphaerolites* had deposited in the previously coherent, scaly and slightly double-refracting layer on the object glass, which exhibited the dark cross of the phytosterol. In order to explain this phenomenon, I think I must assume a *dimorphism* of the solid substance. Moreover, liquid crystals are formed here, as has also been observed by Prof. Lehmann.

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1) Schey. Dissertatie, Leiden (1899) p. 51, 54.

According to Prof. LEHMANN, normal phytosterol-valerate forms very beautiful liquid crystals, which are analogous to those of cholesterol-oleate; like these they are not formed until the fused mass is undercooled. Consequently, the anisotropous liquid phase is here also *labile* in regard to the isotropous one.

I do not think it at all improbable that the changes in the melting points observed by SCHEY with his higher tryglicerides also owe their origin to the occurrence of labile, double-refracting liquid phases. A further investigation is certainly desirable.

§ 8. We now arrive at the discussion of the mutual behaviour of both series of fatty esters in regard to each other.

It has been sufficiently proved by BÖMER that the meltingpoint-line of *cholesterol* and of *phytosterol* is a *rising* line. In connection with MÜGGE's and my own crystal determinations we should have here indeed a gradual mixing between heterosymmetric components! In mixtures which contain about 3 parts of cholesterol to 1 part of phytosterol, the microscopical research appears to point to a new solid phase, which seems to crystallise in trigonal prisms. This compound (?) also occurs with a larger proportion of cholesterol [1]). Whether we must conclude that there is a miscibility of this new kind of crystal with both components, or whether an eventual transformation in the solid mixing phases proceeds so slowly that a transition point in the meltingpoint-line escapes observation, cannot be decided at present.

The matter is of more interest with the esters of both substances. According to BÖMER [2]) the formiates give a meltingpoint-line with a eutectic point; the acetates, however, a continuously rising melting point-line.

The method of experimenting and the theoretical interpretation is, however, rather ambiguous, as BÖMER prepares mixed solutions of the components, allows these to crystallise and determines the meltingpoint of the solid phase first deposited. By his statement of the proportion of the components in the solution used, he also gives an incomplete and confusing idea of the connection between the meltingpoint and the concentration.

Although a *rising* of the binary meltingpoint-line may, of course, be ascertained in this manner quite as well as by other means — and BÖMER's merit certainly lies in the discovery of the fact

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[1]) Compare BÖMER, Z. f. Nahr. u. Gen. M. (1901) 546.

[2]) BÖMER, Z. f. Nahr. u. Gen. Mitt. (1901) 1070. In connection with the dimorphism of the formiates, a mixing series with a blank is however very probable in this case.

itself — the determination of the binary meltingpoint-line must be reckoned faulty as soon as it is to render *quantitative* services, which is of importance for the analysis of butter; for if the meltingpoint-curve is accurately known, the quantity of phytosterol added may be calculated from the elevation of the melting point of the cholesterol acetate. I have, therefore, now determined the binary melting point line in the proper manner. (Fig. 4).

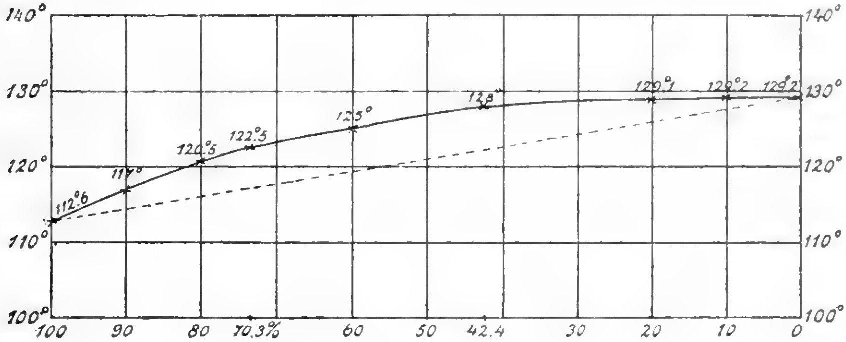

Fig. 4.
Cholesterol-, and Phytosterol-Acetate.

Although the curve takes an upward course it still deviates considerably from the straight line which connects the two meltingpoints. As the course of the curve from 40 % cholesterol-acetate to 0 % is nearly *horizontal*, it follows that the composition of mixtures can be verified by the melting-point, when the admixture of phytosterol in the animal fat does not exceed 60 %. The results are the most accurate when the quantity of phytosterol-ester[1]) amounts to 2 %—40 %. In practice, this method is therefore applicable in most cases. The cholesterol-acetate used in these experiments melted at 112.°8; the phytosterol-acetate at 129.°2.

A	mixture	of	90	%	Chol.	Acet.	+ 10	%	Phyt.	Acet.	melts	at	117°
»	»	»	80	»	»	»	+ 20	»	»	»	»	»	120.°5
»	»	»	73.3	»	»	»	+ 26.7	»	»	»	»	»	122.°5
»	»	»	60	»	»	»	+ 40	»	»	»	»	»	125°
»	»	»	42.4	»	»	»	+ 57.6	»	»	»	»	»	128°
»	»	»	20	»	»	»	+ 80	»	»	»	»	»	129.°1
»	»	»	10	»	»	»	+ 90	»	»	»	»	»	129.°2

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[1] It should be observed that although BÖMER, in several parts of his paper, recommends the said method for qualitative purposes only, it is plain enough in other parts that he considers the process suitable for quantitative determinations in the case of small concentrations. In his interpretation of the melting point line this is, however, *not* the case, for his experiments give no explanation as to the mixing proportion of the components in mixtures of definite observed melting point. Quantitative determinations are only rendered possible by a complete knowledge of the binary melting point line. When the concentration of cholesterol-acetate is 0,5 — 1 %, the meltingpoint is practically not altered; when it is 2 % however, the amount is easy to determine.

Probably, a case of isomorphotropous relation occurs here with the acetates; both esters are, probably, monoclinic, although this is not quite certain for the cholesterol-ester. This is pseudotetragonal and

according to VON ZEPHAROVICH: *monoclinic*, with $\beta = 73°38'$;
according to OBERMAYER: *triclinic*, with $\beta = 106°17'$, $\alpha = 90°20'$, $\gamma = 90°6'$,
while the axial relations are $1{,}85 : 1 : 1{,}75$.

The phytosterol-ester has been approximately measured microscopically by BEYKIRCH and seems to possess a monoclinic or at least a triclinic symmetry with monoclinic limit-value. In my opinion both compounds are certainly *not* isomorphous. In any case it might be possible that even though a direct isomorphism does not exist in the two ester-series, there are other terms which exhibit isomorphotropous miscibility in an analogous manner, as found for the acetates by BÖMER. I have extended the research so as to include the isovalerates; the result however is negative and the case of the acetic esters seems to be the only one in this series.

The following instance may be quoted:

31.8°/₀ cholesterol-butyrate + 68,2°/₀ phytosterol-butyrate indicate for t_1 81° and for t_2 83° etc. etc.

For the formiates, the lowering had been already observed by BÖMER; other esters, also those of the iso-acids behave in an analogous manner: at both sides of the melting-diagram occurs a lowering of the initial melting points. It is, however, highly probable that in some, perhaps in all cases, there exists an iso*di*morphotropous mixing with a blank in the series of the mixed crystals.

The anisotropous liquid phase of cholesterol-esters gives rise in this case to anisotropous liquid mixed crystals. I just wish to observe that for some of the lower-melting esters, such as the butyrate, capronate, caprinate, normal valerate, etc., the temperature t_1 for these mixed crystals may be brought to about 50° or 60° or lower and this creates an opportunity for studying liquid mixed crystals at such temperatures, which greatly facilitates microscopical experiments.

In all probability, I shall shortly undertake such a study of these substances. Of theoretical importance is also the possibility, to which Prof. BAKHUIS ROOZEBOOM called my attention, that in those substances where t_2 answers to the more-labile condition, the at first more labile liquid mixed crystals, on being mixed with a foreign substance, become, finally, stable in regard to the isotropous fused mass. Experiments with these preparations, in this sense, will be undertaken elsewhere. Perhaps, a study of the low-melting derivatives or else a similar study of the low-melting liquid mixed crystals by means of the *ultra-microscope* might yield something of importance.

Zaandam, May 1906.

Physics. — "*Researches on the thermic and electric conductivity power of crystallised conductors.*" I. By Dr. F. M. JAEGER. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 26, 1906).

1. Of late years, it has been attempted from various sides to find, by theoretical means, a connection between the phenomena of the thermic and electric conductivity of metallic conductors, and this with the aid of the more and more advancing electron theory.

In 1900 papers were published successively by P. DRUDE [1]), J. J. THOMSON [2]) and E. RIECKE [3]) and last year by H. A. LORENTZ [4]).

One of the remarkable results of these researches is this, that *the said theory has brought to light that the quotient of the electric and thermic conductivity power of all metals, independent of their particular chemical nature, is a constant, directly proportional to the absolute temperature.*

When we assume that the electrons in such a metal can move freely with a velocity depending on the temperature, such as happens with the molecules in ideal gases and also that these electrons only strike against the much heavier metallic atoms, so that in other words, their mutual collision is neglected, whilst both kinds of particles are considered as perfectly elastic globes, the quotient of the thermic conductivity power λ and the electric conductivity power σ may be indeed represented by a constant, proportional to the absolute temperature T.

The theories of DRUDE and LORENTZ only differ as to the absolute value of the quotient; according to DRUDE $\frac{\lambda}{\sigma} = \frac{4}{3}\left(\frac{\alpha}{e}\right)^2 T$; according to LORENTZ $\frac{\lambda}{\sigma} = \frac{8}{9}\left(\frac{\alpha}{e}\right)^2 T$. In these expressions λ, σ and T have the above cited meaning, whilst α is a constant and e represents the electric charge of the electron.

By means of a method originated by KOHLRAUSCH, JAEGER and DIESSELHORST have determined experimentally the values for $\frac{\lambda}{\sigma}$ with

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[1]) P. DRUDE, Ann. Phys. (1900). **1**. 566; **3**. 369.

[2]) J. J. THOMSON, Rapport du Congrès de physique Paris (1900). **3**. 138.

[3]) E. RIECKE, Ann. Phys. Chem. (1898). **66**. 353, 545, 1199; Ann. Phys. (1900). **2**. 835.

[4]) H. A. LORENTZ, Proc. 1905, Vol. VII, p. 438, 585, 684.

various metals [1]). The agreement between theory and observation is in most cases quite satisfactory, only here and there, as in the case of bismuth [2]), the difference is more considerable. From their measurements for silver at 18°, the value 47×10^5 may be deduced in C.G.S. units, for the expression $\frac{aT}{e}$. (Compare LORENTZ, loco cit. p. 505); according to DRUDE's formula: 38×10^5.

§ 2. I hope, shortly, to furnish an experimental contribution towards these theories by means of a series of determinations of an analogous character, but more in particular with crystallised conductors, and in the different directions of those crystal-phases.

If we take the most common case in which may be traced three mutual perpendicular, thermic and electric main directions in such crystals, the propounded theories render it fairly probable for all such conducting crystals that:

$$\frac{\lambda_x}{\sigma_x} = \frac{\lambda_y}{\sigma_y} = \frac{\lambda_z}{\sigma_z}, \text{ and therefore also: } \lambda_x : \lambda_y : \lambda_z = \sigma_x : \sigma_y : \sigma_z.$$

In conducting crystals, the directions of a greater electric conductivity should, therefore, not only be those of a greater thermic conductivity, but, theoretically, the quotient of the electric main-conductivities should be numerically *equal* to that of the thermic main-conductivities.

Up to the present but little is known of such data. The best investigated case is that of a slightly titaniferous *Haemitate* of

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[1]) W. JAEGER und DIESSELHORST, Berl. Sitz. Ber. (1899). 719 etc. Comp. REINGANUM, Ann. Phys. (1900) 2, 398.

[2]) With Al, Cu, Ag, Ni, Zn, the value of $\frac{\lambda}{\sigma}$ at 18° varies between 636×10^8 and 699×10^8; with Cd, Pb, Sn, Pt, Pd between 706×10^8 and 754×10^8; with Fe between 802 and 832×10^8, therefore already more. With *bismuth* $\frac{\lambda}{\sigma}$ at $18° = 962 \times 10^8$. Whilst in the case of the other metals mentioned the values of $\frac{\lambda}{\sigma}$ at 100° and at 18° are in the average proportion of 1,3 : 1, with *bismuth* the proportion is only 1.12. In their experiments, JAEGER and DIESSELHORST employed little rods, and bearing in mind the great tendency of bismuth to crystallise, their results with this metal cannot be taken as quite decisive, as the values of the electric and thermic conductivity power in the chief directions of crystallised bismuth differ very considerably.

Swedish origin which has been investigated by H. Bäckström and K. Angström [1]) as to its thermic and electric conductivity power. In this ditrigonal mineral, they found for the quotient of the thermic conductivity power in the direction of the chief axis (c) and in that perpendicular to it (a) at 50°:

$$\frac{\lambda_a}{\lambda_c} = 1.12.$$

For the quotient of the electric resistances w at the same temperature they found:

$$\frac{w_c}{w_a} = 1.78, \text{ and, therefore: } \frac{\sigma_a}{\sigma_c} = 1.78.$$

From this it follows that in the case of the said conductor, the theory agrees with the observations as to the relation between the conductivity powers only *qualitatively*, but not *quantitatively*, and — contrary to the usually occurring deviations — the proportion of the quantities λ is *smaller* than that of the quantities σ.

Jannettaz's empirical rule, according to which the conductivity for heat in crystals is greatest parallel to the directions of the more complete planes of cleavage, applies here only in so far as haematite which does *not* possess a distinct plane of cleavage, may still be separated best along the base {111} (Miller), that is to say parallel to the plane of the directions indicated above with a.

§ 3. In order to enrich somewhat our knowledge in this respect the plan was conceived to investigate in a series of determinations the thermic and electric conductivity-power of some higher and also of some lower-symmetrical crystalline conductors, and, if possible, of metals also. For the moment, I intend to determine the quotient of the conductivities in the different main directions, and afterwards perhaps to measure those conductivities themselves in an absolute degree.

I. On the thermic and electric conductivities in crystallised Bismuth and in Haematite.

Measurements of the thermic and electric conductivity of bismuth are already known.

Matteucci [2]) determined the thermic conductivity, by the well-

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[1]) H. Bäckström and K. Ångström, Ofvers. K. Vetensk. Akad. Förh. (1888) No. 8, 533; Bäckström, ibid. (1894), No. 10, 545.

[2]) Matteucci, Ann. Chim. et Phys. (3). **43**. 467. (1855).

well-known method of INGENHOUSZ, by measurement of the length of the melted off waxy layer which was put on the surface of cylindrical rods of bismuth, cut // and $\perp$ to the main axis, whilst the one end was plunged into mercury heated at 150°. For the average value of the quotient of the main conductivities — perpendicular and normal to the main axis — he found the value 1,08. JANNETTAZ's rule applies in this case, because the complete cleavability of ditrigonal bismuth takes place along {111} (MILLER), therefore, perpendicularly to the main axis. JANNETTAZ [1]) has applied the SÉNARMONT method to bismuth. He states that in bismuth the ellipses have a great eccentricity but he did not take, however, exact measurements.

A short time ago, LOWNDS [2]) has again applied the SÉNARMONT method to bismuth. He finds for the quotient of the demi-ellipsoidal axes 1.19 and, therefore for the quotient of the conductivities 1.42.

The last research is from PERROT [3]). By the SÉNARMONT method he finds as the axial quotient of the ellipses about 1.17 and consequently for the quotient of the conductivities $\perp$ and // axis 1.368, which agrees fairly well with the figure found by LOWNDS. Secondly, PERROT determined the said quotient by a method proposed by C. SORET, which had been previously recommended by THOULET [4]), namely, by measuring the time which elapses between the moments when two substances with known melting points ϑ_1 and ϑ_2 placed at a given distance at different sides of a block of the substance under examination begin to melt. As indices were used; *a-Naphtylamine* ($\vartheta = 50°$ C.), *o-Nitroaniline* ($\vartheta = 66°$ C.), and *Naphthalene* ($\vartheta = 79°$ C.).

As the mean of all the observations, PERROT finds as the quotient of the main conductivities 1,3683, which agrees perfectly with his result obtained by SÉNARMONT's method.

He, however, rightly observes that this concordance between the two results is quite *an accidental one*, and that the method of THOULET and SORET must *not* be considered to hold in all cases. The proof thereof has been given by CAILLER in a theoretical paper; [5]) the agreement is caused here by the accidental *small* value of a quotient $\frac{hl}{k}$, in which l represents the thickness of the little plate of bismuth

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[1]) JANNETTAZ, Ann. de chim. phys. **29**. 39. (1873).

[2]) L. LOWNDS, Phil. Magaz. V. 152. (1903).

[3]) L. PERROT, Archiv. d. Science phys. et nat. Généve (1904 . (4). **18**. 445.

[4]) THOULET, Ann. de Chim. Phys. (5). **26**. 261. (1882)

[5]) C. CAILLER, Archiv. de Scienc. phys. et nat. Genève (1904). (4). **18**. 457.

and h and k the coefficients of external and internal conductivity.

§ 4. I have endeavoured to determine the quotient of the chief conductivities by the method proposed by W. VOIGT.

As is wellknown, this method is based on the measurement of the angle, formed by the two isotherms at the line of demarcation between two little plates which have been joined to an artificial twin, when the heat current proceeds along the line of demarcation. If λ_1 and λ_2 are the two chief conductivities of a plate of bismuth cut parallel to the crystallographic main axis, and if the angle which the two main directions form with the line of demarcation equals 45°, then according to a former formula[1]):

$$\frac{\lambda_1}{\lambda_2} = tg\left(45^\circ + \frac{\varepsilon}{2}\right)$$

§ 5. The bismuth used was kindly furnished to me by Dr. F. L. PERROT, to whom I again wish to express my hearty thanks.

The prism investigated by me is the one which Dr. PERROT in his publications[2]) indicates with M, and for which, according to SÉNARMONT's method, he found for $\frac{\lambda_a}{\lambda_c}$ the value 1,390. The prism given to Dr. VAN EVERDINGEN yielded in the same manner for $\frac{\lambda_a}{\lambda_c}$ the value 1,408.

Two plates were cut parallel to the crystallographic axis, in two directions forming an angle of 90° and these were joined to twin plates with $\varphi = 45^\circ$.

It soon appeared that in this case the VOIGT method[3]) was attended by special difficulties which, as Prof. VOIGT informed me, is generally the case with *metals*. First of all, it is difficult to find a coherent coating of elaidic acid + wax; generally the fused mixture on the polished surface forms droplets instead of congealing to an even layer. Secondly, the isotherms are generally curved and their form presents all kinds of irregularities, which are most likely caused by the great specific conductivity of the metals, in connection with the peculiarity just mentioned. On the advice of Prof. VOIGT I first covered the metallic surface with a very thin coating of varnish; this dissolves in the fused acid, and causes in many cases a better cohesion, but even this plan did not yield very good results.

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[1]) These Proceedings. (1906). March p. 797.

[2]) p. 4, note 10.

[3]) VOIGT, Göttinger Nachr. (1896). Heft 3, p. 1—16; ibid. (1897). Heft 2. 1—5

However, at last, I succeeded in getting a satisfactory coating of the surface by substituting for white wax the ordinary, yellow bees-wax. This contains an adhesive substance probably derived from the honey, and, when mixed in the proper proportion with elaidic acid it yields the desired surface coating.

I have also coated [1]) the bottoms of the plate and the sides, except those which stand $\perp$ on the line of demarcation with a thick layer of varnish mixed with mercury iodide and copper iodide. During the operation the heating was continued to incipient darkening (about 70°).

The plates should have a rectangular or square form, as otherwise the isotherms generally become curved.

It is further essential to heat *rapidly* and to raise the copper bolt to a fairly high temperature; the isotherms then possess a more straight form and give more constant values for ε.

I executed the measurements on the double object table of a LEHMANN's crystallisation microscope on an object glass wrapped in thick washleather, to prevent the too rapid cooling and solidification of the coating.

After numerous failures, I succeeded at last in obtaining a long series of constant values. As the mean of 30 observations, I found $\varepsilon = 22°12'$ and therefore:

$$\frac{\lambda_a}{\lambda_c} = 1{,}489.$$

§ 6. The value now found is somewhat greater than that found by PERROT. I thought it would be interesting to find out in how far a similar deviation was present in other cases, and whether when compared with the results obtained by the methods of SÉNARMONT, JANETTAZ and ROENTGEN, it has always the same direction.

In fact, the investigation of many minerals has shown me that all values obtained previously, are *smaller* than those obtained by the process described here.

I was inclined at first to believe that these differences were still greater than those which are communicated here. Although a more extended research, including some plates kindly lent to me by Prof. VOIGT, showed that these differences are not so serious as I suspected, at first the deviation exists *always in the same direction.*

For instance, I measured the angle ε of a plate of an *Apatite*-crystal from Stillup in Tyrol and found this to be 17°. From the

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[1]) RICHARZ's method of experimenting (Naturw. Rundschau, **17**, 478 (1902)) did not give sufficiently sharply defined isotherms and was therefore not applied.

position of the isotherms it also follows that $\lambda_c > \lambda_a$ so that $\frac{\lambda_c}{\lambda_a} = 1,35$.

In a quartz-plate obtained from Prof. VOIGT I found $\varepsilon = 30\frac{1}{2}°$, therefore $\frac{\lambda_c}{\lambda_a} = 1,75$. In a plate of *Antimonite* from Skikoku in Japan cut parallel to the plane {010}, $\frac{\lambda_c}{\lambda_a}$ was found to be even much larger than 1,74, which value is deduced from the experiments of SÉNARMONT and JANNETTAZ as they find for the quotient of the demi ellipsoidal axes 1.32.

For *Apatite* they find similarly 1,08, for quartz 1,73, whilst TUCHSCHMIDT determined the heat-conductivity of the latter mineral according to WEBER's method in absolute degree. His experiments give the value 1,646 for the quotient $\frac{\lambda_c}{\lambda_a}$.

The deviations are always such that if $\lambda_1 > \lambda_2$ the values of the quotient $\frac{\lambda_1}{\lambda_2}$ turn out to be *larger* when VOIGT's method is employed instead that of DE SÉNARMONT. The method employed here is, however, so sound in principle, and is so much less liable to experimental errors, that it certainly deserves the preference over the other processes.

Finally, a sample of *Haematite* from Elba was examined as to its conducting power. A plate cut parallel to the *c*-axis was found not to be homogeneous and to contain gas-bubbles. I repeatedly measured the angles ε of a beautifully polished preparation of Prof. VOIGT, and found fairly constantly $10\frac{1}{2}°$, whilst the position of the isotherms showed that λ_a was again larger than λ_c.

For the *Haematite* we thus obtain the value: $\frac{\lambda_a}{\lambda_c} = 1,202$. The value found by BÄCKSTRÖM and ANGSTRÖM for their mineral with the aid of CHRISTIANSEN's method was 1,12. In this case the deviation also occurs in the above sense.

From the experiments communicated we find for the quotient $\varkappa_a : \varkappa_c$ in both crystal phases, if by this is meant $\left(\frac{\lambda}{\sigma}\right)_a : \left(\frac{\lambda}{\sigma}\right)_c$ the values:

With *Bismuth*: $\frac{\varkappa_a}{\varkappa_c} = 1,128$.

With *Haematite*: $\frac{\varkappa_a}{\varkappa_c} = 1,480$.

In this my measurements of $\frac{\lambda_a}{\lambda_c}$ are combined with the best value found by VAN EVERDINGEN [1]) with PERROT's prism, namely $\frac{\sigma_a}{\sigma_c} = 1{,}68$, and with the value found by the Swedish investigators for haematite· 1,78 at 50° C.

7. If there were a perfect concordance between theory and observation, we should have in both cases $\frac{\varkappa_a}{\varkappa_c} = 1$. The said values 1,128 and 1,480 are, therefore, in a certain sense a measure for the extent of the divergence between the observation and the conclusion which is rendered probable by the electron theory.

In the first place it will be observed that the agreement is much better with *bismuth* than with *haematite*. However, this may be expected if we consider that the theory has been proposed, in the first instance, for *metallic* conductors. The influence of the peculiar nature of the *oxide* when compared with the true *metal* is shown very plainly in this case.

The question may be raised whether, perhaps, there may be shown to exist some connection between the crystal structure and the chemical nature on one side, and the given values of $\frac{\varkappa_a}{\varkappa_c}$ on the other side.

Such a connection would have some significance because it may be, probably, a guide for the detection of special factors situated in the crystalline structure, which stand in the way of a complete agrement of electron theory and observations.

§ 8. First of all, it must be observed that we are easily led to compare the structures of the two phases. Both substances investigated crystallise ditrigonally and have an analogous axial quotient; for *bismuth*: $a : c = 1 : 1{,}3035$ (G. ROSE); for *haematite* $a : c = 1 : 1{,}3654$ (MELCZER). In both substances, the habit is that of the rhomboid, which in each of them approaches very closely to the regular hexahedron. The characteristic angle α is 87°34′ for *bismuth* for haematite 85°42′. Particularly in bismuth the pseudo-cubic construction is very distinct; the planes of complete cleavage which answer the forms $\{111\}$ and $\{11\overline{1}\}$ approach by their combination the regular octahedron in a high degree. Although haematite does not

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[1]) VAN EVERDINGEN, Archives Néerland. (1901) 371 ; Versl. Akad. v. Wet. (1895—1900) ; Comm. Phys. Lab. Leiden, 19, 26, 37, 40 and 61. See Archiv. Nêerl. p. 452 ; rods No. 1 and No. 5.

possess a perfect plane of cleavage, it may be cleaved in any case along {111} with testaceous plane of separation. It admits of no doubt that the elementary parallelepipeds of the two crystal structures are in both phases pseudo-cubic rhombohedral configurations and the question then rises in what proportion are the molecular dimensions of those cells in both crystals?

If, in all crystal-phases, we imagine the whole space divided into volume-units in such a manner that each of those, everywhere joined, mutually congruent, for instance cubic elements, just contains a single chemical molecule, it then follows that in different crystals the size of those volume elements is proportionate to $\frac{M}{d}$, in which M represents the molecular weight of the substances and d the sp. gr. of the crystals. If, now, in each crystal phase the content of the elementary cells of the structure is supposed to be equal to this equivalent-volume $\frac{M}{d}$, the dimensions of those cells will be reduced for all crystals to a same length unit, namely all to the length of a cubic-side belonging to the volume-element of a crystal phase, whose density is expressed by the same number as its molecular weight; then in that particular case $V=\frac{M}{d}=1$. If we now calculate the dimensions of such an elementary parallelopiped of a BRAVAIS structure whose content equals the quotient $\frac{M}{d}$ and whose sides are in proportion to the crystal parameters $a:b:c$, the dimensions χ, ψ and ω thus found will be the so-called *topic parameters* of the phase which, after having been introduced by BECKE and MUTHMANN independently of each other, have already rendered great services in the mutual comparison of chemically-different crystal-phases. In the particular case, that the elementary cells of the crystal-structure possess a rhombohedral form, as is the case with ditrigonal crystals, the parameters χ, ψ and ω become equal to each other $(=\varrho)$. The relations applying in this case are

$$\varrho=\left(\frac{V}{sin^2\,\alpha\,.\,sin\,A}\right)^{\frac{1}{3}},\quad \text{with}\quad sin\,\frac{A}{2}=\frac{sin\,\frac{\alpha}{2}}{sin\,\alpha}.$$

If now these calculations are executed with the values holding here: $Bi=207{,}5$; $Fe_2O_3=159{,}64$; $d_{Bi}=9{,}851$ (PERROT); $d_{Fe_2O_3}=4{,}98$, then

$$V_{Bi} = 21,064 \text{ and } V_{Fe_2O_3} = 32,06,$$

and with the aid of the given relations and the values for a and A we find for each phase:[1])

$$\frac{\varrho_{Bi}}{\varrho_{Fe_2O_3}} = \frac{2,7641}{3,1853}.$$

If now we just compare these values for the sides of the rhombohedral elementary cells of the crystal structure with those of the quotients $\frac{\varkappa_a}{\varkappa_c}$ in the two phases, they curiously enough show the following relation:

$$\left(\frac{\varkappa_a}{\varkappa_c}\right)_{Fe_2O_3} : \left(\frac{\varkappa_a}{\varkappa_c}\right)_{Bi} = \varrho^2_{Fe_2O_3} : \varrho^2_{Bi} = 1,32.$$

Allowing for experimental errors, the agreement is all that can be desired: in the first term of the equation the value is exactly: 1.312, in the last term: 1,328.

In our case the quotient $\frac{\varkappa_a}{\varkappa_c}$ may therefore be written for both phases in the form: $C.\varrho^2$, in which C is a constant independent of the particular chemical nature of the phase.

Instead of the relation

$$\varrho_1^2 : \varrho_2^2, \text{ perhaps } \varrho_1^2 \sin \alpha_1 : \varrho_2^2 \sin \alpha_2 = 1.305$$

is still more satisfactory. These expressions, however, represent nothing else *but the surface of the elementary mazes of the three chief planes of the trigonal molecule structure,* for these are in our case squares whose flat axis $= \alpha$. The quotient $\frac{\varkappa_a}{\varkappa_c}$ in the two phases should then be directly proportional to the reticular density of the main net-planes of BRAVAIS's structures.

A choice between this and the above conception cannot yet be made, because α_1 and α_2 differ too little from 90°. Moreover, a further investigation of other crystals will show whether we have to do here with something more than a mere accidental agreement. Similar investigations also with lower-symmetric conductors are at this moment in process and will, I hope, be shortly the subject of further communications.

Zaandam, May 1906.

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[1]) For bismuth $\alpha = 87°:34'$ and $A = 87°40'$: for haematite $\alpha = 85°42'$ and $A = 86°0'$. The angle A is the supplement of the right angle on the polar axes of the rhombohedral cells and α is the flat angle enclosed between the polar axes.

Chemistry. — *"Three-phaselines in chloralalcoholate and aniline-hydrochloride"*. By Prof. H. W. Bakhuis Roozeboom.

It is now 20 years since the study of the dissociation phenomena of various solid compounds of water and gases enabled me to find experimentally the peculiar form of that three-phaseline which shows the connection between temperature and pressure for binary mixtures in which occurs a solid compound in presence of solution and vapour, The general significance of that line was deduced, thermodynamically, by van der Waals and the frequency of its occurrence was proved afterwards by the study of many other systems.

That this three-phaseline is so frequently noticed in practice in the study of dissociable compounds is due to the circumstance that, in the majority of the most commonly occurring cases, the volatility of the two components or of one of them, is so small, that at the least dissociation of the compound both liquid and vapour occur in its presence.

In the later investigations, which have led to a more complete survey of the many equilibria which are possible between solid liquid and gaseous phases, pressure measurements have been somewhat discarded. When, however, the survey as to the connection of all these equilibria in binary mixtures got more and more completed and could be shown in a representation in space on three axes of concentration, temperature and pressure, the want was felt to determine for some equilibria, theoretically and also experimentally, the connection between temperature and pressure, in order to fill up the existing voids.

Of late, the course and the connection of several p,t-lines, have been again studied by van der Waals, Smits and myself either qualitatively or qualitative-quantitatively.

To the lines, which formerly had hardly been studied, belonged the equilibria lines which are followed, when, with a constant volume, the compound is exposed to change of temperature in presence of vapour only. They can be readily determined experimentally only when the volatility of the least volatile component is not too small. Stortenbeker at one time made an attempt at this in his investigation of the compounds of iodine with chlorine, but did not succeed in obtaining satisfactory data.

In the second place it was desirable to find some experimental confirmation for the peculiar form of the three-phaseline of a compound, recently deduced by Smits for the case in which a minimum occurs in the pressure of the liquid mixtures of its components.

Mr. Leopold has now succeeded in giving experimental contributions in regard to both questions, by means of a series of very accurately conducted researches where chloralalcoholate and anilinehydrochloride occur as solid compounds.

Solid compounds which yield two perceptibly volatile components (such as PCl_5, $NH_3.H_2S$, $PH_3.HCl$, $CO_2.2\,NH_3$ etc.) have been investigated previously, but either merely as to their condition of dissociation in the gaseous form, or as to the equilibrium of solid in presence of gaseous mixtures of different concentration at constant temperature; but liquids occur only at higher pressures, so that the course of the three-phase lines had never been studied.

These two compounds were selected because in their melting points neither temperature nor pressure were too high. Moreover, the difference in volatility of the two components in the first example (chloral + alcohol) was much smaller than in the second (aniline + hydrogen chloride). It was also safe to conclude from the data of both compounds that the liquid mixtures of their components would show a minimum pressure.

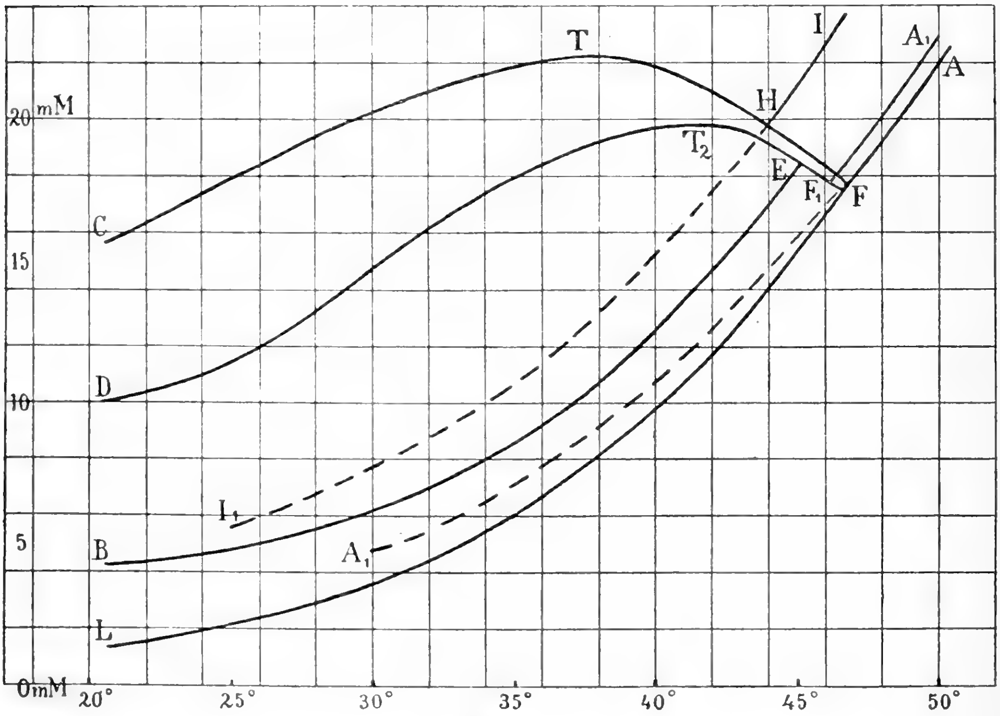

Fig. 1.

This last point was ascertained first of all by a determination of the boiling point lines, in which a maximum must occur. In both cases this was found to exist and to be situated at the side of the least volatile component, respectively chloral or aniline.

The investigation of the three-phase lines showed first of all that these possess the expected form in which two maxima and one minimum of pressure occur.

In the first system (Fig 1) CFD is the three-phase line, T and T_2 are the respective maxima for the vapour pressure of solutions with excess of either alcohol or chloral and saturated with chloralalcoholate; the minimum is situated very close to the melting point F.

In the second system (anilinehydrochloride Fig. 2) the first maximum, in presence of excess of HCl is situated at such an elevated

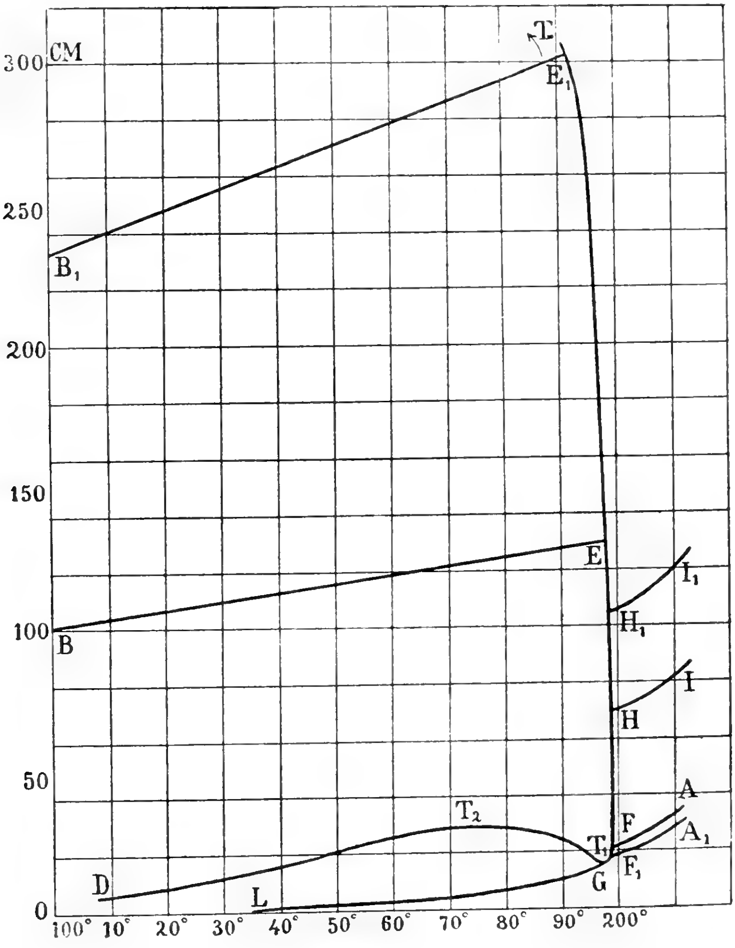

Fig. 2.

pressure that this has not been determined, the second T_2 at a moderate pressure is situated at the side of the aniline. The minimum T_1 is situated at the same side and is removed further from the melting point than in Fig. **1**.

	T_1 minimum	F melting point
p	16 cM.	22.5 cM.
t	197°	199°2

The determination of these lines and also that of the equilibria-lines for compound + vapour or liquid + vapour which also occur in both figures can only take place on either side of point F, for in measuring the pressures, we can only have in the apparatus a larger, or smaller, excess of either component. Moreover, it is possible to fill the apparatus with the compound in a dry and pure condition. In the case of the compounds employed, this was attained by preparing very pure crystals by repeated sublimation in vacuo.

In the second example, the sublimation line LG of aniline hydrochloride was thus determined. On this line then follows the piece GF of the three-phase line, because beyond G, no vapour can exist which has the same composition as the compound, except in the presence of some excess of HCl, so that a little liquid is formed with a slight excess of aniline. If, however, the apparatus is properly filled with the compound so that there remains but little space for the vapour then the three-phase line G may be traced to very near the melting point F, where one passes on to the line FA, for the equilibrium of the fused compound with its vapour.

We have here, therefore, the first experimental confirmation of the normal succession of the p,t-lines when those are determined with a pure compound which dissociates more or less.

Theoretically, the minimum T_1 in the three-phaseline must be situated at the left of the terminal point G of the sublimationline. The difference here, although small, is yet perfectly distinct:

	T_1	G
p	16 cM.	16.5 cM.
t	197°	198°

In the case of chloralalcoholate the points T_1 and G both coincide so nearly with F that this point is practically undistinguishable from the triple point of a non-dissociating compound, both LF and FA, or their metastable prolongation FA' appear to intersect in F. Moreover, the investigation of the melting point line proved that chloralalcoholate in a melted condition is but little dissociated.

In both compounds the p,t-lines have also been determined with excess of chloral or aniline. A very small quantity of these suffices to cause the occurrence of liquid in presence of the compound at temperatures far below the melting point and we then move on the lowest branch of the three-phaseline.

In the case of a slight excess of chloral (Fig. 1) this was followed from D over T_2 to F_1 just a little below the melting point, and from there one passed on to the liquid-vapour line F_1A_1, which was situated a little above FA.

In the case of a slight excess of aniline the piece $DT_2T_1GF_1$ could be similarly followed (Fig. 2). In this occurred the minimum T_1, whilst the piece GF_1 coincided entirely with the corresponding part of GF, which had already been determined in the experiment with the pure compound. Just below F the compound had disappeared entirely and one passed on to the liquid-vapour line F_1A_1, which, unlike that in Fig. 1, was situated below FA.

If the excess of the component is very trifling, liquid is formed only at higher temperatures of the three-phaseline, and below this temperature a sublimationline is determined, with excess of the component in the vapour, which line must, therefore, be situated higher than the pure sublimationline.

With chloralalcoholate a similar line BE (Fig 1) was determined, situated decidedly above LF. At E, liquid occurred and a portion of the three-phaseline EF was followed up to a point situated so closely to F that the liquid-vapourline, which was then followed, was situated scarcely above FA.

The excess of chloral was, therefore, exceedingly small, but in spite of this, BE was situated distinctly above LF. The position of BE depends, in a large measure, on the gas-volume above the solid compound, as this determines the extra pressure of the excess of the component, which is totally contained in the same; so long as no liquid occurs. It appeared, in fact, to be an extremely difficult matter to prepare chloralalcoholate in such a state of purity that it exhibited the lowest imaginable sublimationline LF, which meets the three-phaseline in F.

Similar sublimation lines may also occur with mixtures containing excess of alcohol. But also in this case, even with a very small excess of alcohol we shall retain liquid even at low temperatures and, therefore, obtain branch CTF of the three-phaseline. Such happens, for instance, always when we use crystals of the compound which have been crystallised from excess of alcohol. They then contain sufficient mother-liquor.

We then notice the peculiar phenomenon that the compound is apparently quite solid till close to the melting point and we find for the vapour pressure the curve CTF, whilst the superfused liquid gives the vapour pressureline FA_1 which is situated much lower. Ramsay has found this previously without being able to give an explanation, as the situation of the three-phaseline was unknown at that period.

In the case of anilinehydrochloride, it was not difficult, on account of the great volatility of HCl, to determine sublimationlines when an excess of this component was present. In Fig. 2 two such lines are determined BE and B_1E_1. From E_1 the three-phaseline was followed over the piece E_1H_1 afterwards the liquid-vapourline H_1I_1. From E also successively EH and HI. With a still smaller excess of hydrogen chloride we should have stopped even nearer to F on the three-phaseline.

In the case of chloralalcoholate we noticed also the phenomenon that a solid substance which dissociates after fusion may, when heated not too slowly, be heated above its meltingpoint, a case lately observed by Day and Allen on melting complex silicates, but which had also been noticed with the simply constituted chloralhydrate.

An instance of the third type of a three-phaseline where the maximum and minimum have disappeared in the lower branch of the three-phase line has not been noticed as yet.

The two types now found will, however, be noticed frequently with other dissociable compounds such as those mentioned above, and therefore enable us to better understand the general behaviour of such substances.

Physics. — *"On the polarisation of Röntgen rays."* By Prof. H. Haga.

In vol. 204 of the Phil. Trans. Royal Soc. of London p. 467, 1905 Barkla communicates experiments which he considers as a decisive proof that the rays emitted by a Röntgen bulb are partially polarised, in agreement with a prediction of Blondlot founded upon the way in which these rays are generated.

In these experiments Barkla examined the secondary rays emitted by air or by some solids: paper, aluminium, copper, tin, by means of the rate of discharge of electroscopes. In two directions perpendicular to one another and both of them perpendicular to the direction of the primary rays, he found a maximum and a minimum for the action of the secondary rays emitted by air, paper and aluminium.

The difference between the maximum and minimum amounted to about 20°/$_0$.

I had tried to examine the same question by a somewhat different method. A pencil of RÖNTGEN rays passed through a tube in the direction of its axis, without touching the wall of the tube. A photographic film, bent cylindrically, covered the inner wall of the tube in order to investigate whether the secondary rays emitted by the air particles showed a greater action in one direction than in another. I obtained a negative result and communicated this fact to BARKLA, who advised me to take carbon as a very strong radiator for secondary rays. I then made the following arrangement.

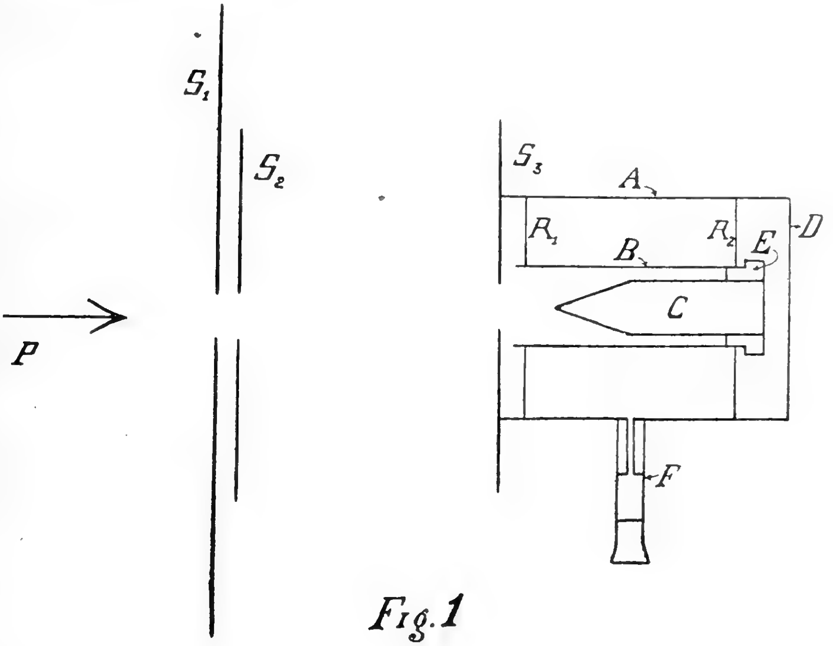

Fig. 1

Let S_1 (fig. 1) be the front side of a thick-walled leaden box, in which the RÖNTGEN bulb is placed; S_2 and S_3 brass plates 10 × 10 c.m. large and 4 m.m. thick. Their distance is 15 c.m. and they are immovably fastened to the upper side of an iron beam. In the middle of these plates apertures of 12 m.m. diameter were made. A metal cylinder A is fastened to the back side of S_3; a brass tube B provided with two rings R_1 and R_2 slides into it 1).

An ebonite disk E in which a carbon bar is fastened fits in tube B. This bar is 6 c.m. long and has a diameter of 14 m.m. At one end it has been turned off conically over a length of 2 c.m.

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1) Fig. 1 and 2 are drawn at about half their real size.

The aperture in S_3 was closed by a disk of black paper; the back side of A was closed by a metal cover, which might be screwed off.

The dimensions were chosen in such a way, that the boundary of the beam of Röntgen rays, which passed through the apertures in S_1, S_2 and S_3, lay between the outer side of the carbon bar and the inner side of the tube B. The photographic film covering the inside of B was therefore protected against the direct Röntgen rays.

If we accept Barkla's supposition on the way in which the secondary beams are generated in bodies of small atomic weight, and if the axis of the primary beam perfectly coincided with that of the carbon bar, then a total or partial polarisation of the Röntgen rays would give rise to two maxima of photographic action on diametrically opposite parts of the film and between them two minima would be found. From the direction of the axis of the cathode rays the place of these maxima and minima might be deduced.

A very easy method proved to exist for testing whether the primary beam passed symmetrically through the tube B or not. If namely the inner surface of cover D was coated by a photographic plate or film, which therefore is perpendicular to the axis of the carbon bar then we see after developing a sharply defined bright ring between the dark images of the carbon bar and of the ebonite disk. This ring could also be observed on the fluorescent screen — but in this case of course as a dark one, — and the Röntgen bulb could easily be placed in such a way, that this ring was concentric with the images of the carbon bar and of the ebonite disk.

This ring proved to be due to the rays that diverged from the anticathode but did not pass through the carbon bar perfectly parallel to the axis and left it again on the sides; these rays proved to be incapable of penetrating the ebonite, but were totally absorbed by this substance; when the ebonite disk was replaced by a carbon one, then the ring disappeared; it is therefore a very interesting instance of the selective absorption of Röntgen rays[1]).

When in this way the symmetrical passage of the Röntgen rays had been obtained, then the two maxima and minima never appeared, neither with short nor with long duration of the experiment, though a strong photographic action was often perceptible on the film. Such an action could for instance already be observed after one hour's exposure, if an induction-coil of 30 cm. striking distance was used with a turbine interruptor. A storage battery of 65 volts was used;

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[1]) Take for this experiment the above described arrangement, but a carbon bar of 1 cm. diameter and 4 cm. long.

the current strength amounted to 7 ampères; the Röntgen bulb was "soft".

Sometimes I obtained one maximum only or an irregular action on the film, but this was only the case with an asymmetric position of the apparatus.

From these experiments we may deduce: 1st that the primary Röntgen rays are polarised at the utmost only to a very slight amount, and 2nd that *possibly* an asymmetry in the arrangement caused the maxima and minima observed in the experiments of Barkla, who did not observe at the same time in two diametrical opposite directions.

With nearly the same arrangement I repeated Barkla's experiments on the polarisation of secondary rays, which he has shown also by means of electroscopes and described Proc. Roy. Soc. Series A vol. 77, p. 247, 1906.

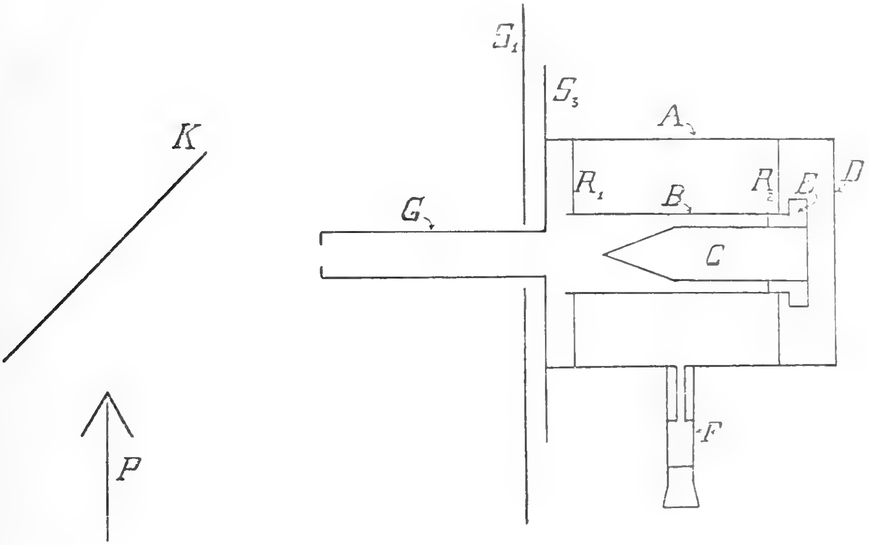

Fig. 2

Let the arrow (fig. 2) indicate the direction of incidence of the Röntgen rays on the carbon plate *K* large 8 × 8 cm. and thick 12 mm. The secondary rays emitted by this plate could pass through the brass tube *G*, which was fastened to S_3. This tube was 6 cm. long and on the frontside it was provided with a brass plate with an aperture of 5 mm. It was placed within the leaden case at 8 cm. distance from the middle of the carbon plate; leaden screens protected the tube against the direct action of the primary rays. In these experiments the above mentioned induction-coil was used with a

Wehnelt interruptor; the voltage of the battery amounted to 65 Volts and the current to 7 Ampères. A very good photo was obtained in 30 hours and it shows very clearly two maxima and two minima, the distance between the centra of the maxima is exactly half the inner circumference of the tube, and it may be deduced from their position that they are caused by the tertiary rays emitted by the conic surface of the carbon bar.

In this experiment the centre of the anticathode, the axis of the carbon bar and the centre of the carbon plate lay in one horizontal plane, and the axis of the cathode rays was in one vertical plane with the centre of the carbon plate; the axes of the primary and the secondary beams were perpendicular to one another. According to Barkla's supposition we must expect that with this arrangement the maximum of the action of the tertiary rays will be found in the horizontal plane above mentioned. In my experiment this supposition really proved to be confirmed. In order to know what part of the photographic film lay in this plane, a small side-tube *F* was adjusted to the outside of cylinder *A*, and this tube *F* was placed in an horizontal position during the experiment. A metal tube with a narrow axial hole fitted in tube *F*, so that in the dark room, after taking away a small caoutchouc stopper which closed *F*, I could prick a small hole in the film with a long needle through this metal tube and through small apertures in the walls of *A* and *B*. This hole was found exactly in the middle of one of the maxima.

So this experiment confirms by a photographic method exactly what Barkla had found by means of his electroscopes and it proves that the secondary rays emitted by the carbon are polarised.

In some of his experiments Barkla pointed out the close agreement in character of primary and secondary Röntgen rays; in my experiments also this agreement was proved by the radiogram obtained on the film placed in cover *D*. Not only did the secondary rays act on the film after having passed through the carbon bar of 6 cm., but also the bright ring was clearly to be seen, which proves that ebonite absorbs all secondary rays which have passed through carbon [1]). The ring was not so sharply defined as in the experiments with primary rays; this fact finds a natural explanation in the different size of the sources of the radiation: in the case of the primary rays the source is a very small part of the anticathode, in the case of the secondary rays it is the rather large part of the carbon plate which emits rays through the apertures in *G* and S_3.

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[1]) The ring was perfectly concentric: the arrangement proved therefore to be exactly symmetrical.

This agreement makes it already very probable that the RÖNTGEN rays also consist in *transversal* vibrations; these experiments however yield a firmer proof for this thesis. If namely we accept the supposition of BARKLA as to the way of generation of secondary rays in bodies with a small atomic weight, then it may easily be shown, that the supposition of a *longitudinal* vibration of the primary RÖNTGEN rays would, in the experiment discussed here, lead to a maximum action of the tertiary rays in a *vertical* plane and not in an *horizontal* plane, as was the case.

Groningen, Physical Laboratory of the University.

Chemistry. — "*Triformin* (*Glyceryl triformate*)". By Prof. P. VAN ROMBURGH.

Many years ago I was engaged in studying the action of oxalic acid on glycerol [1]) and then showed that in the preparation of formic acid by LORIN's method diformin is produced as an intermediate product.

Even then I made efforts to prepare triformin, which seemed to me of some importance as it is the most simple representative of the fats, by heating the diformin with anhydrous oxalic acid, but I was not successful at the time. Afterwards LORIN [2]) repeated these last experiments with very large quantities of anhydrous oxalic acid and stated that the formic acid content finally rises to 75 %, but he does not mention any successful efforts to isolate the triformin.

Since my first investigations, I have not ceased efforts to gain my object. I confirmed LORIN's statements that on using very large quantities of anhydrous oxalic acid, the formic acid content of the residue may be increased and I thought that the desired product might be obtained after all by a prolonged action.

Repeated efforts have not, however, had the desired result, although a formin with a high formic acid content was produced from which could be obtained, by fractional distillation in vacuo, a triformin still containing a few percent of the di-compound.

I will only mention a few series of experiments which I made at Buitenzorg, first with Dr. NANNINGA and afterwards with Dr. LONG. In the first, a product was obtained which had a sp.gr. 1.309 at 25°, and gave on titration 76.6 % of formic acid, whilst pure triformin requires 78.4 %. The deficiency points to the presence of fully 10 % of diformin in the product obtained.

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[1]) Compt. Rend. 93 (1881) 847.

[2]) Compt. Rend. 100 (1885) 282.

In the other, the diformin, was treated daily, during a month, with a large quantity of anhydrous oxalic acid, but even then the result was not more favourable.

The difficulty in preparing large quantities of perfectly anhydrous oxalic acid coupled with the fact that carbon monoxide is formed in the reaction, which necessitates a formation of water from the formic acid, satisfactorily explains the fact that the reaction does not proceed in the manner desired. A complete separation of di- and triformin cannot be effected in vacuo as the boiling points of the two compounds differ but little.

I, therefore, had recourse to the action of anhydrous formic acid on diformin. I prepared the anhydrous acid by distilling the strong acid with sulphuric acid in vacuo and subsequent treatment with anhydrous copper sulphate. Even now I did not succeed in preparing the triformin in a perfectly pure condition, for on titration it always gave values indicating the presence of some 10°/₀ of diformin.

Afterwards, when 100°/₀ formic acid had become a cheap commercial product, I repeated these experiments on the larger scale, but, although the percentage of diformin decreased, a pure triformin was not obtained.

I had also tried repeatedly to obtain a crystallised product by refrigeration but in vain until at last, by cooling a formin with high formic acid content in liquefied ammonia for a long time, I was fortunate enough to notice a small crystal being formed in the very viscous mass. By allowing the temperature to rise gradually and stirring all the while with a glass rod, I succeeded in almost completely solidifying the contents of the tube. If now the crystals are drained at 0° and pressed at low temperature between filter paper and if the said process is then repeated a few times, we obtain, finally, a perfectly colourless product melting at 18°, which on being titrated gave the amount of formic acid required by triformin.

The sp. gr. of the fused product at 18° is 1.320.

$$n_{18}^{d} = 1.4412.$$

MR. 35.22 ; calculated 35.32.

The pure product when once fused, solidifies on cooling with great difficulty unless it is inoculated with a trace of the crystallised substance. On rapid crystallisation needles are obtained, on slow crystallisation large compact crystals are formed.

In vacuo it may be distilled unaltered; the boiling point is 163° at 38^{mm}. On distillation at the ordinary pressure it is but very slightly decomposed. The boiling point is then 266°. A product contaminated with diformin, however, cannot be distilled under those circumstances, but is decomposed with evolution of carbon monoxide and dioxide and formation of allyl formate.

If triformin is heated slowly a decided evolution of gas is noticed at 210° but in order to prolong this, the temperature must rise gradually. The gas evolved consists of about equal volumes of carbon monoxide and dioxide. The distillate contains as chief product allyl formate, some formic acid, and further, small quantities of allyl alcohol. In the flask a little glycerol is left [1]).

Triformin is but slowly saponified in the cold by water in which it is insoluble, but on warming saponification takes place rapidly.

Ammonia acts with formation of glycerol and formamide. With amines, substituted formamides are formed, which fact I communicated previously [2]).

The properties described show that triformin, the simplest fat, differs considerably in its properties from the triglycerol esters of the higher fatty acids.

Chemistry. — "*On some derivatives of* 1-3-5-*hexatriene*". By Prof. P. VAN ROMBURGH and Mr. W. VAN DORSSEN.

In the meeting of Dec. 30 1905 it was communicated that, by heating the diformate of s-divinylglycol we had succeeded, in preparing a hydrocarbon of the composition C_6H_8 to which we gave the formula:

$$CH_2 = CH - CH = CH - CH = CH_2.$$

Since then, this hydrocarbon has been prepared in a somewhat larger quantity, and after repeated distillation over metallic sodium, 50 grams could be fractionated in a LADENBURG flask in an atmosphere of carbon dioxide.

The main portion now boiled between 77°—78°.5 (corr.; pressure 764.4 mm.).

$$\text{Sp. gr.}_{13.5} \quad 0.749$$
$$n_{D13.5} \quad 1.4884$$

Again, a small quantity of a product with a higher sp. gr. and a larger index of refraction could be isolated.

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[1]) This decomposition of triformin has induced me to study the behaviour of the formates of different glycols and polyhydric alcohols on heating. Investigations have been in progress for some time in my laboratory.

[2]) Meeting 30 Sept. 1905.

In the first place the action of bromine on the hydrocarbon was studied.

If to the hydrocarbon previously diluted with chloroform we add drop by drop, while agitating vigorously with a WITT stirrer, a solution of bromine in the same solvent, the temperature being — 10°, the bromine is absorbed instantly and as soon as one molecule has been taken up the liquid turns yellow when more is added. If at that point the addition of bromine is stopped and the chloroform distilled off in vacuo, a crystalline product is left saturated with an oily substance. By subjecting it to pressure and by recrystallisation from petroleum ether of low boiling point, fine colourless crystals are obtained which melt sharply at 85°.5—86° [1]).

A bromine determination according to LIEBIG gave 66.84°/₀, $C_6H_8Br_2$ requiring 66.65°/₀.

A second bromine additive product, namely, a tetrabromide was obtained by the action of bromine in chloroform solution at 0° in sunlight; towards the end, the bromine is but slowly absorbed. The chloroform is removed by distillation in vacuo and the product formed is recrystallised from methyl alcohol. The melting point lies at 114°—115° and does not alter by recrystallisation. Analysis showed that four atoms of bromine had been absorbed.

Found: Br: 80.20. Calculated for $C_6H_8Br_4$ 79.99.

A third bromine additive product was found for the first time in the bromine which had been used in the preparation of the hydrocarbon to retain any hexatriene carried over by the escaping gases. Afterwards it was prepared by adding 3 mols of bromine to the hydrocarbon diluted with 1 vol. of chloroform at 0° and then heating the mixture at 60° for 8 hours. The reaction is then not quite completed and a mixture is obtained of tetra- and hexabromide from which the latter can be obtained, by means of ethyl acetate, as a substance melting at 163°.5—164°.

Found: Br. 85.76. Calculated for $C_6H_8Br_6$ 85.71.

On closer investigation, the dibromide appeared to be identical with a bromide obtained by GRINER [1]) from s. divinyl glycol with phosphorus tribromide; of which he gives the melting point as 84°.5—85°. A product prepared according to GRINER melted at 85°.5—86° and caused no lowering of the meltingpoint when added to the dibromide of the hydrocarbon.

GRINER obtained, by addition of bromine to the dibromide prepared from his glycol, a tetrabromide melting at 112° together with a

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[1]) Not at 89° as stated erroneously in the previous communication.

product melting at 108°—109°, which he considers to be a geometrical isomer. On preparing [2]) the tetrabromide according to GRINER the sole product obtained was that melting at 112°, which proved identical with the tetrabromine additive product prepared from the hydrocarbon, as described above. For a mixture of these two bromides exhibited the same meltingpoint as the two substances separately.

Prolonged action of bromine on the tetrabromide according to GRINER, yielded, finally, the hexabromide melting at 163°—164°, which is identical with the one prepared from the hydrocarbon.

The bromine derivatives described coupled with the results of GRINER prove that our hydrocarbon has indeed the formula given above.

According to THIELE's views on conjugated double bonds we might have expected from the addition of two atoms of bromine to our hexatriene the formation of a substance with the formula

$$CH_2Br - CH = CH - CH = CH - CH_2Br \quad . \quad . \quad . \quad (1)$$

or

$$CH_2Br - CH = CH - CHBr - CH = CH_2. \quad . \quad . \quad (2)$$

from the first of which, on subsequent addition of two bromine atoms the following tetrabromide would be formed.

$$CH_2Br - CHBr - HC = CH - CHBr - CH_2Br. \quad . \quad . \quad (3)$$

As, however, the dibromide obtained is identical with that prepared from s. divinyl glycol, to which, on account of its mode of formation, we must attribute the formula

$$CH_2 = CH - CHBr - CHBr - CH = CH_2 \quad . \quad . \quad . \quad (4)$$

(unless, what seems not improbable considering certain facts observed, a bromide of the formula (1) or (2) should have really formed by an intramolecular displacement of atoms) the rule of THIELE would not apply in this case of two conjugated systems.

Experiments to regenerate the glycol from the dibromide have not as yet led to satisfactory results, so that the last word in this matter has not yet been said. The investigation, however, is being continued.

Meanwhile, it seems remarkable that only the first molecule of bromine is readily absorbed by a substance like this hexatriene, which contains the double bond three times.

By means of the method of SABATIER and SENDERENS, hexatriene may be readily made to combine with 6 atoms of hydrogen. If its

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[1]) Ann. chim. phys. [6] **26**. (1892) 381.

[2]) Investigations on a larger scale will have to decide whether an isomer, melting at 108°, really occurs there as a byproduct which then exerts but a very slight influence on the melting point of the other product.

vapour mixed with hydrogen is passed at 125°—130° over nickel reduced to a low temperature, the hydrogen is eagerly absorbed and a product with a lower boiling point is obtained, which, however, contains small quantities of unsaturated compounds (perhaps also cyclic ones). In order to remove these, the product was treated with bromine and after removal of the excess and further purification it was fractionated. As a main fraction, there was obtained a liquid boiling at 68°.5—69°.5 at 759.7 mm.

$$Sp.\ gr._{12°} = 0{,}6907 \qquad n_{D_{12°}} = 1.3919.$$

Although the boiling point agrees with that of the expected hexane the sp. gr. and the refraction differ still too much from the values found for hexane by BRÜHL and by EYKMAN[1]).

Therefore, the product obtained from hexatriene was shaken for some time with fresh portions of fuming sulphuric acid until this was no longer coloured. After this treatment were obtained one fraction of

B. p. 69°—70°, $Sp. gr._{14}$ 0.6718 $n_{D_{14}}$ 1.38250.

and another of

B. p. 69°.7—70°5, $Sp. gr._{14}$ 0.6720, $n_{D_{14}}$ 1.38239.

An *n*-hexane prepared in the laboratory, according to BRÜHL[2]) by Mr. SCHERINGA gave the following values

B. p. 69°, $Sp. gr._{14}$ 0.664 $n_{D_{14}}$ 1.3792

whilst an *n*-hexane prepared, from diallyl according to SABATIER and SENDERENS, by Mr. SINNIGE gave

B. p. 68.5°—70,° $Sp. gr._{10}$ 0.6716, $n_{D_{10}}$ 1.38211.

It is, therefore, evident that the hexane obtained by SABATIER'S, and SENDERENS' process still contains very small traces of impurities.

There cannot, however, exist any doubt that 1-3-5-hexatriene absorbs 6 atoms of hydrogen with formation of normal hexane.

Of greater importance, however, for the knowledge of the new hydrocarbon is the reduction by means of sodium and absolute alcohol.

If, as a rule, unsaturated hydrocarbons are not likely to take up hydrogen under these circumstances, it becomes a different matter when a conjugated system is present. Now, in 1-3-5-hexatriene, two conjugated systems are found and we might therefore expect the occurrence of a 2-4-hexadiene:

$$CH_3—CH=CH—CH=CH—CH_3$$

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[1]) BRÜHL (B. B. **27**, (1894) 1066) finds $Sp. gr._{20} = 0.6603$, $n_{D_{20}} = 1.3734$.; EYKMAN (R. **14**, (1881) 187) $Sp. gr._{14} = 0.6652$ $n_{D_{14}} = 1.37725$.

[2]) Ann. **200**. 183.

or, of a 2-5-hexadiene:

$$CH_3—CH=CH—CH_2—CH=CH_2.$$

The first, still having a conjugated system can again absorb two atoms of hydrogen and then yield hexene 3.

$$CH_3—CH_2—CH=CH—CH_2—CH_3$$

whilst the other one cannot be hydrogenated any further [1]).

The results obtained seem to point out that both reactions have indeed taken place simultaneously, and that the final product of the hydrogenation is a mixture of hexadiene with hexene.

10 grams of 1-3-5-hexatriene were treated with 100 grams of boiling absolute alcohol and 15 grams of metallic sodium. After the sodium had dissolved, a current of steam was passed, which caused the ready separation of the hydrocarbon formed, which, however, still contained some alcohol. After redistillation, the hydrocarbon was washed with water, dried over calcium chloride and distilled over metallic sodium.

At 75°.5 it commenced to boil and the temperature then slowly rose to 81°. The liquid was collected in two fractions.

fraction I. B.p. 75°.5—78°, $Sp.gr._{10}$ 0.7326 $n_{D_{10}}$ = 1.4532
„ II. „ 78° —79°.5. „ — „ = 1.4665

These fractions were again united and once more treated with sodium and alcohol. But after purification and drying no liquid of constant boiling point was obtained, for it now commenced to boil at 72°.5, the temperature rising to 80°. The main fraction now possessed the following constants:

B.p. 72°.5—74°, $Sp.gr._{12}$ 0.7146 $n_{D_{12}}$ 1.4205

The fraction 75°—80 gave $n_{D_{12}}$ 1.4351.

An elementary analysis of the fraction boiling at 72°.5—74° gave the following result:

Found	Calculated for C_6H_{10}	Calculated for C_6H_{12}
C 87.06	87.7	85.6
H 13.32	12.3	14.4

The fraction investigated consists, therefore, probably of a mixture of C_6H_{10} and C_6H_{12}. The quantity collected was insufficient to effect another separation. We hope to be able to repeat these experiments on a larger scale as soon as we shall have again at our disposal a liberal supply of the very costly primary material.

Utrecht, Org. Chem. Lab. University.

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[1]) If $CH_2=CH—CH_2—CH_2—CH=CH_2$ should be formed, this will not readily absorb more hydrogen either.

Mathematics. — *"The force field of the non-Euclidean spaces with negative curvature"*. By Mr. L. E. J. BROUWER. (Communicated by Prof. D. J. KORTEWEG).

A. *The hyperbolic Sp_3*.

I. Let us suppose a rectangular system of coordinates to be placed thus that $ds = \sqrt{A^2\,du^2 + B^2\,dv^2 + C^2\,dw^2}$, and let us assume a line-vector distribution X with components X_u, X_v, X_w, then the integral of X along a closed curve is equal to that of the planivector Y over an arbitrary surface bounded by it; here the components of Y are determined by:

$$Y_u = \frac{1}{BC}\left\{\frac{\partial\,(X_v\,B)}{\partial w} - \frac{\partial\,(X_w\,C)}{\partial v}\right\}, \text{ etc.}$$

For, if we assume on the bounded surface curvilinear coordinates ξ and η, with respect to which the boundary is convex, the surface integral is

$$\int\sum\left(\frac{\partial v}{\partial\xi}\cdot\frac{\partial w}{\partial\eta} - \frac{\partial v}{\partial\eta}\cdot\frac{\partial w}{\partial\xi}\right)\left(\frac{\partial\,(X_v\,B)}{\partial w} - \frac{\partial\,(X_w\,C)}{\partial v}\right)d\xi\,d\eta.$$

Joining in this relation the terms containing $X_w\,C$ and adding and subtracting $\frac{\partial\,(X_w\,C)}{\partial w}\cdot\frac{\partial w}{\partial\xi}\cdot\frac{\partial w}{\partial\eta}$ we obtain:

$$\int d\xi\,d\eta\left\{\frac{\partial\,(X_w\,C)}{\partial\eta}\cdot\frac{\partial w}{\partial\xi} - \frac{\partial\,(X_w\,C)}{\partial\xi}\cdot\frac{\partial w}{\partial\eta}\right\}.$$

Integrating this partially, the first term with respect to η, the second to ξ, we shall get $\int X_w\,C\,dw$ along the boundary, giving with the integrals $\int X_v\,B\,dv$ and $\int X_u\,A\,du$ analogous to them the line integral of X along the boundary.

In accordance with the terminology given before (see Proceedings of this Meeting p. 66—78) [1]) we call the planivector Y the first derivative of X.

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[1]) The method given there derived from the indicatrix of a convex boundary that for the bounded space by front-position of a point of the interior; and the method understood by the vector $X_{pqr\ldots}$ a vector with indicatrix $opqr\ldots$. We can however determine the indicatrix of the bounded space also by post-position of a point of the interior with respect to the indicatrix of the boundary; and moreover assign to the vector $X_{pqr\ldots}$ the indicatrix $pqr\ldots o$. We then find:

Analogously we find quite simply as second derivative the scalar:

$$Z = \frac{1}{ABC} \sum \frac{\partial \{X_u . BC\}}{\partial u}.$$

According to the usual way of expressing, the first derivative is the rotation vector and the second the divergency.

II. If X is to be a ${}_{2}^{1}X$, i. e. a second derivative of a planivector Ξ, we must have:

$$X_u = \frac{1}{BC} \left\{ \frac{\partial (\Xi_v B)}{\partial w} - \frac{\partial (\Xi_w C)}{\partial v} \right\}, \text{ etc.,}$$

and it is easy to see that for this is necessary and sufficient

$$Z = 0.$$

III. If X is to be a ${}_{0}^{1}X$, i. e. a first derivative (gradient) of a scalar distribution φ, we must have:

$$X_u = -\frac{\partial \varphi}{A \partial u} \quad , \quad X_v = -\frac{\partial \varphi}{B \partial v} \quad , \quad X_w = -\frac{\partial \varphi}{C \partial w}$$

and it is easy to see, that to this end it will be necessary and sufficient that

$$Y = 0.$$

IV. It is easy to indicate (comp. SCHERING, Göttinger Nachrichten, 1870) the ${}_{0}^{1}X$, of which the divergency is an isolated scalar value in the origin.

It is directed according to the radius vector and is equal to:

$$\frac{1}{sinh^2 r},$$

when we put the space constant $= 1$ ²).

$$Y_{\alpha_1 \alpha_2 \dots \alpha_p \alpha_{p+1}} = \sum_{\alpha_{q_{p+1}} = \alpha_1 \dots \alpha_{p+1}} \frac{\partial X_{\alpha_{q_1} \dots \alpha_{q_p}}}{\partial x_{\alpha_{q_{p+1}}}} ;$$

$$Z_{\alpha_1 \dots \alpha_{p-1}} = - \sum_{\alpha_q = \alpha_p \dots \alpha_n} \frac{\partial X_{\alpha_1 \dots \alpha_{p-1} \alpha_q}}{\partial x_{\alpha_q}} .$$

These last definitions include the well known *divergency* of a vector, and the *gradient* of a potential also as regards the sign; hence in the following we shall start from it and we have taken from this the extension to non-Euclidean spaces.

²) For another space constant we have but to substitute in the following formulae $\frac{r}{R}$ for r.

It is the first derivative of a scalar distribution:

$$-1 + coth\, r,$$

and has in the origin an isolated divergency of 4π.

V. In future we shall suppose that X has the *field property* and shall understand by it, that it vanishes at infinity in such a manner that in the direction of the radius vector it becomes of lower order than $\frac{1}{r}$ and in the direction perpendicular to the radius vector of lower order than e^{-r}.

For a ${}_0^1X$ this means that it is derived from a scalar distribution, having the *potential property*, i.e. the property of vanishing at infinity.

Now the theorem of GREEN holds for two scalar distributions (comp. FRESDORF, diss. Göttingen, 1873):

$$\int \varphi \frac{\partial \psi}{\partial v}\, dO - \int \varphi \nabla^2 \psi \,.\, d\tau = \int \psi \frac{\partial \varphi}{\partial v}\, dO - \int \psi \nabla^2 \varphi \,.\, d\tau$$

$$\left(= \int S\{grad.\ \varphi,\ grad.\ \psi\}\, dt.\right).$$

If now φ and ψ both vanish at infinity whilst at the same time $lim.\ \varphi\, \psi\, e^{2r} = 0$, then the surface integrals disappear, when we apply the theorem of GREEN to a sphere with infinite radius and

$$\int \varphi \,.\, \nabla^2 \psi \,.\, d\tau = \int \psi \,.\, \nabla^2 \varphi \,.\, d\tau,$$

integrated over the whole space, is left.

Let us now take an arbitrary potential function for φ and $-1 + coth\, r$ for ψ, where r represents the distance to a point P taken arbitrarily, then these functions will satisfy the conditions of vanishing at infinity and $lim.\ \varphi\, \psi\, e^{2r} = 0$, so that we find:

$$4\pi \,.\, \varphi_P = \int (-1 + coth\, r) \nabla^2 \varphi \,.\, d\tau.$$

So, if we put $-1 + coth\, r \equiv F_1(r)$, we have:

$${}_0^1X = \nabla_1 \int \frac{\nabla_2\, {}_0^1X}{4\pi} F_1(r)\, d\tau. \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

VI. We now see that there is no vector distribution with the field property, which has in finite nowhere rotation and nowhere divergency. For, such a vector distribution would have to have a potential, having nowhere rotation, but that potential would have to be everywhere 0 according to the formula, so also its derived vector.

From this ensues: a vector field is determined uniformly by its rotation and its divergency.

VII. So, if we can indicate elementary distributions of divergency and of rotation, the corresponding vector fields are elementary fields, i. e. the arbitrary vector field is an arbitrary space-integral of such fields.

For such elementary fields we find thus analogously as in a Euclidean space (l. c. p. 74 seq.):

1. a field E_1, of which the second derivative consists of two equal and opposite scalar values, close to each other.

2. a field E_2, of which the first derivative consists of equal planivectors in the points of a small circular current and perpendicular to that same current.

At finite distance from their origin the fields E_1 and E_2 are here again of the same identical structure.

VIII. To indicate the field E_1 we take a system of spherical coordinates and the double point in the origin along the axis of the system. Then the field E_1 is the derivative of a potential:

$$\frac{\cos\varphi}{\sinh^2 r}.$$

It can be regarded as the sum of two fictitious "fields of a single agenspoint", formed as a derivative of a potential $-1+\coth r$, which have however in reality still complementary agens at infinity.

IX. The field E_2 of a small circular current lying in the equator plane in the origin is outside the origin identical to the above field E_1. Every line of force however, is now a closed vector circuit with a line integral of 4π along itself. We shall find of this field E_2 a planivector potential, lying in the meridian plane and independent of the azimuth.

In order to find this in a point P with a radius vector r and spherical polar distance φ we have but to divide the total current between the meridian plane of P and a following meridian plane with difference of azimuth $d\vartheta$, passing between P and the positive axis of revolution, by the element of the parallel circle through P over $d\vartheta$. For, if ds is an arbitrary line element through P in the meridian plane making with the direction of force an angle $\digamma$, if dh is the element of the parallel circle, Σ the above mentioned current and H the vector potential under consideration, we find:

$$d\Sigma = dh\,.\,Xds\sin\digamma,$$

whilst the condition for H is:

$$d\,(Hdh) = dh\; ds\; X \sin F.$$

So we have but to take $\frac{\Sigma}{dh}$ for H.

To find Σ we integrate the current of force within the meridian zone through the spherical surface through P. The force component perpendicular to that spherical surface is $2 \cos \varphi \frac{\cosh r}{\sinh^3 r}$, therefore:

$$\Sigma = \int_0^{\varphi} 2 \cos \varphi \frac{\cosh r}{\sinh^3 r} \,.\, \sinh r\, d\varphi \,.\, \sinh r \sin \varphi\, d\vartheta = d\vartheta \coth r \,.\, \sin^2 \varphi.$$

So:

$$H = \frac{\Sigma}{dh} = \frac{\Sigma}{\sinh r \sin \varphi d\vartheta} = \frac{\cosh r}{\sinh^2 r} \sin \varphi.$$

X. From this ensues, that if two arbitrary vectors of strength unity are given in different points along whose connecting line we apply a third vector $= \frac{\cosh r}{\sinh^2 r}$, the volume product of these three vectors, i. e. the volume of the parallelepipedon having these vectors as edges taken with proper sign, represents the linevector potential according to the first (second) vector, caused by an elementary magnet with moment unity according to the second (first) vector.

To find that volume product, we have first to transfer the two given vectors to a selfsame point of their connecting line, each one parallel to itself, i. e. in the plane which it determines with that connecting line, along which the transference is done, and maintaining the same angle with that connecting line.

The volume product $\psi(S_1, S_2)$ is a symmetric function of the two vectors unity of which we know that with integration of S_1 along a closed curve s_1 it represents the current of force of a magnet unity according to S_2 through s_1, in other words the negative reciprocal energy of a magnet unity in the direction of S_2 and a magnetic scale with intensity unity within s_1, in other words the force in the direction of S_2 by a magnetic scale with intensity unity within s_1, in other words the force in the direction of S_2 by a current with intensity unity along s_1. So we can regard $\psi(S_1, S_2)$ as a force in the direction of S_2 by an element of current unity in the direction of S_1.

With this we have found for the force of an element of current with intensity unity in the origin in the direction of the axis of the system of coordinates:

$$\frac{\cosh r}{\sinh^2 r} \sin \varphi,$$

directed perpendicular to the meridian plane.

XI. For the fictitious field of an element of current (having meanwhile everywhere current, i. e. rotation) introduced in this way we shall find a linevector potential V, everywhere "parallel" (see above under § X) to the element of current and the scalar value of which is a function of r only.

Let us call that scalar value U, and let us regard a small elementary rectangle in the meridian plane bounded by radii vectores from the origin and by circles round the origin, then the line integral of V round that rectangle is:

$$-\frac{\partial}{\partial r}\{U \sin \varphi \sinh r \, d\varphi\} \, dr - \frac{\partial}{\partial \varphi}\{U \cos \varphi \, dr\} \, d\varphi.$$

This must be equal to the current of force through the small rectangle:

$$\frac{\cosh r}{\sinh^2 r} \sin \varphi \, . \sinh r \, d\varphi . \, dr,$$

from which we derive the following differential equation of U with respect to r:

$$U - \frac{\partial}{\partial r}\{U \sinh r\} = \coth r,$$

the solution of which is:

$$U = \operatorname{cosech} r - \tfrac{1}{2} r \operatorname{sech}^2 \tfrac{1}{2} r + c \, . \operatorname{sech}^2 \tfrac{1}{2} r.$$

Let us take $c = 0$, we shall then find as vector potential V of an element of current unity E:

$$\operatorname{cosech} r - \tfrac{1}{2} r \operatorname{sech}^2 \tfrac{1}{2} r = F_2 (r),$$

directed parallel to E.

Let us now apply in an arbitrary point of space a vector G, then the vector V has the property that, when integrated in G along an elementary circuit whose plane is perpendicular to G, it indicates the force in the direction of G, caused by the element of current E, or likewise the vector potential in the direction of E caused by an elementary magnet with intensity unity in the direction of G.

So, if we call of two vectors unity E and F the potential $\chi(E, F)$, the symmetric function $F_2 (r, \cos \varphi$, where r represents the distance of the points of application of the two vectors and φ their angle after parallel transference to a selfsame point of their connecting line, we know that this function χ gives, by integration of e.g. E over a closed curve e not only the negative energy of a magnetic scale with intensity unity bounded by e in the field of an element of current unity F, but also the component along F of the vector potential caused by a current unity along e.

From this ensues for the vector V of an element of current, that when the element of current is integrated to a closed current it becomes the vector potential of that current determined uniformly on account of its flux property.

So really *the* vector potential of a ${}_2^1X$, i. e. of a field of currents is obtained as an integral of the vectors V of the elements of current.

XII. We can now write that in an arbitrary point:

$$ {}_2^1X = \overline{\overset{2}{\nabla}} \int \frac{\overline{\overset{1}{\nabla}}\, {}_2^1X}{4\pi} F_2(r)\, d\tau, \quad . \quad . \quad . \quad . \quad . \qquad (II) $$

where we first transfer in a parallel manner the vector elements of the integral to the point under consideration and then sum up.

Let us now consider an arbitrary force field as if caused by its two derivatives (the magnets and currents), we can then represent to ourselves, that both derivatives, propagating themselves according to a function of the distance vanishing at infinity, generate the potential of the field.

The field X is namely the total derivative of the potential:

$$ \int \frac{\overline{\overset{2}{\nabla}}\, X}{4\pi} F_1(r)\, d\tau + \int \frac{\overline{\overset{1}{\nabla}}\, X}{4\pi} F_2(r)\, d\tau. $$

The extinguishment of the scalar potential is greater than that of the vector potential; for, the former becomes at great distances of order e^{-2r}, the latter of order re^{-r}. Farther the latter proves not to decrease continuously from ∞ to 0, but at the outset it passes quickly through 0 to negative, it then reaches a negative maximum and then according to an extinguishment re^{-r} it tends as a negative (i. e. directed oppositely to the generating element of current) vector to zero.

XIII. The particularity found in Euclidean spaces, that $F_1(r) = F_2(r) = \frac{1}{r}$, is founded upon this, that in Euclidean spaces the operation of twice total derivation is found to be alike for scalar distributions and vector distributions of any dimensions (l.c. p. 70).

Not so in non-Euclidean spaces; e. g. in the hyperbolic Sp_3 we find for the ∇^2 of a scalar distribution u in an arbitrary point when choosing that point as centre of a system of RIEMANN normal coordinates

$$\left(\text{i. e. a system such that } ds = \frac{\sqrt{dx^2+dy^2+dz^2}}{1-\frac{x^2+y^2+z^2}{4}}\right)$$

$$\nabla^2 u = -\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right),$$

but as ∇^2 of a vector distribution with components X, Y and Z, we find for the x-component X_{∇^2}:

$$X_{\nabla^2} = -\left(2\,X+\frac{\partial^2 X}{\partial x^2}+\frac{\partial^2 X}{\partial y^2}+\frac{\partial^2 X}{\partial z^2}\right).$$

The hyperbolic Sp_2.

I. As first derivative Y of a vector distribution X we find a planivector determined by a scalar value:

$$\frac{1}{AB}\left\{\frac{\partial\,(X_u\,A)}{\partial v}-\frac{\partial\,(X_v\,B)}{\partial u}\right\}.$$

As second derivative Z we find the scalar:

$$\frac{1}{AB}\left\{\frac{\partial\,(X_u\,B)}{\partial u}+\frac{\partial\,(X_v\,A)}{\partial v}\right\}.$$

II. If X is to be a ${}_2^1X$, i. e. a second derivative of a planivector with scalar value ψ we must have:

$$X_u = -\frac{\partial\psi}{B\partial v} \quad ; \quad X_v = \frac{\partial\psi}{A\partial u},$$

to which end is necessary and sufficient: $Z=0$.

If X is to be a ${}_0^1X$, i. e. a first derivative of a scalar φ we must have:

$$X_u = -\frac{\partial\varphi}{A\partial u} \quad ; \quad X_v = -\frac{\partial\varphi}{B\partial v},$$

to which end is necessary and sufficient: $Y=0$.

III. The ${}_0^1X$, of which the divergency is an isolated scalar value in the origin, becomes a vector distribution in the direction of the radius vector:

$$\frac{1}{\sinh r}.$$

It is the first derivative of a scalar distribution:

$$l\,coth\,\tfrac{1}{2}\,r.$$

The divergency in the origin of this field is 2π.

The scalar distribution $l \coth \frac{1}{2} r$ has thus the potential property. (This was not the case for the field of a single agens point in the Euclidean Sp_2).

IV. In the following we presuppose again for the given vector distribution the field property (which remains equally defined for 2 and for n dimensions as for 3 dimensions); no vector field is possible that has nowhere rotation and nowhere divergency; so each vector field is determined by its rotation and its divergency and we have first of all for a gradient distribution:

$$ {}_{0}^{1}X = \overline{\nabla^{1}} \int \frac{\overline{\nabla^{2}}\, {}_{0}^{1}X}{2\pi} \, l \coth \tfrac{1}{2} r \, d\tau, $$

$$ {}_{0}^{1}X = \overline{\nabla^{1}} \int \frac{\overline{\nabla^{2}}\, {}_{0}^{1}X}{2\pi} \, F_1(r) \, d\tau \quad . \quad . \quad . \quad . \quad . \quad . \qquad (I) $$

V. For the field E_1 of an agens double point we find the gradient of the potential:

$$ \frac{\cos\varphi}{\sinh r}. $$

It can be broken up into "fields of a single agens point" formed as a derivative of a potential $l \coth \frac{1}{2} r$.

VI. Identical outside the origin to the above field E_1 is the field E_2 of a double point of rotation, whose axis is perpendicular to the axis of the agens double point of the field E_1. For that field E_2 we find as scalar value of the planivector potential in a point P the total current of force between P and the axis of the agens double point, that is:

$$ \sin\varphi \coth r. $$

So if are given a vector unity V and a scalar unity S and if we apply along their connecting line a vector $\coth r$, the volume product ψ of V, S and the vector along the connecting line is the scalar value of the planivector potential in S by a magnet unity in the direction of V.

Of ψ we know that when summing up S out of a positive scalar unity S_2 and a negative S_1 it represents the current of force of a magnet unity in the direction of V passing between S_1 and S_2, in other words the negative reciprocal energy of a magnet unity in the direction of V and a magnetic strip $S_1 S_2$ with intensity unity, in other words the force in the direction of V by a couple of rotation $S_1 \rightarrow S_2$. So we can regard ψ as the force in the direction of V by an isolated rotation in S. So that we must take as fictitious "force field of an element of rotation unity"

$$coth\ r,$$

directed perpendicularly to the radius vector. In reality, however, this force field has rotation everywhere in Sp_2.

VII. Let us now find the scalar value U, function of r, which we must assign to a planivector potential, that the "field of an element of rotation unity" be its second derivative. We must have:

$$-\frac{dU}{dr} = coth\ r.$$

$$U = l\ cosech\ r.$$

And we find for an arbitrary ${}_2^1X$:

$${}_2^1X = \overline{\nabla}^{2} \int \frac{\overline{\nabla}^{1}\, {}_2^1X}{2\pi}\, l\ cosech\ r\, d\tau,$$

$${}_2^1X = \overline{\nabla}^{2} \int \frac{\overline{\nabla}^{1}\, {}_2^1X}{2\pi}\, F_2\,(r)\, d\tau. \quad \ldots\ldots \quad (II)$$

And an arbitrary vector field X is the total derivative of the potential

$$\int \frac{\overline{\nabla}^{2} X}{2\pi}\, F_1\,(r)\, d\tau + \int \frac{\overline{\nabla}^{1} X}{2\pi}\, F_2\,(r)\, d\tau.$$

VIII. We may now wonder that here in Sp_2 we do not find F_1 and F_2 to be identical, as the two derivatives and the two potentials of a vectordistribution are perfectly dually related to each other in the hyperbolic Sp_2 as well as in the Euclidean Sp_2. The difference, however, is in the principle of the field property, which postulates a vanishing at infinity for the scalar potential, not for the planivector potential; and from the preceding the latter appears not to vanish, so with the postulation of the field property the duality is broken.

But on the other hand that postulation in Sp_2 lacks the reasonable basis which it possesses in spaces of more dimensions. For, when putting it we remember the condition that the total energy of a field may not become infinite. As soon as we have in the infinity of Sp_n forces of order e^{-r}, this furnishes in a spherical layer with thickness dr and infinite radius described round the origin as centre an energy of order $e^{-2r} \times e^{(n-1)r}\, dr = e^{(n-3)r}\, dr$; which for $n \geqq 3$ would give when integrated with respect to r an infinite energy at infinity of Sp_n. So for $n \geqq 3$ are excluded by the field property only vector distributions which cannot have physical meaning.

For $n = 2$ however the postulation lacks its right of existence; more sense has the condition (equivalent for $n > 2$ to the field property) that for given rotation and divergency the vector distribution must have a minimum energy. Under these conditions we shall once more consider the field and we shall find back there too the duality with regard to both derivatives and both potentials.

IX. Let us consider first of all distributions with divergency only and let us find the potential function giving a minimum energy for given ∇^2.

We consider the hyperbolical Sp_2 as a conform representation of a part of a Euclidean Sp_2 bounded by a circle; if we then apply in corresponding points of the representation the same potential, we retain equal energies and equal divergencies in corresponding plane elements. So the problem runs:

Which potential gives within a given curve (in this case a circle) in the Euclidean Sp_2 under given divergency distribution a minimum energy?

According to the theorem of GREEN we have for this:

$$\tfrac{1}{2}\int \delta \Sigma \left(\frac{\partial u}{\partial x}\right)^2 d\tau = \int \Sigma \frac{\partial u}{\partial x} \cdot \frac{\partial \delta u}{\partial x} \cdot d\tau = \int u \cdot \frac{\partial . \delta u}{\partial v} \cdot dO - \int u \nabla^2 \delta u \, . \, d\tau ,$$

so that, as $\nabla^2 \delta u$ is 0 everywhere within the boundary curve, the necessary and sufficient condition for the vanishing of the variation of the energy is:

$$u = 0, \text{ along the boundary curve.}$$

For the general vector distribution with divergency only in the hyperbolical Sp_2 we thus find under the condition of minimum energy also, that the potential at infinity must be 0. So we find it, just as under the postulation of the field property, composed of fields E_1, derived from a potential $\dfrac{\cos \varphi}{\sinh r}$.

The lines of force of this field E_1 have the equation,

$$\sin \varphi \coth r = c.$$

Only a part of the lines of force (in the Euclidean plane all of them) form a loop; the other pass into infinity. None of the equipotential lines, however, pass into infinity; they are closed and are all enclosed by the circle at infinity as the line of 0-potential.

The same holds for the arbitrary ${}^{1}_{0}X$; of the lines of force one part goes to infinity; the potential lines however are closed.

X. If we now have to find the field with rotation only, giving for given rotation distribution a minimum energy, it follows from a consideration of the rotation as divergency of the normal vector, that the scalar value of the planivector potential at infinity must be 0, and the general ${}^{1}_{2}X$ is composed of fields E_2, derived from a planivector potential $\dfrac{sin\ \varphi}{sinh\ r}$ (whilst we found under the postulation of the field property $sin\ \varphi\ \ coth\ r$).

In contrast to higher hyperbolical spaces and to any Euclidean and elliptic spaces the fields E_1 and E_2 cannot be summed up here to a single isolated vector.

For this field E_2 and likewise for the arbitrary ${}^{1}_{2}X$ the lines of force (at the same time planivector potential lines) are closed curves.

XI. We have now found

$$ {}^{1}_{0}X = \overset{1}{\overline{\nabla}} \int \frac{\overset{2}{\overline{\nabla}}\ {}^{1}_{0}X}{2\pi}\, l\ coth\ \tfrac{1}{2}\ r\ d\tau, $$

$$ {}^{1}_{2}X = \overset{2}{\overline{\nabla}} \int \frac{\overset{1}{\overline{\nabla}}\ {}^{1}_{2}X}{2\pi}\, l\ coth\ \tfrac{1}{2}\ r\ d\tau. $$

And from this ensues that also the general vector distribution X having under given rotation and divergency a minimum energy is equal to:

$$ X_{div.} + X_{rot.} = \overset{1}{\overline{\nabla}} \int \frac{\overset{2}{\overline{\nabla}} X}{2\pi}\, l\ coth\ \tfrac{1}{2}\ r\ d\tau + \overset{2}{\overline{\nabla}} \int \frac{\overset{1}{\overline{\nabla}} X}{2\pi}\, l\ coth\ \tfrac{1}{2}\ r\ d\tau. $$

For, if V is an arbitrary distribution without divergency and without rotation in finite, it is derived from a scalar potential function, so it has (according to § VIII) no reciprocal energy with $X_{div.}$; neither (as according to § IX all lines of force of $X_{rot.}$ are closed curves and a flux of exclusively closed vector tubes has no reciprocal energy with a gradient distribution) with $X_{rot.}$; so that the energy of $X_{div.} + X_{rot.} + V$ is larger than that of $X_{div.} + X_{rot.}$.

So finally we have for the general vector distribution of minimum energy X:

$$ X = \nabla \int \frac{\triangle X}{2\pi}\, .\ l\ coth\ \tfrac{1}{2}\ r\ d\tau. $$

C. *The hyperbolic* Sp_n.

I. Let us suppose a system of rectangular coordinates, so that

$$ds = \sqrt{A_1 u_1^2 + \dots A_n u_n^2},$$

and let us suppose a linevector distribution X with components $X_1 \dots X_n$, then the integral of X along a closed curve is equal to that of a planivector Y over an arbitrary surface bounded by it, in which the components of Y are determined by:

$$Y_{\alpha_1\alpha_2} = \frac{1}{A_{\alpha_1} A_{\alpha_2}} \left\{ \frac{\partial (X_{\alpha_2} A_{\alpha_2})}{\partial x_{\alpha_1}} - \frac{\partial (X_{\alpha_1} A_{\alpha_1})}{\partial x_{\alpha_2}} \right\}.$$

Y is the *first derivative* or *rotation* of X.

Further the starting vector current of X over a closed curved Sp_{n-1} is equal to the integral of the scalar Z over the bounded volume of that Sp_{n-1}; here

$$Z = \frac{1}{A_1 \dots A_n} \sum \frac{\partial (X_{\alpha_1} . A_{\alpha_2} \dots A_{\alpha_n})}{\partial x_{\alpha_1}}$$

Z is the *second derivative* or *divergency* of X.

II. If X is to be a ${}^1_2X$, i. e. a second derivative of a planivector Ξ, we must have:

$$X_{\alpha_1} = \frac{1}{A_{\alpha_2} \dots A_{\alpha_n}} \sum \frac{\partial . (\Xi_{\alpha_1 \alpha_{q_1}} A_{\alpha_{q_2}} \dots A_{\alpha_{q_{n-1}}})}{\partial_{\alpha_{q_1}}}.$$

The necessary and sufficient condition for this is:

$$Z = 0.$$

If X is to be a ${}^1_0X$, i. e. a first derivative of a scalar φ, we must have:

$$X_\alpha = - \frac{\partial \varphi}{A_\alpha \partial x_\alpha}.$$

The necessary and sufficient condition for this is:

$$Y = 0.$$

III. The ${}^1_0X$, which has as divergency an isolated scalar value in the origin (comp. Opitz., Diss. Göttingen, 1881), is directed along the radius vector, and if we put the space constant equal to 1 is equal to

$$\frac{1}{sinh^{n-1} r}.$$

It is the first derivative of a scalar distribution

$$\int_r^\infty \frac{dr}{\sinh^{n-1} r} \equiv w_n(r),$$

and it has in the origin an isolated divergency of k_n (if $k_n r^{n-1}$ expresses the spherical surface of the Euclidean space Sp_n).

IV. For two scalar distributions φ and ψ the theorem of GREEN holds (comp. Opitz., l.c.):

$$\int \varphi \frac{\partial \psi}{\partial \nu} \, . \, dO_{n-1} - \int \varphi \nabla^2 \psi \, . \, d\tau_n = \int \psi \frac{\partial \varphi}{\partial \nu} \, . \, dO_{n-1} - \int \psi \nabla^2 \varphi \, . \, d\tau_n$$

$$\left(= \int S(\nabla \varphi, \nabla \psi) \, . \, d\tau_n \right).$$

If at infinity φ and ψ both become 0 whilst at the same time

$$\lim \varphi \psi e^{(n-1)r} = 0,$$

then for an ${}^{n-1}$sphere with infinite radius the surface integrals disappear and we have left

$$\int \varphi \, . \, \nabla^2 \psi \, . \, d\tau_n = \int \psi \, . \, \nabla^2 \varphi \, . \, d\tau_n,$$

integrated over the whole space.

If here we take an arbitrary potential function for φ and $w_n(r)$ for ψ, where r represents the distance to an arbitrarily chosen point P — these functions satisfying together the conditions of the formula — we have:

$$k_n \varphi_P = \int w_n(r) \, . \, \nabla^2 \varphi \, . \, d\tau_n.$$

If thus we postulate for the vector distributions under consideration the *field property* (which remains defined just as for Sp_3) we have, if we put $w_n(r) \equiv F_1(r)$, for an arbitrary ${}^1_0X$:

$$ {}^1_0X = \overline{\nabla\!/} \int \frac{\overline{\nabla^2\!/}\, {}^1_0X}{k_n} F_1(r) \, d\tau \, ; \qquad \ldots\ldots \quad (I)$$

from which we deduce (compare A § VI) that there is no vector field which has in finite nowhere rotation nor divergency; so that a vector field is uniformly determined by its rotation and its divergency.

V. So a vectorfield is an arbitrary integral of:

1. Fields E_1, of which the second derivative consists of two equal and opposite scalar values close to each other.

2. Fields E_2, of which the first derivative consists of planivectors distributed regularly in the points of a small ${}^{n-2}$sphere and perpendicular to that ${}^{n-2}$sphere.

At finite distance from their origin the fields E_1 and E_2 are of identical structure.

VI. In order to indicate the field E_1 we assume a spherical system of coordinates [1]) and the double point in the origin along the first axis of the system. Then the field E_1 is the derivative of a potential:

$$\frac{\cos\varphi}{\sinh^{n-1} r}.$$

The lines of force of this field run in the meridian plane. It can be regarded as the sum of two fictitious "fields of a single agens-point" constructed as derivative of a potential $w_n(r)$ to which, however, must be assigned still complementary agens at infinity.

VII. The field E_2 of a small vortex-${}^{n-2}$sphere according to the space perpendicular to the axis of the double point just considered is identical outside the origin to the field E_1. Each line of force is now however a closed vector tube with a line integral k_n along itself. We shall find for this field E_2 a planivector potential H, lying in the meridian plane and dependent only on r and φ. It appears then simply that this H is a ${}^2_1X$.

Let ε be an $(n-2)$-dimensional element in the $n-2$ coordinates existing besides r and φ, then it defines for each r and φ an element on the surface of an ${}^{n-2}$-sphere of a size $dh = c\varepsilon \sinh^{n-2} r \sin^{n-2}\varphi$, and for the entire Sp_n what may be called a "meridian zone".

We then obtain for the current of force Σ, passing inside a meridian zone between the axis of the system and a point P with coordinates r and φ, if ds represents an arbitrary line element through P in the meridian plane under an angle $\digamma$ with the direction of force:

$$d\Sigma = dh \,.\, X\, ds \sin\digamma,$$

whilst we can easily find as necessary and sufficient condition for H:

$$d\,(Hdh) = dh \,.\, ds \,.\, X \sin\digamma\,;$$

so we have but to take $\dfrac{\Sigma}{dh}$ for H.

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[1]) By this we understand in Sp_n a system which with the aid of a rectangular system of numbered axes determines a point by 1. r, its distance to the origin, 2. φ, the angle of the radius vector with X_1, 3. the angle of the projection of the radius vector on the coordinate space $X_2 \ldots X_n$ with X_2, 4. the angle of the projection of the last projection on the coordinate space $X_3 \ldots X_n$ with X_3; etc. The plane through the X_1-direction and the radius vector we call the *meridian plane.*

To find Σ we integrate the current of force inside the meridian zone passing through the ${}^{n-1}$spherical surface through P between the axis of the system and P. As we have $(n-1)\cos\varphi\,\frac{\cosh r}{\sinh^{n} r}$ for the force component perpendicular to that spherical surface we find:

$$\Sigma = \int_{0}^{\varphi}(n-1)\cos\varphi\,\frac{\cosh r}{\sinh^{n} r}\,.\,\sinh r\,d\varphi\,.\,c\varepsilon\,\sinh^{n-2} r\,\sin^{n-2}\varphi = c\varepsilon\,\sin^{n-1}\varphi\,\coth r.$$

$$H = \frac{\Sigma}{dh} = \frac{\cosh r}{\sinh^{n-1} r}\,\sin\varphi.$$

VIII. If thus are given in different points a line vector L unity and an ${}^{n-2}$vector W unity and if we put along their connecting line a line vector $\frac{\cosh r}{\sinh^{n-1} r}$, then the volume product ψ of L, W and the vector along the connecting line is the ${}^{n-2}$vector potential in the direction of W caused by an elementary magnet with moment unity in the direction of L.

We know of $\psi(L, W)$ that with integration of W along a closed curved $Sp_{n-2}\,Q$ it represents the current of force of a magnet unity in the direction of L through Q, in other words the negative reciprocal energy of a magnet unity in the direction of L and a magnetic ${}^{n-1}$scale with intensity unity, bounded by Q, in other words the force in the direction of L by a magnetic ${}^{n-1}$scale bounded by Q, in other words the force in the direction of L by a vortex system, regularly distributed over Q and perpendicular to Q. So we can regard $\psi(L, W)$ as the force in the direction of L by a vortex unity, perpendicular to W. With this we have found for the force of a plane vortex with intensity unity in the origin:

$$\frac{\cosh r}{\sinh^{n-1} r}\,\sin\varphi,$$

directed parallel to the operating vortex element and perpendicular to the "meridian plane", if now we understand by that plane the projecting plane on the vortex element; whilst φ is here the angle of the radiusvector with the Sp_{n-2} perpendicular to the vortex element.

IX. For the fictitious field of a vortex element in the origin introduced in this way (which meanwhile has vorticity everywhere in space) we shall find a planivector potential, directed everywhere "parallel" to the vortex element and of which the scalar value U is a function of r only.

Let us suppose a point to be determined by its azimuth parallel to the vortex element and then farther in the Sp^{n-1} of constant azimuth by a system of spherical coordinates, of which we take the first axis in the "meridian plane" (see above under § VIII), and in the plane of the vortex element, the second in the meridian plane perpendicular to the first, and the rest arbitrarily; let us understand meanwhile by φ here the angle of the radius vector with the Sp_{n-2}, perpendicular to the vortex element; let further ε be an $(n-3)$-dimensional element in the $n-3$ last coordinates, then this defines for each r and φ an element on the surface of an ${}^{n-3}$sphere, of a size

$$dk = c\varepsilon \sinh^{n-3} r \cos^{n-3}\varphi .$$

We then consider a small elementary rectangle in the meridian plane bounded by radii vectores out of the origin and circles about the origin and a Sp_{n-1} element consisting of the elements dk erected in each point of this small elementary rectangle. Applying to this Sp_{n-1}-element the reduction of an $(n-2)$-fold integral along the boundary to a $(n-1)$-fold integral over the volume according to the definition of second derivative, we find:

$$-\frac{\partial}{\partial\varphi}\{U\cos\varphi \,.\, dr \,.\, c\varepsilon \sinh^{n-3} r \cos^{n-3}\varphi\}\, d\varphi \,-$$

$$-\frac{\partial}{\partial r}\{U\sin\varphi \,.\, \sinh r\, d\varphi \,.\, c\varepsilon \sinh^{n-3} r \cos^{n-3}\varphi\}\, dr =$$

$$= c\varepsilon \sinh^{n-3} r \cos^{n-3}\varphi \;.\; \sinh r\, d\varphi \,.\, dr \,.\, \frac{\cosh r}{\sinh^{n-1} r} \sin\varphi .$$

$$(n-2)\, U - \frac{dU}{dr} \sinh r - (n-2)\, U \cosh r = \frac{\cosh r}{\sinh^{n-2} r} .$$

$$\frac{dU}{dr} + (n-2) \tanh \tfrac{1}{2} r \,.\, U = - \frac{\cosh r}{\sinh^{n-1} r} .$$

The solution of this equation is:

$$U = -\frac{1}{2^{n-3}} \,.\, \cosh^{-2(n-2)} \tfrac{1}{2} r \,.\int \coth^{n-3} \tfrac{1}{2} r \,.\, d\, \tfrac{1}{2} r + \frac{1}{(n-2) \sinh^{n-2} r} .$$

So we find as planivector potential V of a plane vortex:

$$\frac{1}{(n-2)\sinh^{n-2} r} - \frac{1}{2^{n-3} \cosh^{2(n-2)} \frac{1}{2} r} \int \coth^{n-3} \tfrac{1}{2} r \,.\, d\, \tfrac{1}{2} r \equiv F_2 (r),$$

directed parallel to that plane vortex.

Let us now call E the ${}^{n-2}$vector, perpendicular to the plane vortex, the field of which we have examined, and let us also set off the vector potential V as an ${}^{n-2}$vector; let us then bring in an arbitrary point of space a line vector G; then the vector V has the property that when integrated in G along a small curved closed Sp_{n-2} in a Sp_{n-1} perpendicular to G, it indicates the force in the direction of G caused by the current element E, or also the vector potential in the direction of E, caused by an elementary magnet with intensity unity in the direction of G.

Let us now call the potential $\chi(E, F)$ of two ${}^{n-2}$vectors unity E, F the symmetric function $F_2(r)\cos\varphi$, where r represents the distance of the points of application of both vectors and φ their angle after parallel transference to one and the same point of their connecting line, then we know that this function χ gives, when e. g. E is integrated over a closed curved Sp_{n-2} which we shall call e, not only the negative energy of a magnetic ${}^{n-1}$scale with intensity unity bounded by e in the field of a vortex unity perpendicular to F but also the component along F of the vector potential caused by a system of vortices about e with intensity unity.

From this ensues again for the vector potential V of a vortex element, that when the vortex element is integrated to a system of vortices about a closed curved Sp_{n-2} it becomes the vector potential determined according to § VII of that vortex Sp_{n-2}; so that the vector potential of an arbitrary ${}^1_2X$ is obtained as integral of the vectors V of its vortex elements, in other words:

$$ {}^1_2X = \overline{\nabla}^{2} \int \frac{\overline{\nabla}^{1}\, {}^1_2X}{k_n}\, F_2(r)\, d\tau, \quad . \quad . \quad . \quad . \quad . \qquad (II)$$

where for each point the vector elements of the integral are first brought over to that point parallel to themselves and there are summed up.

X. So let us consider an arbitrary force field as if caused by its two derivatives (the magnets and the vortex systems), we can then imagine that both derivatives are propagated through the space according to a function of the distance vanishing at infinity, causing thereby the potential of the field.

For, the field X is the total derivative of the potential:

$$\int \frac{\overline{\nabla}^{2}\, X}{k_n}\, F_1(r)\, d\tau + \int \frac{\overline{\nabla}^{1}\, X}{k_n}\, F_2(r)\, d\tau.$$

The extinguishment of the scalar potential is the stronger, as it is at great distances of order $e^{-(n-1)r}$, the vector potential only of order $re^{-(n-2)r}$.

Astronomy. — *"The luminosity of stars of different types of spectrum."* By Dr. A. Pannekoek. (Communicated by Prof. H. G. van de Sande Bakhuyzen).

The investigation of the spectra of stars which showed that, with a few exceptions, they can be arranged in a regular series, has led to the general opinion that they represent different stages of development gone through by each star successively. Vogel's classification in three types is considered as a natural system because these types represent the hottest and earliest, the further advanced, and the coolest stage. This, however, does not hold for the subdivisions: the difference in aspect of the lines, the standard in this case, does not correspond to the different stages of development mentioned above. Much more artificial is the classification with letters, which Pickering has adopted in his Draper Catalogue; it arose from the practical want to classify the thousands of stellar spectra photographed with the objective prism. After we have allowed for the indistinctness of the spectra which, arising from insufficient dispersion and brightness, influenced this classification, the natural affinity between the spectra will appear and then this classification has the advantage over that of Vogel that the 2nd type is subdivided. The natural groups that can be distinguished are: class A: the great majority of the white stars (Sirius type), Vogel's I*a*; class B: the smaller number of those stars distinguished by the lines of helium, called Orion stars, Vogel's I*b*. In the continuous series the latter ought to go before the first type and therefore they are sometimes called type 0. Class F forms the transition to the second type (Procyon); class G is the type of the sun and Capella (the E stars are the indistinct representatives of this class); class K contains the redder stars of the 2d type, which approach to the 3d type, such as Arcturus (Pickering reckons among them the H and I as indistinct representatives). The 3d type is called in the Draper Catalogue class M.

The continuity of the stellar spectra is still more evident in the classification given by Miss A. Maury. (Annals Harv. Coll. Obs. Bd. 28). Miss Maury arranges the larger number of the stellar spectra in 20 consecutive classes, and accepts groups intermediate to these. The classes I—IV are the Orion stars, VI—VIII constitute the first type, IX—XI the transition to the 2d type, XIII—XIV the 2d type itself such as the sun, XV corresponds to the redder Arcturus stars, XVII—XX constitute the third type. If we consider that from class I to III a group of lines is gradually falling out, namely the hydrogen lines of the other series, which are characteristic of the Wolf-Rayet stars or the so-called fifth type stars (Vogel II*b*), it is obvious that we must place these stars at the head of the series, as it has also been done by Miss Cannon in her investigation of the southern spectra (H. C. O. Ann. Bd. 28) [1]).

Some of these stars show a relative intensity of the metallic lines different from that of the ordinary stellar spectra; Vogel and Scheiner have found this before in *α* Cygni and *α* Persei (Public. Potsdam Bd. 7, part 2). Maury found representatives of this group in almost all the classes from III to XIII, and classed them in a parallel series designated by III*c*—XIII*c*, in contradistinction to which the great majority are called *a* stars.

According to the most widely spread opinion a star goes successively through all these progressive stages of development. It commences as an extremely tenuous mass of gas which grows hotter by contraction, and after having reached a maximum temperature decreases in temperature while the contraction goes on. Before the maximum temperature is reached, there is a maximum emission of light; past the maximum temperature the brightness rapidly decreases owing to the joint causes: fall of temperature and decrease in volume. That the first type stars are hotter than the stars of the second type may be taken for certain on the strength of their white colour; whether the maximum temperature occurs here or in the Orion stars is however uncertain.

This development of a tenuous mass of gas into a dense and cold body, of which the temperature first increases and then decreases is in harmony with the laws of physics. In how far, however, the different spectral types correspond to the phases of this evolution is a mere hypothesis, a more or less probable conjecture; for an actual transition of a star from one type into the other has not yet been

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[1]) According to Campbell's results (Astronomy and Astrophysics XIII, p. 448), the characteristic lines of the Wolf-Rayet stars must be distinguished in two groups and according to the relative intensity of the two groups these stars must be arranged in a progressive series. One group consists of the first secondary series and the first line of the principal series of hydrogen: Hβ' 5414, Hγ' 4542, Hδ' 4201, principal line 4686); it is that group which in Maury's classes I—III occurs as dark lines and vanishes and which in the classes towards the other side (class O*e*—O*b* Cannon) is together with the ordinary H lines more and more reversed into emission lines. The other group, which as compared with the hydrogen lines becomes gradually stronger from this point, consists of broad bands of unknown origin of which the middle portions according to Cannon's measurements of *γ* Velorum have the wavelengths 5807, 5692, 5594, 5470, 4654, 4443. The brightest band is 4654; its relative intensity as compared with the H line 4689 gradually increases in the series: 4, 47, 5, 48, 42 (Campbell's star numbers).

observed. The hypothesis may be indirectly tested by investigating the brightness of the stars. To answer to a development as sketched here the brightness of a star must first increase then decrease; the mean apparent brightness of stars, reduced to the same distances from our solar system must vary with the spectral class in such a way that a maximum is reached where the greatest brightness is found while the apparent brightness decreases in the following stages of development.

§ 2. For these investigations we cannot make use of directly measured parallaxes as a general measure for the distance because of the small number that have been determined. Another measure will be found in the proper motions of the stars when we assume that the real linear velocity is the same for different spectral classes. In 1892 W. H. S. MONCK applied this method to the Bradley-stars in the Draper Catalogue [1]. He found that the proper motions of the B stars were the smallest, then followed those of the A stars; much larger are the mean proper motions of the F stars [2] which also considerably surpasses that of the G, H and K stars and that of the M stars. He thence concluded that these F stars (the 2d type stars which approach to the 1st type) are nearest to us and therefore have a smaller radiating power than the more yellow and redder stars of the 2d type. "Researchés on binary stars seem to establish that this is not due to smaller average mass and it would therefore appear, that these stars are of the dullest or least light-giving class — more so not only than the Arcturian stars but than those of the type of Antares or Betelgeux" (p. 878). This result does not agree with the current opinion that the G, K and M stars have successively developed from the F stars by contraction and cooling.

It is, however, confirmed by a newly appeared investigation of EJNAR HERTZSPRUNG: Zur Strahlung der Sterne [3], where MAURY's classification of the spectra has been followed. He finds for the mean magnitude, reduced to the proper motion 0″,01, the values given in the following table where I have added the corresponding proper motions belonging to the magnitude 4.0.

Here also appears that for the magnitude 4,0 the proper motion is largest and hence the brightness smallest for the classes XII and

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[1] Astronomy and Astrophysics XI p. 874.

[2] He constantly calls them incorrectly "Capellan stars" because in the Dr. Cat. Capella is called F, though this star properly belongs to the sun and the G stars.

[3] Zeitschrift für wissenschaftliche Photographie Bd. III. S. 429.

Spectrum		Magn. for	P. M. for
Maury	Draper C.	P. M. 0″.01	Magn. 4.0 ″
II—IV	B	4.37	0.012
V—VI	B—A	7.25	0.045
VII—VIII	A	8.05	0.065
IX—XI	F	9.06	0.103
XII—XIII	F—G	11.23	0.279
XIII—XIV[1]	G	7.93	0.061
XV	K	9.38	0.119
XV—XVI	K—M	7.77	0.057
XVII—XVIII	M	8.28	0.072

XIII that form the transition from F to G; for the later stages of development the brightness again increases.

§ 3. A better measure than the proper motion for the mean distance of a group of stars is the parallactic motion. This investigation was rendered easy by means of N°. 9 of the "Publications of the astronomical Laboratory at Groningen", where the components τ and v of the proper motion are computed with the further auxiliary quantities for all the Bradley-stars. Let τ and v be the components of the proper motion at right angles with and in the direction of the antapex, λ the spherical distance of the star-apex, then

$$q = \frac{\Sigma \, v \sin \lambda}{\Sigma \sin^2 \lambda}$$

is the parallactic motion for a group of stars, i.e. the velocity of the solar system divided by the mean distance of the group. The mean of the other component $\frac{1}{n} \Sigma \tau$ is, at a random distribution of the directions, equal to half the mean linear velocity divided by the distance.

The mean magnitudes of the different groups are also different. Because we here especially wish to derive conclusions about the brightness, and as both the magnitude and the proper motion depend on the distance the computation was made after the reduction to

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[1] The Roman figures in italics in MAURY's classification designate the transition to one class higher.

magnitude 4.0; that is to say, we have imagined that every star was replaced by one which in velocity and in brightness was perfectly identical with the real one, but placed at such a distance that its apparent magnitude was 4.0. If the ratio in which we then increase the proper motion is

$$p = 10^{0.2\,(m-4)}$$

we have

$$q_{4.0} = \frac{\Sigma\; pv \sin\lambda}{\Sigma \sin^2\lambda} \quad \text{and} \quad \tau_{4.0} = \frac{\Sigma\; p\tau}{n}.$$

In this computation we have used MAURY's classes as a basis. We have excluded 61 Cygni on account of its extraordinary great parallax, while instead of the whole group of Ursa Major ($\beta\;\gamma\;\delta\;\varepsilon\;\zeta$) we have taken only one star (ε). In the following table are combined the results of the two computations.

Spectrum MAURY	Spectrum Dr Cat.	Typical star	n	mean m	mean τ	q	$\tau_{4.0}$	$q_{4.0}$
					″	″	″	″
I—III	B	ε Orionis	33	3.57	0.007	0.018	0.007	0.013^5
IV—V	B—A	γ Orionis	48	4.31	0.011	0.035	0.014	0.036
VI—VIII	A	Sirius	93	3.92	0.040	0.054	0.038	0.061
IX—XII	F	Procyon	94	4.14	0.089	0.153	0.095	0.136
XIII—XIV	G	Capella	69	4.08	0.141	0.157	0.160	0.199
XV	K	Arcturus	101	3.90	0.123	0.119	0.120	0.096
XVI—XX	M	Betelgeuze	61	3.85	0.049	0.068	0.050	0.061

In both the series of results the phenomenon found by MONCK and HERTZSPRUNG manifests itself clearly. I have not, however, used these numbers $\tau_{4.0}$ and $q_{4.0}$, but have modified them first, because it was not until the computation was completed that I became acquainted with HERTZSPRUNG's remark that the above mentioned c stars show a very special behaviour; their proper motions and parallaxes are so much smaller than those of the a stars of the same classes that they must be considered as quite a separate group of much greater brilliancy and lying at a much larger distance[1]). We have

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[1]) In his list of parallaxes HERTZSPRUNG puts the question whether perhaps the bright southern star α Carinae (Canopus) belongs to the c stars; but he finds no indication for this except in its immeasurably small parallax and small proper motion. In her study of the southern spectra Miss CANNON has paid no regard

Class	n	$\tau_{4.0}$	$q_{4.0}$	$2\tau/q$
		″	″	
I	5	0.009	0.022	0.8
II	13	005	009	1.1
III	14	006	015	0.8
IV	18	014	023	1.2
IV	16	016	044	0.7
V	11	009	042	0.4
VI	16	030	068	0.9
VII	30	040	086	0 9
VIII	41	043	055	1.6
IX	25	050	064	1.6
X	16	070	171	0.8
XI	22	103	061	3.3
XII	23	170	282	1 2
XIII	18	297	346	1.7
XIV	21	192	305	1.3
XIV	20	077	025	6.2
XV *A*	26	234	148	3.2
XV *B*	35	105	070	3.0
XV *C*	40	059	087	1 4
XVI	19	049	071	1.4
XVII	19	049	032	3.1
XVIII	16	050	075	1.3
XIX—XX	7	057	078	1.5

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to the difference between the *a* and the *c* stars. Yet all the same this question may be answered in the affirmative; on both spectrograms of this star occurring in her work, we see very distinctly the line 4053.8, which in Capella and Sirius is absent and which is a typical line for the *c* stars. Hence follows that *α* Carinae is indeed a *c* star.

therefore repeated the computation after exclusion of the *c* and the *ac* stars.

The table (see p. 139) contains the results for all the classes of MAURY separately; class XV is divided into three subdivisions: XV *A* are those whose spectra agree with that of *α* Boötis, XV *C* are those which agree with the redder *α* Cassiopeiae, while XV *B* embraces all those that cannot with certainty be classed among one of the other two groups.

The values for $\tau_{4.0}$ and $q_{4.0}$ differ very little from those of the preceding table. If we take the value of the velocity of the solar system $= 4.2$ earth's distances from the sun, the q's divided by 4.2 yield the mean parallax of stars of different spectral classes for the magnitude 4.0 ($\pi_{0.4}$). Reversely, we derive from the q's the relative brightness of these stellar types, for which we have here taken the number which expresses how many times the brightness exceeds that of magnitude 4.0 when placed at a distance for which $q = 0''.10$, hence with the parallax $0''.024$. Finally the last column $2\tau/q$ contains the relation between the mean linear velocities of the group of stars and our solar system.

In the following table we have combined these values in the same way as before.

Spectrum MAURY	 Dr. Cat.	Typical star	n	$\tau_{4.0}$	$q_{4.0}$	$\pi_{4.0}$	L for $q = 0''.10$	$2\tau/q$
				″	″	″		
I—III	B	ε Orionis	32	0.005^5	0.014	0.0033	51	0.8
IV—V	B—A	γ Orionis	45	0.013	0.036	0.0086	7.7	0.7
VI—VIII	A	Sirius	87	0.040	0.063	0.015	2.5	1.3
IX—XII	F	Procyon	86	0.101	0.141	0.034	0.50	1.4
XIII—XIV	G	Capella	59	0.182	0.224	0.053	0.20	1.6
XV	K	Arcturus	101	0.120	0.096	0.023	1.1	2.5
XVI—XX	M	Betelgeuze	61	0.050	0.061	0.015	2.7	1.6

§ 4. Conclusions from this table. The numbers of the last column are not constant but show a systematic variation. Hence the mean linear velocity is not constant for all kinds of stars but increases as further stages of development in the spectral series are reached. (Whether the decrease for the 3rd type, class M, is real must for the present be left out of consideration). That the linear speed of the Orion stars is small is known and appears moreover from the radial velocities. While CAMPBELL found 19.9 kilometres for the velocity of the solar motion, and 34 kilometres for the mean velocity of all the stars, FROST and ADAMS derived from the radial velocities of 20 Orion stars measured by them, after having applied the correction for the solar motion: 7.0 kilometres as mean value [1]), hence for the actual mean speed in space 14 kilometres, whence follows the ratio 0.7 for $2\tau/q$. Hence the Orion stars are the particularly slow ones and the Arcturian stars (class XV) are those which move with the greatest speed.

§ 5. When we look at the values of $q_{4.0}$ or those of $\pi_{4.0}$ or $L_{0.10}$, derived from them, we find, as we proceed in the series of development from the earliest Orion stars to the Capella or solar type G, that the brightness constantly decreases. That q was larger for the 2^d^ type as a whole than for the first (the Orion stars included) has long been known; some time ago KAPTEYN derived from the entire Bradley-Draper material that on an average the 2^{d} type stars (F G K) are 2,7 times as near and hence 7 times as faint as the 1st type stars (A and B). This result perfectly agrees with the ordinary theory of evolution according to which the 2^{d} type arises from the 1st type through contraction and cooling.

A look at the subdivisions shows us first of all that the Orion stars greatly surpass the A stars in brightness, and also that among the Orion stars those which represent the earliest stage greatly surpass again in brightness those of the later stages. As compared with the solar type G the Sirius stars are 12 times, the stars which form the transition to the Orion stars 38 times and lastly the ε Orionis type 250 times as bright. This result is in good harmony with the hypothesis that one star goes successively through the different conditions from class I to class XIV; we then must accept that the density becomes less as we come to the lower classes. Whether the temperature of the Orion stars is higher than that of the Sirius stars or lower cannot be derived from this result; even in the latter case it may be that the larger surface more than counterbalances the effect of smaller radiation. This must be decided by photometric measurements of the spectra. As the Wolf-Rayet stars follow next to class I, an investigation of their proper motion, promised by KAPTEYN, will be of special interest.

Past the G stars, the solar type of the series, the brightness again increases. The values obtained here for q confirm in this respect the results of MONCK and HERTZSPRUNG.

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[1]) Publications Yerkes Observatory. Vol. II. p. 105.

Against the evidence of the q's only one objection can be made, namely that these classes K and M might have a proper motion in common with the sun, so that q would not be a good measure for the distance. A priori this objection is improbable but it may be tested by material, which, though otherwise of small value, may for this kind of investigations yield very valuable conclusions on this point, namely the directly measured parallaxes. **Hertzsprung** gives mean values of the measured parallaxes reduced to magnitude 0,0; by the side of these we have given the values for somewhat different groups derived from our $\pi_{4.0}$:

	Observed $\pi_{0.0}$	
II—IV	0″.0255	(6)
IV—VI	0 .106	(5)
VII—VIII	0 .153	(10)
IX—XI	0 .226 1)	(6)
XII—XIII	0 .442	(2)
XIV	0 .567	(5)
XV	0 .151	(8)
XVI	0 .171	(3)
XVII—XVIII	0 .115	(3)

	Derived from q $\pi_{0.0}$
I—III	0″.021
IV—V	0 .054
VI—VIII	0 .094
IX—XII	0 .21
XIII—XIV	0 .33
XV	0 .14
XVI—XX	0 .096

In general **Hertzsprung**'s numbers are somewhat larger, this can be easily explained by the circumstance that many parallaxes measured in consequence of their large proper motions will probably be above the mean. It appears sufficiently clear from this, at any rate, that also the directly measured parallaxes markedly point at an increase of brightness past class XIV, and that there is not the least ground to assume for the other groups a motion in common with the sun.

It is therefore beyond doubt that the K and M stars have a greater intrinsic brilliancy than the F and G stars. **Monck** derives from this fact that they have a greater radiating power, because about the same value for the masses is derived from the double stars.

That the latter cannot be derived from the double stars will appear hereafter. Moreover **Monck**'s conclusion of the greater radiating power of the K and M stars is unacceptable. In incandescent bodies this radiating power depends on the temperature of the radiating layers and of the atmospheric absorptions. With unimpaired radiance a greater amount of radiation is accompanied with bluer light (because the maximum of radiation is displaced towards the smaller wavelengths) as both are caused by the higher temperature. The general absorption by an atmosphere is also largest for the smaller wavelengths, so that when after absorption the percentage of the remaining light is less, the colour of the radiated light will be redder.

Therefore it is beyond doubt that a redder colour corresponds at any rate with a less degree of radiance per unit of surface.

Then only one explanation remains: *the K and M stars (the redder 2nd type stars like Arcturus and the 3rd type) possess on an average a much larger surface and volume than the other 2nd type stars of the classes F and G.* This result is at variance with the usual representation of stellar evolution according to which the redder K and later the M stars are developed from the yellow-white F and G stars by further *contraction* and cooling.

§ 6. A further examination of the constitution of these stars shows us that it is improbable that they should possess a very small density; the low temperature, the strongly absorbing vapours point to a stage of high condensation. These circumstances lead to expect greater (with regard to the F and G stars) rather than less density. From the larger volumes it then follows *that the K and M stars have much larger masses than the F's and G's.* This result is the more remarkable in connection with the conclusion derived above about their greater mean velocity. If the stars of our stellar system form a group in the sense that their velocities within the group depend on their mutual attraction, we may expect that on an average the velocities will be the greater as the masses are smaller. No difficulty from this arises for the Orion stars with small speed, because the same circumstances which allow us to ascribe to them a mass equal to that of the A, F and G stars, enable us likewise to ascribe to them a larger mass. The K stars which have both a greater mass and a greater velocity are characterized by this thesis as belonging to a separate group, which through whatever reason must *originally* have been endowed with a greater velocity. Arcturus with its immeasurably small parallax and large proper motion is therefore through its enormously great linear velocity and extraordinary luminosity an exaggerated type of this entire class, of which it is the brightest representative. Therefore it would be worth while to investigate separately the systematic motions of the K stars which hitherto have been classed without distinction with the F and G stars as 2nd type.

If this result with regard to the greater masses of the K and M stars should not be confirmed, the only remaining possibility is the supposition *that the density of these star is extremely small.* In this case their masses might be equal to that of other stars and they may represent stages of evolution of the same bodies. Where they ought to be placed in the series of evolution remains a riddle. There is a regular continuity in the series F—G—K—M; and according as we suppose the development to take place in one direction or in the other we find in the transition G—K either cooling accompanied with expansion, or heating accompanied with contraction. The puzzling side of this hypothesis can also be expressed in the following way: while in the natural development of the celestial bodies, as we conceive it, the temperature has a maximum but the density continuously increases, the values obtained here would according to this interpretation point at a maximum density in the spectral classes F and G.

In Vol. XI of Astronomy and Astrophysics **Maunder** has drawn attention to several circumstances, which indicate that the spectral type rather marks a difference in constitution than difference in the stage of development. "There seems to me but one way of reconciling all these different circumstances, viz.: to suppose that spectrum type does not primarily or usually denote epoch of stellar life, but rather a fundamental difference of chemical constitution" [1]). One of the most important of these facts is that the various stars of the Pleiades, which widely differ in brightness and, as they are lying at the same distance from the sun, also in actual volume show yet the same spectrum. The result found here confirms his supposition.

One might feel inclined to look for a certain relation between these K and M stars and the *c* stars, which, according to **Hertzsprung**, have also a much greater luminosity, hence either less density or greater mass than the similar *a* stars; and the more so as these *c* stars reach no further than class XIII. Yet to us this seems improbable; the K stars are numerous, they constitute 20 °/₀ of all the stars, while the *c* stars are rare. Moreover the spectra of all the K stars are with regard to the relative intensity of the metallic lines perfectly identical with the *a* stars of preceding classes such as the sun and Capella. Therefore it as yet remains undecided to which other spectra we have to look for other phases in the K star lives and to which spectra for those in the *c* star lives. The *c* stars, except a few, are all situated in or near the Milky Way: this characteristic feature they have in common with the Wolf-Rayet stars and also with the 4th type of **Secchi** (Vogel's III*b*), although these spectra have no lines in common which would suggest any relation between them.

§ 7. The constitution found here for the Arcturian stars among the third type stars may perhaps be tested by means of other

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[1]) Stars of the first and second types of spectrum. p. 150.

data, namely by those derived from the double stars. The optically double stars cannot however teach us anything about the masses of the stars themselves as will appear from the following consideration (also occurring in "The Stars" by NEWCOMB). Let us suppose that a binary system is n times as near to us, while all its dimensions become n times as small, but that the density and the radiation remain the same. Then the mass will diminish in the proportion of n^3 to 1, the major axis of the orbit a in the proportion of n to 1 and hence the time of revolution remains the same; the luminosity becomes n^2 times as small, therefore the apparent brightness remains the same as well as the apparent dimensions of the orbit, in other words: it will appear to us exactly as it was before. Hence the mass cannot be found independently of the distance. Let a be the angular semi-major axis, M the mass, P the time of revolution, δ the density, λ the radiating power, π the parallax and ϱ the radius of the spherical volume of the star, then we shall have: $\pi^3 M = \frac{a^3}{P^2}$; the mass M is a constant value $\times \varrho^3 \delta$, the apparent brightness H is a constant $\times \pi^2 \varrho^2 \lambda$. Eliminating from this the parallax and the radius, we find

$$H^3 \frac{P^4}{a^6} = c \frac{\lambda^3}{\delta^2}.$$

Thus from the known quantities: elements of orbit and brightness, we derive a relation between the physical quantities: density and radiating power, independently of the mathematical dimensions. This relation has been derived repeatedly. In the paper cited before MAUNDER gives values for the density $\delta = c \left(\frac{\lambda}{H}\right)^{3/2} \frac{a^3}{P^2}$ in the supposition of equal values of λ; he found for the Sirius stars (1st type) 0,0211, for the solar stars (all of the 2nd type) 0,3026, hence 14 times as large on an average; we can also say that when we assume the same density the radiating power of the Sirius stars would be 6 times as large; the exact expression would be that the quotient λ^3/δ^2 is 200 times as large for the Sirius stars as for the solar stars.

In a different form the same calculation has been made by HERTZSPRUNG by means of AITKEN's list of binary system elements [1]). By means of $-2{,}5 \log H = m$ he introduces into his formula the stellar magnitudes; if we put in the logarithmical form

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[1]) Lick Observatory Bulletin Nr. 84.

$$3 \log H + 4 \log P - 6 \log a = const. + 3 \log \lambda - 2 \log \delta$$
$$m - {}^{10}/_{3} \log P + 5 \log a = m_r$$

then we have $m_r = const. - 2{,}5 \log \lambda + {}^{5}/_{3} \log \delta$.

If we arrange the values of m_r after the spectra according to the Draper Catalogue (for the Southern stars taking CANNON; according to the brightest component α Centauri was reckoned to belong to class G), we find as mean values:

Class A	— 2.92	(9 stars	— 4.60 to	— 1.09)
,, F	— 1.32	(19 ,,	— 3.61 ,,	+ 0.14)
,, G and E	— 0.49	(11 ,,	— 1.60 ,,	+ 1.28)

The 3 stars of the type K (with H) give — 4.88 (γ-Leonis), — 1.05 and + 0,87, hence differ so widely that no valuable result is to be derived from them. To the extraordinarily high value for λ^3/δ^2 given by γ Leonis attention has repeatedly been drawn. While for a great number of stars of the other classes the extreme values of m_r differ by 3.5 magnitudes we find that γ Leonis differs by 5 magnitudes from the mean of the two other values, that is to say: its radiating power is a hundred times as large, or its density is a thousand times as small as for these other stars. For the classes A and F we find that λ^3/δ^2 is 640 and 8 times respectively as large as for class G; conclusions about class K as a whole, such as are especially wanted here, cannot be derived from it. It may be that an investigation of binary systems with partially known orbit motion (for which we should require auxiliary hypotheses) would yield more results.

About the mass itself, however, something may be derived from the spectroscopic binary systems. The elements derived from observation $a \sin i$ and P directly yield $M \sin^3 i$; as it is improbable that there should be any relation between the type of spectrum and the angle between the orbit and the line of sight we may accept the mean of $\sin^3 i$ to be equal for all groups. For systems of which only one component is visible, the element derived from observation contains another unknown quantity, viz. the relation β of the mass of the invisible to that of the visible star. If a is the semi major axis of the orbit of the visible star round the common centre of gravity, we have

$$\frac{a^3 \sin^3 i}{P^2} = M \frac{\beta^3}{(1+\beta)^2} \sin^3 i.$$

It is not perfectly certain, of course, that on an average β is the same for all classes of spectrum; if this is not the case the M's may behave somewhat different from the values of $\frac{a^3 \sin^3 i}{P^2}$ computed here.

Unfortunately, of the great number of spectroscopic double stars discovered as yet (in Lick Observatory Bulletin N°. 79 a number of 147 is given) the orbit elements of only very few are known. They give, arranged according to their spectra:

Group II—IV (B)		Group VI—VIII (A)	
Orion type		Sirius type	
ο Persei	0.61	β Aurigae	0.56
η Orionis	2.51	ζ Ursae	(3.41) 1)
δ Orionis	0.60	Algol	0.72
β Lyrae	7.85	α Androm.	0.36 2)
α Virginis	0.33	α_2 Gemin.	0.002
V Puppis	34.2		

Group XII—XIV *a* (F—G)		Group XII—XIV *ac*	
Solar type		α Ursae min.	0.00001
α Aurigae	0.185	ζ Geminorum	0.0023
χ Draconis	0.120	η Aquilae	0.0029
(W Sagittarii	0.005)	δ Cephei	0.0031
(X Sagittarii	0.001)		
ι Pegasi	0.117	Group XV (K)	
η Pegasi	0.234	β Herculis	0.061

Of the K stars only one representative occurs here, so neither this material offers anything that could help us to test the results obtained about this stellar type. But all the same, some remarkable conclusions may be derived from this table. It appears here that notwithstanding their small number the Orion stars evidently surpass the others in mass, while the Sirius stars seem also to have a somewhat greater mass than the solar stars. Very striking, however, is the small mass of the *c* stars approaching towards *a*. Hence *the c stars combine a very great luminosity with a very small mass, and consequently their density must be excessively small.* If it should be not merely accidental that the three regularly variable stars of short period, occurring in Maury, all happen to show *c* characteristics and a real connection should exist between this particularity of spectrum and the variability, we may reasonably include into the

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1) In the case of ζ Ursae *a* has been taken equal to the semi major axis of the relative orbit; hence this number is proportionally too large by an unknown number of times.

2) Assumed period 100 days, velocity in orbit 32.5 kilometres.

group W and X Sagittarii which also yield small values; as has been remarked, for the southern stars no distinction is made between the a and the c stars [1]).

We may expect that within a few years our knowledge of the orbits of the spectroscopic double stars will have augmented considerably. Then it will be possible to derive conclusions like those found here from much more abundant material, and also to arrive at some certainty about the mean mass of the K stars. With regard to the latter our results show at any rate that in investigations on grouping of stars and stellar motions it will be necessary not to consider the 2nd type as one whole, but always to consider the F and G stars apart from the redder K stars.

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[1]) In this connection may be mentioned that in 1891 the author thought he detected a variability of α Ursae minoris with a period of a little less than 4 days. The small amplitude and the great influence of biased opinions on estimations of brightness after ARGELANDER's method in cases of short periods of almost a full number of days, made it impossible to obtain certainty in either a positive or a negative sense. CAMPBELL's discovery that it is a spectroscopic binary system with a period of $3^d\,23^h\,14^m$ makes me think that it has not been wholly an illusion.

ERRATA.

In the Proceedings of the Meeting of June, 1905, p. 81:
line 7 from top, read: "cooled by conduction of heat",
,, 16 ,, ,, for: "*Exh'* Pl. IV" read: "*Exh'* Pl. VI".

In Plate V belonging to Communication N°. 83 from the physical laboratory at Leiden, Proceedings of the Meeting of February 1903, p. 502, the vacuum glass B'_0 has been drawn 18 cm. too long.

(August 21, 1906).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday September 29, 1906.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 29 September 1906, Dl. XV).

CONTENTS.

Botany. — *"On the harmful consequences of the secretion of sugar with some myrmecophilous plants."* By Mrs. M. Nieuwenhuis-von Uexküll-Güldenband. Ph. D. (Communicated by Prof. J. W. Moll).

(Communicated in the meeting of June 30, 1906).

During my residence of about eight months at Buitenzorg in 1901 I occupied myself chiefly with an investigation of the structure and peculiarities of the sugar-secreting myrmecophilous plants. The results of these observations, extending over some 70 plants, are inconsistent with the opinion expressed by Delpino, Kerner, Trelease, Burck and many others, that the extrafloral secretion of sugar by plants would serve to attract ants which in return would protect the plants against various harmful animals.

For I was unable to observe in a single instance that the secretion of sugar is useful to the plant; on the other hand it appeared to me that the ants feed on the sugar, but that, instead of being useful at the same time, they injure the plant indirectly by introducing and rearing lice; moreover the extrafloral nectaries attract not only ants but also numbers of beetles, bugs, larvae, etc. and these are not content with the sugar alone, but at the same time eat the nectaries themselves and often consume the leaves and flowers to no small extent.

In about one third of the plants, investigated with this purpose, the secretion of sugar in this way certainly does much harm; with another third the plants experience only little harm by attracting the undesirable visitors, while with the last third no indication at all could be found that by secreting sugar they were worse off than other plants.

Of those that were indirectly injured by secreting sugar I here only mention a few examples out of the many which I shall consider more extensively elsewhere.

Spathoglottis plicata Bl. is a common orchid in the Indian archipelago. In the environs of Buitenzorg it is e.g. found on the Salak, and it is used in the Botanical Garden to set off the beds in the orchid quarter. Its leaves (all basal leaves) have a length of as much as 1.20 M., according to Smith, they are narrow, have a long point and are folded lengthwise; their inflorescence is erect, reaches a height of about 2 metres and bears at its extremity, in the axils of coloured bracts, a number of flowers, the colour of which varies from red violet to white. The bracts and perianth leaves have blunt, thick and darker coloured points. On the inflorescences two kinds of ants always abound, one large and one small species. Even when the flower-buds are still closed the ants are already found on the bracts and no sooner are the flowers open than the ants also attack the perianth leaves. It appeared that sugar was secreted as a bait here.

In order to prove this the flowers were placed for some time under a damp glass bell-jar; after a few hours by means of FEHLING's reagent sugar could be proved to be present in the liquid secreted by the leaves at the exterior side. I could find no special organs for this secretion, however; probably the secretion is an internal one the product being brought out by the epiderm or the stomata.

It was already known to DELPINO that some orchids secrete sugar on the perianth; the remarkable point with the just mentioned *Spathoglottis* is that the ants have such an injurious influence on it. Whereas namely the small species remains on the flowers and is content with the sugar there secreted, the big species also descends to the basal-leaves and attacks these also, often to such an extent that only a skeleton of them remains. These harmful big ants are not expelled at all by the much more numerous small ones. It further appeared most clearly that the secretion of sugar was the reason indeed why such important organs as the leaves were eaten by the big species. The proof was namely afforded by those plants that had finished flowering and bore fruit; with these secretion of sugar took place no longer and the leaves, which were produced in this period, remained consequently uninjured. So it was the secretion of sugar during the flowering period which attracted the ants, while the leaves as such were no sufficient bait.

A second instance of the great harm that may be caused to the plants themselves by the secretion of sugar, is seen with various tree- and shrublike *Malvaceae*. In the Botanical Garden stands an unnamed tree, a *Malvacea* from Indo-China. This not only has nectaries on the leaves and calyx, but also offers the ants a very suitable dwelling-place in the stipules, which occur in pairs and are bent towards each other. The spaces formed in this way are indeed inhabited by ants, but not by so many as might be expected. The reason is that in spite of the abundance of nectaries they find no sufficient food, since on these trees a species of bugs occurs which not only consume the secreted sugar but also eat the nectaries themselves. These bugs moreover injure the leaves to such an extent that the tree suffers from it, as may be seen by a cursory examination. The same may be stated of a tree named "*Malvacea Karato*" and of some other species of this family.

In order to prove that the secretion of sugar by attracting harmful insects is indeed injurious to these trees it would still be necessary to show that they remain uninjured when the secretion of sugar does not take place. This proof is readily afforded by some other *Malvaceae.*

Two shrublike *Malvaceae* of common occurrence in India, namely *Hibiscus rosa sinensis L.* and *Hibiscus tiliaceus L.* have nectaries on their leaves. They are not frequented by ants or other harmful insects, however, because in the nectaries, as far as my observations go, a fungus always occurs, which may be recognised already from the outside by its black colour. This fungus prevents the secretion of sugar, and the nectaries cease to have an attraction for insects which otherwise would be harmful to the plant. These shrubs by their healthy appearance contrast strongly with the above mentioned plants in the *Malvaceae* quarter, which are frequented by ants and other insects.

On account of the circumstance that the extrafloral nectaries are found chiefly on and near the inflorescences, BURCK proposed the hypothesis, that in some cases they would serve to attract ants into the neighbourhood of the flowers in order to protect these against bees and wasps, which would bore them and rob honey. But even with the plants investigated by him I could find no confirmation of his hypothesis. First the nectaries only rarely occur on the inflorescences exclusively; also the plants mentioned by him as proof as: *Thunbergia grandiflora* Roxb., *Gmelina asiatica L.*, and *Gmelina bracteata, Nycticalos macrosyphon* and *Nycticalos Thomsonii* cannot serve as examples, since these plants also on their vegetative parts such as leaves and stems possess nectaries, which according to him are not present there or are not mentioned. In regard to the so-called "food-bodies" (BURCK'sche Körperchen) on the calyx of *Thunbergia grandiflora,* it appeared to me that these are no "food-bodies" at all, but ordinary sugar-secreting deformed hairs which I also found on the bracts, leaves and leaf-stalks of this plant.

Further it appeared to me that the number of bored flowers stands in no relation to the number of nectaries occurring on the calyx, as should be the case according to BURCK. It is much more dependent on external factors, as e. g. the more or less free situation of the plants, the weather etc.

As an example the creeper *Bignonia Chamberlaynii* may be mentioned. Of this plant on many days only 1,6 °/₀ of the fallen flowers appeared not to have been bored by *Xylocopa coerulea,* although numerous ants always occur on the nectaries of the calyx.

An example of the fact that the more or less free situation influences the number of perforations of the flowers is found in two species of the genus *Faradaya,* both having nectaries on the calyx and the leaves. With *Faradaya papuana* Scheff., which stands in the Botanical Garden at Buitenzorg surrounded by many other richly flowering plants, the flowers are often perforated by a boring wasp: of the fallen flowers only 1 °/₀ was undamaged. This was different with another still unnamed species of the same genus which, as far as the nectaries were concerned, showed no difference with the former and grew at some distance from it in a less open site. Its branches hung partly to the ground and bore far fewer flowers than *Faradaya papuana.* Now of this three 19,3 °/₀ of the flowers remained unperforated.

And in regard to the weather it appeared that the number of bored flowers closely depends on it. After a sunny day a much larger number of flowers had been bored the next morning than when rain had prevented the insects from flying out. This was e. g. very conspicuous with *Ipomoea carnea* Jacq., a shrub having nectaries as well on the leaves as on the calyx, the latter being bored by *Vespa analis* and two *Xylocopas.* Collected in the morning without regard to the weather of the preceding day 90°/₀ of the fallen flowers were bored; after rainy days 57 °/₀ of the flowers were damaged and after sunny days even 99,1 °/₀ were bored.

From this appears most clearly how little value must be assigned to statistical data about the perforation of flowers and about their being eventually protected by ants if not at the same time all other circumstances which may influence the results have been taken into account.

When trying to fix the part, either favourable or otherwise, played by insects with regard to a plant, one meets with greater difficulties in the tropics than e.g. in Middle Europe, because the vegetative period lasts so much longer. So one may meet an abundance of definite insects during one part of that period which are not found during another part. This special difficulty of the question whether special arrangements in a plant form an adaptation to a definite animal species is still enhanced in a botanical garden by the circumstance that there nearly all the plants are in a more or less uncommon site or surroundings. Yet here also the mutual behaviour of the animals frequenting the plants may be investigated as well as their behaviour towards the plants themselves, while the results enable us to draw some justified conclusion as to the mutual relations in the natural sites of these plants. I took this point of view when I began my investigation and among others put myself the following questions to which the here briefly mentioned answers were obtained:

1. On what parts of plants is extrafloral secretion of sugar found?

In the cases examined by me I found secretion of sugar on the branches, leaves, stipules, bracts of different kind, peduncles and pedicels, ovaries and the inner and outer side of calyx and corolla, in each of these organs separately or in a great number of different combinations. The most commonly occurring of these combinations were: *a.* on leaf-sheaths and calyx together, *b.* on the leaf-blade only *c.* on the leaf-stalks, peduncle and calyx. Of other combinations I only found from one to three examples each.

2. Does the structure or place of the nectaries clearly indicate that they are made for receiving ants?

Except in a few cases (as the nectaries occurring in the closely assembled flowers of *Gmelina asiatica* Scheff. on that side of the calyx, that is turned away from the axis of the inflorescence) this question must be decidedly answered negatively. Although it seems as if the very common cup shape of the nectaries were eminently suitable for storing the secreted honey, yet on the lower side of the leaves these nectaries are for the greater part found with their opening turned downward. I remind the reader of the two large, also downwardly directed cup-shaped nectaries at the base of the side leaves of some species of *Erythrina*.

The frequent occurrence of nectaries on the calyces, which only in the budding period secrete honey, seems to indicate that these buds require special protection. But inconsistent with this view is the fact that sometimes, according to my observations, only half of the flowers has nectaries in the calyces (e.g. *Spathodea campanulata* Beauv.).

With many species of *Smilax* only part of the branches attracts ants and these are branches that carry no flowers and so, according to the prevailing conception, would least require protection. It is difficult to make the idea of the protection of the flowers agree with the fact that nectaries occur on the inner and outer side of the upper edge of the tube of the corolla of *Nycticalos macrosyphon*, *Spathodea serrulata* and others. Attracting ants to the entrance of the corolla, which is the very place where the animals causing cross-fertilisation have to enter, has certainly to be called unpractical from the biologist's point of view.

Against the conception that these plants should require protection, also the fact pleads that exactly with young plants, where protection would be most necessary, these baits for protective ants are absent.

A short time ago ULE[1]) has drawn attention to this as a result of his investigation of American plants.

3. Is sugar secreted in *all* nectaries?

This is not the case; in some nectaries I could detect no secretion even after they had stayed for a long time under a bell-jar; this was the case e.g. with the leaves of *Gmelina asiatica*. Consequently they are not frequented by ants, although these insects always occur on the similarly shaped but strongly secreting nectaries of the calyx.

The quantity of the secreted substances moreover fluctuates with the same nectaries of the same plant and depends on many external and internal influences.

4. Are all the products secreted by the nectaries always and eagerly consumed by the ants?

Evidently this also is not always the case, for whereas the nectaries of some plants are constantly frequented by ants, with others the nectaries so to say overflow, without a single animal visiting them. (So with some species of *Passiflora*).

5. At what age of the organs do the nectaries secrete sugar?

As a rule the nectaries of the inflorescences cease to secrete as soon as the flowers are opened; those of the leaves even only functionate in the youngest stages of development.

6. Are the ants that frequent the plants with nectaries hostile towards other visitors?

Although I daily watched the behaviour of the ants with the extrafloral nectaries for hours, I have never observed that they hindered other animals in any way. On the *Luffa* species one may see the ants at the nectaries peacefully busy by the side of a species of beetles which does great damage to the plant by eating leaves and buds.

The results of my investigations of some wild plants in Java in their natural sites agreed entirely with those obtained in the Buitenzorg Botanical Garden.

Exactly those species of ants that occur on the so-called "ant-plants" of the Indian archipelago, seem to belong to the harmless ones; the dangerous species with powerful mouth-apparatus, e.g. those which are called *semut rangrang* in West Java and according to Dr. VORDERMAN are used by the Malay for defending Mango trees against beetles, are carnivorous. So these ants have to be specially allured by hanging animal food (dead leguans) in the trees to be protected.

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[1]) ENGLER's Bot. Jahrbücher. Heft III, Bd. 37, 1906.

What the real meaning is of the often so highly differentiated organs as many extrafloral nectaries are and of the secretion of sugar which they present in most cases, can only be settled by new investigations which however will have to bear not only on the biology but also on the physiology of the plant.

Physics. — *"Methods and apparatus used in the cryogenic laboratory at Leiden. X. How to obtain baths of constant and uniform temperature by means of liquid hydrogen."* By Prof. H. KAMERLINGH ONNES. Communication N°. 94*f* from the Physical Laboratory at Leiden.

(Communicated in the meeting of 28 May, 1906).

§ 1. *Introduction.* Communication N°. 14 of Dec. '94 treated of the results I had obtained after I had employed regenerators for the cascade method, and especially discussed the way how to obtain a permanent bath of liquid oxygen to be used in measurements at the then observed lowest temperatures. At the end of that paper I expressed the hope to be able to construct a cycle of hydrogen similar to that of oxygen. A mere continuation of the cascade method would not do. By means of liquid oxygen or nitrogen, even when they evaporate in vacuo, we practically cannot reach the critical temperature of hydrogen; for the liquefaction of this gas we had therefore to avail ourselves of cooling by adiabatic expansion.

In Comm. N°. 23 of Jan. '96 I made some remarks on what could be derived from VAN DER WAALS' law of corresponding states for the liquefaction of hydrogen following this method. I had found that an apparatus to liquefy hydrogen beginning with — 210° C. might be constructed almost after the same model as an apparatus that had proved suitable for the liquefaction of oxygen beginning with ordinary temperatures and without any further frigorific agents. My efforts, however, to obtain an apparatus for isentropic cooling by combining to a regenerator the outlet- and inflow-tubes of a small expansion motor, fed with compressed gas, had failed. Therefore I directed my attention towards the then newly published (1896) application of the JOULE-KELVIN process (LINDE's apparatus for liquefying air and DEWAR's jet of hydrogen to solidify oxygen).

Though the process of LINDE was the most promising, because he had succeeded with his apparatus to obtain liquid air statically, yet it was evident that only the principle of this method could be followed.

The cooling of an apparatus of dimensions like the first of LINDE (weight 1300 kilogrammes) by means of liquid air (oxygen) evaporating in vacuo could not be thought of. And yet, according to what has been said above, this had to be our starting point.

It rather lay to hand to magnify the spiral (enclosed in a vacuum glass) such as DEWAR had used for his jet of hydrogen to solidify oxygen, and so to get an apparatus with which air could be liquefied, and which could then serve as a pattern for an apparatus to liquefy hydrogen. It was indeed a similar construction with which in 1898 DEWAR had statically liquefied hydrogen for the first time. About the installation which apparently afterwards enabled DEWAR to collect large quantities of liquid hydrogen nothing further has come to my knowledge.

The arrangement of the Leiden hydrogen circulation is based on DEWAR's principle to place the regenerator spiral into a vacuum glass (1896). As to the regenerator spiral itself HAMPSON's apparatus for liquefying air (1896) has been followed because it appeared that the proportions of this spiral have been chosen very favourably, and with its small dimensions and small weight it is exceedingly fit, according to the thesis mentioned above, to serve as a model for a regenerator spiral to liquefy hydrogen of about — 205° at expansion from a higher to the ordinary pressure. The other physicists, who after DEWAR have occupied themselves with liquid hydrogen, — TRAVERS 1900 and 1904, OLSZEWSKI 1902, 1904 and 1905 (the latter rather with a view to obtain small quantities in a short time with simple accessories) — have also built their apparatus after this model.

The Leiden hydrogen liquefactor for constant use has enough peculiar features to occupy a position of its own as an independent construction by the side of the apparatus of TRAVERS and OLSZEWSKI, which do not satisfy the requirements for the Leiden measurements. Moreover I was the first to pronounce the principle according to which this apparatus is built and from which follows that the regenerator spiral fed with hydrogen that has been cooled by liquid oxygen (air) evaporating at a given low pressure, must lead to the goal.

The problem of making a circulation in order to maintain a bath of liquid hydrogen — and of this problem the arrangement of the liquefactor for constant use (which, tested with nitrogen, has really proved efficient) is only a part — has not yet been treated by others.

That also at Leiden we had to wait a long time for its solution cannot be wondered at when we consider the high demands which, I held, had to be satisfied by this cycle. For with a view to the intended measurements I thought it necessary to pour a bath of

1.5 liter into the cryostat (described in VIII of the series "Methods and apparatus used in the Cryogenic Laboratory" of these communications) and to keep it to within 0°.01 at a uniform and constant temperature. The requirements were therefore very much higher than they had formerly been for the bath of liquid oxygen. These requirements could by no means be fulfilled before I had the disposal of a vacuum pump (mentioned as early as Jan. '96 in Comm. N°. 23), (comp. Comm. N°. 83, March '03), suitable to evaporate in a short time large quantities of liquid air at a pressure of a few centimeters, and before I possessed compressors for constant working with extremely pure hydrogen. With the former instrument and the compressors, described in § 3, the liquefactor, described in § 2, delivers 3 à 4 liters of liquid hydrogen per hour. Thus I was able to bring to this assembly (28 May '06) 4 liters of liquid hydrogen prepared at Leiden the day before and to use it in several experiments.

Our installation proved quite satisfactory for operations with the afore mentioned cryostat. After we had succeeded in making with it some measurements in liquid hydrogen boiling under ordinary and under reduced pressure the vacuum glass of the cryostat cracked and only by mere accidence the measuring apparatus were spared. Therefore we have constructed another modified cryostat, to be described in XII, which besides insuring the safety of the measuring apparatus has the advantage of using less liquid hydrogen than the cryostat, described in VIII (Comm. N°. 94^d, June '05). This new cryostat entirely satisfies the requirements; the temperature is kept constant to within 0°,01. It is noteworthy that while the measurements are being made the cryostat shows in no way that we are working with a bath of no less than 1.5 liter of liquid hydrogen.

I wish to express thanks to Mr. G. J. Flim, mechanist at the cryogenic laboratory, for his intelligent assistance. Under his supervision the liquefactor and cryostat, to be described in the following sections, and also other accessories have been built upon my direction in the workshop of the laboratory.

§ 2. *The hydrogen liquefactor for constant use.*

a. The apparatus does not yet entirely realize the original design [1].

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[1] It might be improved by dividing the regenerator spiral in several successive coils, each opening into the next with its own expansion-cock, where the pressures are regulated according to the temperatures. Compare the theory of cooling with the Joule-Kelvin process and the liquefying by means of the Linde process given by van der Waals in the meeting of Jan. 1900.

The latter is represented schematically by fig. 1 on Pl. I and hardly requires further explanation. The compressed hydrogen goes successively through the regenerator coils D_4, D_3, D_2, D_1, C, B, A. B is immersed partially in a bath of liquid air which, being admitted through P, evaporates at a very low pressure; D_4, D_2, C and A are surrounded by hydrogen expanding at the cock M, and D_1 and D_3 by the vapours from the airbath in F. As, however, we can dispose of more liquid air than we want for a sufficient cooling of the admitted hydrogen, and the vacuum pump (comp. Comm. N°. 83, March '03) has a greater capacity than is required to draw off the evaporating air[1]) at reduced pressure, even when we sacrifice the regenerator working of the spirals D_1, D_2, D_3 and D_4, we have for simplicity not yet added the double forecooling regenerator D, by means of which a large quantity of liquid air will be economized, and hence the apparatus consists only of one forecooling regenerator C, the refrigerator F with cooling spiral B and the principal regenerator A in the vacuum glass E with a collecting vessel L, placed in the case V, which forms one complete whole with the case U.

b. The principal regenerator, Pl. I fig. 2, consists of 4 windings of copper tubing, 2.4 m.m. in internal diameter and 3.8 m.m. in external diameter, wound close to each other and then pushed together, indicated by A_1, A_2, A_3 and A_4, (number of layers 81; length of each tube 20 M.). As in the ethylene regenerator (Comm. N°. 14, Dec. '94, and description of Mathias[2]), fig. 1F) and in the methyl chloride regenerator (Comm. N°. 87, March '04, Pl. I) the windings are wound from the centre of the cylinder to the circumference and again from the circumference to the centre round the cock-carrying tube M_4, and are enveloped together in flannel and fit the vacuum glass E_0 (the inner and outer walls are marked with E_{01} and E_{02}). Thence the liquid hydrogen flows at E_1 into the collecting vessel L_0. At M_{00} the four coils are united to one channel which (comp. cock T in fig. 3 of Mathias' description l.c.) is shut by the pivot point M_{11} moved by the handle M_{21}. The packing M_3 hermetically closes the tube M_4 at the top, where it is not exposed to cooling (comp. Mathias' description l.c.). The hydrogen escapes at the side exactly as at the ethylene cock L, fig. 2 in Mathias' description l.c., through 6 openings M_{01} and is prevented from rising or circulating by the screens M_{02} and M_{03}.

c. The new-silver refrigerator case F_1 is suspended in the new-

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[1]) When using oxygen we might avail ourselves of cooling down to a lower temperature, which then must be carried out in two steps (comp. § 4*b*).

[2]) Le laboratoire cryogène de Leyde, Rev. Gen. d. Sc. Avril 1896.

silver case U_1, from which it is insulated by flannel U_{64}. A float F_{31} indicates the level of the liquid air, of which the inflow is regulated through the cock P_{01} with pivot P_{11} and packing P_3 identical with the cock mentioned above, except that the glass tube with cock is replaced by a new-silver one P_4.

The evaporated air is drawn off through a stout copper tube F_2 (comp. § 4*b*). The 2 outlet tubes B_{12} and B_{22} of the spiral B_{11} and B_{21} (each 23 windings, internal diameter of tube 3.6 m.m., external diameter 5,8 m.m., length of each 6 M.) are soldered in the bottom. The two inflow tubes B_{10} and B_{20} are soldered in the new-silver cover, on which the glass tube F_4 covering the index F_{32} of the cork float F_{31} are fastened with sealing wax (comp. for nitrogen Comm. N°. 83 IV, March '03, Pl. VII).

d. The forecooling regenerator spiral C_1, C_2, C_3, and C_4 is wound in 4 windings like A, wrapped in flannel and enclosed in the cylinder of the new-silver case U_2. The four windings (internal diam. of the tubing 2.4 m.m., external diam. 3.8 m.m., number of layers 81, length of each tube 20 M.) branch off at the soldered piece C_{01} from the tube C_{00}, soldered in the cover of U_2. They unite to the two tubes C_7a and C_7b through which the hydrogen is led to the refrigerator. The axis of this spiral is a thin-walled new-silver tube C_6 shut at the top.

The hydrogen blown off is expelled through the tube U_5.

e. The liquid hydrogen is collected in a new-silver reservoir L_1, fitting the vacuum glass L_0, which by means of a little wooden block V_7 rests on the wood-covered bottom of the insulated case V_1, which is coated internally with paper V_{64} and capoc V_{63}. Thanks to L_1 the danger of bursting for the vacuum glass is less than when the hydrogen should flow directly from E_1 into the glass L_{02}. This beaker moreover prevents rapid evaporation in case the glass should burst (comp. § 1).

The level of the liquid hydrogen is indicated by a float L_{200}, which by means of a silk cord L_{21}, slung over the pulleys L_{22} and L_{23} is balanced by an iron weight L_{24}, moving in a glass tube V_{31}, which can also be pulled up and down with a magnet from outside. The float is a box L_{00} of very thin new-silver, the hook L_{201} is a bent capillary tube open at both ends and soldered in the cover. The glass V_{31} fits by means of india rubber on the cylinder V_{32}, which is connected with the case by means of a thin-walled new-silver tube V_{30}.

The hydrogen is drawn off through the new-silver siphon tube N_{61}, which is continued as the double-walled tube N_{51} N_{501}, leading towards the delivery cock N_{01}. Here, as at the ethylene cock (description of MATHIAS l. c. fig. 2), the packing N_3 and the screw-thread are in the portion that is not cooled. The pin N_1, made of a new-silver tube, passes through the cock-carrying tube N_4. Both the outlet tube N_0 and the delivery cock N_4 are surrounded by a portion of the cold hydrogen vapours, which to this end are forced to escape between the double wall of the tube through N_{504} and along Kha (Kd on Pl. II). The outer wall N_{501}, N_{502} of the double-walled tube is insulated from the side tube V_{21} at the case V_{20} by means of wool.

The glass L is covered with a felt cover L_3, fitted at the bottom with a sheet of nickel-paper to prevent radiation towards the liquid hydrogen. This cover fits tightly on the lower end E_2 of E and rests on the tube N_{501} and the pulley-case L_{22}.

f. We still have to describe the various safety arrangements to prevent the apparatus from bursting when the cock M should suddenly admit too much gas, as might occur when the opening has been blocked by frozen impurities in the gas, which suddenly let loose or when one of the tubes breaks down owing to the same blocking or an other cause.

For this purpose serves in the first place the wide glass tube W_1, which ends below mercury. The quantity of gas which of a sudden escapes, and the great force with which the mercury is sometimes flung away rendered it necessary to make a case W_{30} with several screens W_{31} all of varnished card-board to collect the mercury and to reconduct it into the glass W_2 (where a sufficient quantity of it must be present for filling the tube during the exhaustion).

If the pressure in the reservoir rises higher than that for which the safety tube is designed, the thin-walled india rubber tube V_{42}, which is drawn over the perforated brass cylinder wall V_{41} (separated from it by a thin sheet of tissue-paper), breaks. The safety apparatus is connected with the case V_1 by a wide new-silver tube V_{40}.

In order to avoid impurities in the hydrogen in the liquefactor through diffusion of air the india rubber cylinder V_{432} that is drawn over the rings V_{431} and V_{430} after being exhausted is filled through the cock V_{44} with hydrogen under excess of pressure; during the exhaust the india rubber cylinder V_{432} is pressed against the india rubber wall V_{42}.

An arrangement of an entirely identical construction protects the case U_1, which encloses the principal regenerator, and the case U_2 which encloses the forecooling regenerator C.

As to the protection against pressure which may occur in consequence of evaporation of air, it was sufficient to protect the refrigerator space F by means of the tube Y opening below mercury.

g. In protecting the different parts against heat from the surrounding atmosphere, care has been taken that those surfaces of which the temperature might fall below the boiling point of air and which are not sufficiently protected by the conduction from less cooled parts, should not come into contact with air but only with hydrogen. The refrigerator vessel F, for instance, is surrounded with the hydrogen which fills the cases U and V; hydrogen is also to be found in the space between the vacuum glass L and the wall of the case V; and lastly a side tube V_{20} and V_{21} branches off from the case V in order to surround with hydrogen the double-walled siphon tube N_{51}, N_{501} and the double walled cock N_4, N_{501}.

The new-silver case V, from which the vacuum glass L is insulated by layers of paper V_{64} and the refrigerator vessel F by a layer of flannel, and in the same way the new-silver case U, are further protected from conduction of heat from outside by separate wrappings of capoc V_{81}, packed within a card-board cover V_{82} pasted together. To prevent condensation of water vapour, the air in this enclosed space communicates with the atmosphere by means of a drying tube *t.dr* filled with pieces of sodium hydroxide, as in the ethylene- and methyl chloride regenerators (comp. above sub *b*).

The air-tight connection between the case U and the case V is effected by the india rubber ring *Ua*, which fits on the glass and on the strengthened rims U_{50} and V_{50} of the new-silver cases. India rubber of somewhat larger dimensions can only be used for tightening purposes when it is not cooled. In this case the conduction along the new-silver wall, which is insulated from the vacuum glass by layers of paper, is so slight that the ring-shaped strengthened rims remain at the ordinary temperature and the closure can be effected by a stout stretched india rubber ring. When the india rubber is only pressed on the glass this closure is not perfectly tight; therefore the whole connection is surrounded with an atmosphere of almost pure hydrogen, which is obtained and maintained by the india rubber ring *Uc*, which fits tightly on U_1 and V_1 and which is filled with hydrogen under excess of pressure through the cock *Ud*. Thanks to the small conduction of heat of new-silver no cooling is to be feared for the connections of V_{42} and U_{42} no more than for the packings of the cocks M_3 and N_3.

h. The cases V and U are joined and form one firm whole by the three rods *Ub* with the screw-fastenings U_{51} and V_{51}. The vacuum glass E_0, held by the india rubber ring *Ua*, rests with a wooden ring E_1 and a new-silver cylinder U_{31} against the refrigerator vessel F.

The whole construction can stand exhaustion, which is necessary to fill the apparatus with pure hydrogen. After the case U, of which the parts U_1 and U_2 are connected together by beams, and the case V are mounted separately, the vacuum glass E is placed in position and the case V is connected with the case U. The entire liquefactor is suspended from the ceiling by means of some rods and is particularly supported by the stout outlet tube F_3 for air and the outlet tube U_5 for hydrogen.

Plate II represents the circulation schematically: the pieces of apparatus in their true proportions, the connections only schematically. The liquefactor is designated by the letters $\mathfrak{Liq}$. The compressed hydrogen is admitted through Kc, the hydrogen blown off is let out through Khd or Khc.

i. Before the apparatus is set working it is filled with pure hydrogen (the cock M being open) by means of exhaustion and admission of pure hydrogen along Kc. In the drying tubes $\mathfrak{D}a$ and $\mathfrak{D}b$ the pure hydrogen is freed from any traces of moisture which it might have absorbed.

§ 3. *The compressors and the gasometers.*

a. The hydrogen is put under high pressure by means of two compressors in each of which the compression is brought about in two steps.

While other physicists use compressors with water injection running at great speed of the same kind as I have formerly arranged for operations with pure gas (comp. Comm. N°. 14 of Dec. '94, § 10, and N°. 51, Sept. '99, § 3), I have used for the hydrogen circulation slowly running compressors (see Pl. II $\mathfrak{G}$ at 110 and $\mathfrak{H}$ at 80 revolutions per minute) which are lubricated with oil. To enable constant working with hydrogen the highest degree of purity of the gas is required. For if air is mixed with the gas it is deposited in the regenerator spiral and when some quantity of it is collected there it will freeze and melt alternately through the unavoidable variations of temperature in different parts of the spiral, so that even small quantities, taking into consideration that the melted air flows downward, necessarily must cause blocking. And such small quantities of air may easily come in through the large quantity of injection water which is necessary for the above mentioned compressors with water injection or may penetrate into the pieces of apparatus which are required when the same injection water is repeatedly used. Lastly the chance of losing gas is much smaller with the last mentioned compressors and the manipulation much easier. These compressors are made very carefully by the BURCKHARDT company at Basel.

In the first compressor (𝔊 Pl. II, displacing 20 M^3 per hour) the gas is raised in the first cylinder (double-acting with slide) from 1 to 5 and in the second cylinder (plunger and valves) from 5 to 25 atmospheres; in the second compressor 𝔋 (plunger and valves) in the first cylinder from 25 to 50 and in the second from 50 to 250 atmospheres. After each compression the gas is led through a cooling spiral. With the two first cooling spirals (those of 𝔊 Pl. II) an oil-separator is connected.

Safety-valves lead from each reservoir back to the delivery; moreover the packings are shut off with oil-holders (Comm. N°. 14 '94 and N°. 83, Pl. VIII). The hydrogen that might escape from the packing at 𝔋 is collected.

b. The high pressure compressor forces the hydrogen through two steel drying tubes 𝔇*a* and 𝔇*b* filled with pieces of sodium hydroxide (comp. § 2, *i*, and Pl. II), of which the first also acts like an air-chamber for the regenerator spiral. As in all the operations the gas (comp. *c*) originally is almost dry and comes only into contact with oil, we need only now and then run off a small quantity of concentrated sodium hydroxide solution.

c. For the usual working the compressors suck the gas from gasometers. If these should float on water the separation of the water vapour, which is inevitably taken along by the large quantities of gas displaced, which constantly come into contact with water, would give rise to great difficulties in the compression. Therefore we have used for this purpose two zinced gasometers, *Gaz a* and *Gaz b*, Pl. II, with tinned welds (holding each 1 $M.^3$) floating upon oil [1]), which formerly (comp. Comm. N°. 14, Dec. '94) have been arranged for collecting ethylene [2]).

The cock *Kpa* (*Kpb*) is immersed in oil; likewise the connection of the glass tube, through which the oil of the gasholder can be visibly sucked up till it is above the cock, with the cover are immersed in oil. The india rubber outlet tube and the connection with the

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[1]) The drawing sufficiently represents the construction which has been followed for economizing oil. The gasometers can be placed outside the laboratory and therefore they are protected by a cover of galvanized iron and curtains of tarred canvas, which can be drawn round them.

[2]) Formerly it was of the utmost importance that ethylene could be kept pure and dry in the gasometers. But now the purifying of ethylene through freezing in liquid air (comp. Comm. N°. 94*e* IX § 1) has become a very simple operation and weldless reservoirs for the storage of the compressed gas are obtainable in all dimensions.

copper exhaust tube are surrounded by a second india rubber tube filled with glycerine. From the cock onward the conduction can be exhausted; to prevent the tube from collapsing during the exhaust a steel spiral has been placed in it. A float with valve *Kph* (*Kpi*) prevents the oil from being drawn over into the apparatus.

Besides these gasometers we dispose of two other gasometers holding 5 M^3 each to collect hydrogen of a less degree of purity. They are built following the same system as the zinced gasometers for the economizing of liquid, carefully riveted and caulked and float on a solution of calcium chloride. The oil-gasholders serve only for the storage of very pure hydrogen and this only while the apparatus is working.

During the rest of the time the pure hydrogen is kept in the known steel bottles shown on Pl. II at ℜ*ha*. When we wish to liquefy hydrogen, this is blown off into the gasometer through *Kg* (*Khe*, *Kpe* and *Kpb* for instance to *Gaz b*), after this gasometer, which has been left standing filled with hydrogen, is washed out on purpose with pure hydrogen. When we stop working the hydrogen by means of 𝔖 and ℌ is repumped along *Kpf* and *Kpc* through *Ka* and *Kf* into the reservoirs ℜ*ha*.

The gasometers may be connected with the pumps or the liquefactor either separately or together. The former is especially required when the cryostat is worked (comp. XII) and for the purification of hydrogen (comp. XIV).

§ 4. *The cooling by means of liquid air.*

a. The liquid air is sucked into the refrigerator vessel *F* (Pl. I), which by *Ks* (Pl. II) is coupled to the vacuumpump 𝔉, along the tube *Pb* connected with the siphon of a vacuum bottle 𝔄*a* containing liquid air.

This has been filled by catching the jet of liquid air from the apparatus (Pl. IV, fig. 2) in which it is prepared (comp. XIII), into the open glass (see the annexed fig. 1) and is kept, covered with a loose felt stopper *m* (fig. 1). To siphon the liquid air into the apparatus, where it is to be used, the stopper is replaced by a cap *h* (fig. 1) with 3 tubes; one of these *d* is designed to raise the pressure in the bottle with a small handpump, the other *c* is connected to a small mercury manometer, and the third *b* reaches down to the bottom, so that the liquid gas can be let out. (When the bottle is used for other liquid gases, *d* is used for the outlet of the vapours and *c* for the admission of the liquid gas). One of the first two tubes reaches as far as the neck. It may also be used

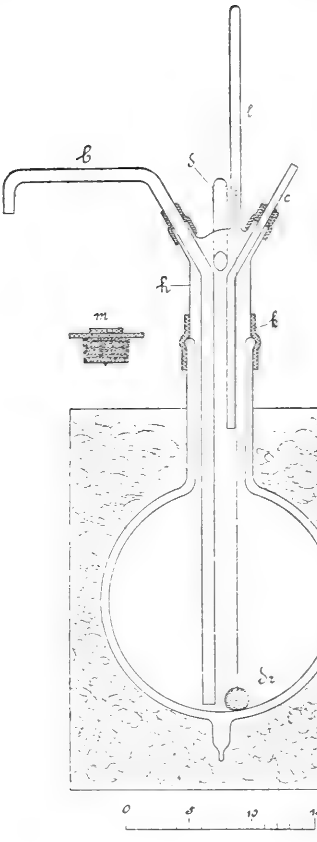

Fig. 1

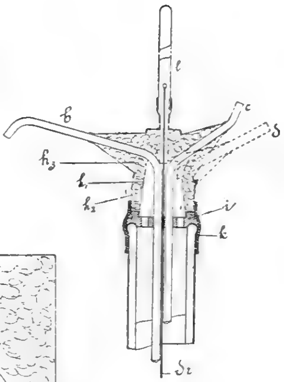

Fig. 2.

to conduct liquid air from a larger stock into the bottle. With the cap a closed glass tube *b* is connected, in which an index of a cork float *dr* indicates the height of the liquid.

The caps, as shown in fig. 1, were formerly blown of glass and the three tubes were fastened into it by means of india rubber. Afterwards the cap h_1, as shown in fig. 2, with the three tubes and with a double wall h_2 of very thin new-silver have been soldered to form one whole, which is fastened on the bottle with an india rubber ring *k*. The space between the walls is filled with capoc h_3 and the whole piece rests on the neck of the bottle by means of a wooden block *i*. After it is placed on the bottle the cap is wrapped round with wool.

With a view to the transport the vacuum glass is placed in a card-board box with fibre packing.

When the siphon is not used it is closed with a piece of india rubber tubing, fitted with a small stopper. When we wish to siphon over, this stopper is removed and the inflow tube *Pb* (Pl. I) is connected with the siphon-tube *b* (fig. 2) with a piece of india rubber tubing. To prevent breaking of the india rubber, which through the cold has become brittle, the new-silver tubes are arranged so that they fit into each other, hence the india rubber is not strained so much.

The admission of liquid air into the refrigerator vessel is further regulated with the cock *P*, Pl. I. When the float indicates that the reservoir is almost empty, another reservoir is put in its place.

The cock *Ks* is regulated according to the readings on the mercury manometer tube *Y*.

b. The air is caused to evaporate at a pressure of 15 mm., which is possible because a BURCKHARDT-WEISS-pump 𝔉 Pl. II is used as vacuumpump.

The vacuumpump is the same as that used in measurements with the cryostat containing a bath at —217° (comp. Comm. No. 94^d June '05) and has been arranged to this end as described in Comm. No. 83 V. March '03. The letters at 𝔉 on Pl. II have the same meaning as on Pl. VIII of Comm. N°. 83. As has been described in Comm. No. 94^d VIII, June '05, this vacuumpump 𝔉, displacing 360 M^3 per hour, is exhausted by a small vacuumpump, displacing 20 M^3 per hour[1]) (indicated by 𝔎 on Pl. II).

§ 5. *How the liquefactor is set working.*

a. When the apparatus is filled with pure hydrogen, as described in § 2, and when air evaporating under low pressure is let into the refrigerator, for convenience the hydrogen, admitted through 𝔊 and ℌ Pl. II along *Kc*, is caused to stream through during some time with wide open cock *M*, Pl. I, for the forecooling of the whole apparatus. Then the cock *M* is regulated so that the pressure in the regenerator spiral rises slowly. It is quite possible for the apparatus to deliver liquid hydrogen at 100 atm., it has done so at 70 atm. As a rule, however, the pressure is kept between 180 and 200 atm. because then the efficiency is some times larger [2]). The liquefactor then delivers about 4 liters liquid hydrogen per hour. Part of the hydrogen is allowed to escape along *Kha* Pl. I fig. 2 (*Kd* Pl. II) for the forecooling of the siphon N_{51} Pl. I and the cock *N*.

As soon as liquid hydrogen begins to separate we perceive that the

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[1]) When we use oxygen (comp. § 2 note 2), and a pressure as low as a few mm should be required, forecooling is required in the second refrigerator like *F*, where oxygen evaporates under low pressure, for instance towards 𝔎.

[2]) V. D. WAALS has shown the way how to compute this (comp. note 1 § 2).

cock *M* must be tightened a little more in order to keep the pressure within the same limits.

When liquid hydrogen collects in *L* rime is seen on the tube N_{503}, Pl. I, fig. 2 near the cock *N*.

b. The gaseous hydrogen escapes along *Khd* (Pl. II) to 𝔊 and to one or to both gasholders. When liquid hydrogen separates, the compressor 𝔊 receives, besides the hydrogen escaping from the liquefactor, a quantity of hydrogen from the gasholders along *Kpa* and *Kpb*. New pure hydrogen is then admitted from ℜ*ha*, Pl. II, along *Kg*.

c. The float (L_{200} Pl. I) does not begin to indicate until a fairly large quantity of liquid hydrogen is collected.

§ 6. *The siphoning of liquid hydrogen and the demonstration of liquid and solid hydrogen.*

a. When the float L_{200}, Pl. I, shows that the glass is filled to the top (this usually happens an hour after the liquefactor is set working) the hydrogen is siphoned into the vacuum glasses *Hydr a*, *Hydr b* etc., Pl. II, which are connected behind each other so that the cold hydrogen vapour, which is led through them, cools them successively before they are filled. When one is full the next is moved one place further.

They are fitted with caps of the same description as the bottles for siphoning liquid air, figs. 1 and 2 in the text of § 4. Pl. III represents on a larger scale 2 bottles coupled behind each other and a third which has been filled, all as on Pl. II, in side- and top-elevation. The evaporated hydrogen escapes along d'_3 and d''_3 and further along K_0 (see Pl. II) to the gasholder. The letters of the figures have the same meaning as in fig. 2; for the explanation I refer to the description of that figure in § 4.

The conduction of heat in the thin new-silver is so little that the new-silver tubes can be soldered in the caps h_2 and that they are sufficiently protected by a double wall h_{11} of new-silver with a layer of capoc between, which is again thickly enveloped in wool.

It has occurred that the india rubber ring k' has burst through the great fall of temperature, but in general the use of india rubber has afforded no difficulties, and hence the somewhat less simple construction, which would lie to hand, and through which we avoid cooling of the india rubber at the place where it must fit, has not yet been made.

b. If we desire to see the jet of liquid hydrogen flowing from the cock *N*, Pl. I, we connect with the tube N_0 and the india rubber tube d_3, instead of the silvered flasks of Pl. II and Pl. III, a transparent vacuum cylinder fig. 3*a*, closed by an india rubber ring with a new-silver cap with inlet tube. After the cock is opened the india rubber outflow tube d_3 covers with rime and becomes as hard as glass; soon the first drops in spheroidal state are seen splashing on the bottom of the glass and the lively liquid fills the glass. If, as shown by fig. 3*b*, a glass cover is placed on the top, the glass may be left standing in the open air without the air condensing into it, which would hasten the evaporation. In the same manner I have sometimes filled non-silvered vacuum flasks holding 1 liter, where the liquid hydrogen boils vividly just as in the glass mentioned before. The evaporation is of course much less and the rising of the bubbles stops when the vacuum glass or the vacuum flask is placed in liquid air.

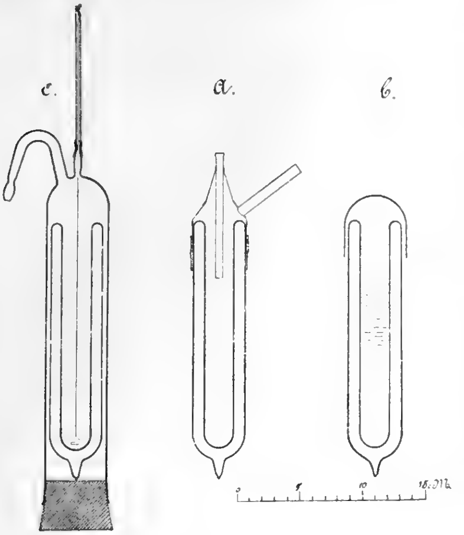

Fig. 3

To demonstrate the pouring of hydrogen from one open vessel into the other, I use a glass, cap round which a collar of thin india rubber sheet is bound (comp. the accompanying fig. 4). The flask from which and the glass into which we want to pour, the latter after being filled with liquid air and quickly turned down and up again (if this is not done quickly a blue deposit of H_2O from the air will come in), are placed under the cap, which fills with hydrogen and hence remains transparent, then with the india rubber round the neck of the bottle and round the glass we take hold of the two, each in one hand. Through the cap we can observe the pouring. The escaping hydrogen rises in the air as clouds.

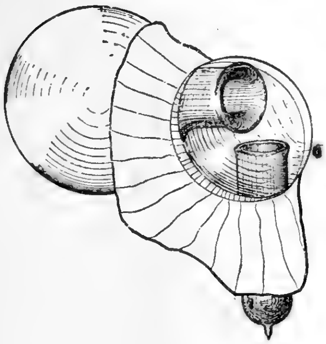

Fig. 4

In order to keep the half filled glass clear it is covered, under the pouring off cap, with a glass cap, and so it can be taken away from the pouring off cap.

c. It is very instructive to see what happens when we proceed to remove this cap and the glass is tilted over a little. Above the level of the liquid hydrogen thick snowy clouds of solid air are formed, the minute solid particles drop on the bottom through the extremely light hydrogen (specific weight $^1/_{14}$), there they collect to a white pulver which, when the hydrogen is shaken, behaves as heavy sand would behave in water. When the hydrogen is evaporated that sand soon melts down to liquid air [1]).

d. Solid hydrogen may be easily demonstrated when we place the glass, fig. 3*a*, under a bell as fig. 3*c* in which a wire can be moved up and down (for instance by fastening it into an india rubber tube) and connect the bell with the airpump. A starch-like white cake is soon formed, which can be moved up and down with the wire.

e. To fill a vacuum flask as shown on Pl. III we first cool it by washing it out with liquid air. The connection at N_0, Pl. I fig. 2 and Pl. III, is brought about simply by drawing a piece of india rubber tubing N_{81} over the new-silver tubes N_0 and C_0 fitting into each other, round which flannel is swaddled. This again is enveloped in loose wool. When some bottles are connected they are filled with pure hydrogen through the tube b_0 of *Hydr. a* after repeated exhaustion and care is also taken that each newly connected bottle is filled with pure hydrogen and that no air can enter the apparatus while the connections are being made.

When from the indications of the float L_{200} (Pl. I, fig. 2) we conclude that a bottle is full, it is disconnected, but as long as the liquid hydrogen is kept in this glass the evaporating hydrogen is allowed to escape into the gasholder, as is represented by Pl. III for *Hydr. c.* The disconnection at N_0 is simply effected by taking off the flannel band C_2, heating the piece of india rubber tubing N_{81} (unvolcanized) with one's fingers (or with a pair of pinchers arranged to this end) till it becomes soft again and can be shoved from the tube N_0.

§ 7. *Transport to the cryostat, closure of the cycle.*

a. The vacuum glasses filled with liquid hydrogen (see *Hydr. d* on Pl. II) are transported to the room where the cryostat $\mathfrak{Cr}$ is mounted

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[1]) All this has been demonstrated by me at the meeting of 28 May. To show the small specific weight of hydrogen I held a very thin-walled glass bulb, which sinks only a little in ether (as a massive glass ball in mercury), suspended by a thin thread in the glass with liquid hydrogen, where it fell like a massive glass ball in water and tapped on the bottom.

into which the hydrogen is siphoned. To this end the tube b''_1 of Pl. III is connected (again by a piece of india rubber tubing, enveloped in flannel and wool) to the inflow tube a_1 of the cryostat and the tube d_0 to an inflow tube of pure hydrogen under pressure, which is admitted from 𝔑*hc*, Pl. II, along *Kwa*. With all these connections and disconnections care must be taken that there should always be an excess of pressure in the tubes that are to be connected, that the disconnected tubes should be immediately closed with stoppers but that first the apparatus after having been exhausted should preliminarily be filled with pure hydrogen. The liquid hydrogen is not admitted into the cryostat ℭ*r* until the latter has been cooled — coupled in another way (see the dotted line on Pl. II) — by means of pure hydrogen which has been led from 𝔑*hc* through a cooling tube immersed in liquid air. This refrigerator is of a similar construction as the nitrogen condenser Pl. VII of Comm. N°. 83 (March '03). Instead of *Nliq* should be read H_2 and instead of *Ox liq*, *Aër liq*, which is siphoned from the vacuum flask 𝔄*c*. (comp. § 6).

During the siphoning of the liquid hydrogen into ℭ*r* the rapidity of the influx is regulated after a mercury manometer, which is connected with the tube *c* on the cap *h*, Pl. III (comp. fig. 2 of § 4).

b. From the cryostat the evaporated hydrogen escapes along Y_{37} into the compressor 𝔖, Pl. II, which can also serve as vacuumpump and which precautiously through 𝔇 and *Kf* at the dotted connection *Kf* stores the gas, which might contain minute impurities, in the separate reservoir 𝔑*hd*; or it escapes along Y_{32} and *Kpe* or *Kpd* into the gasholders *Gaz a* or *Gaz b*.

XI. *The purification of hydrogen for the cycle.*

a. This subject has been treated in Comm. N°. 94*d* IX. To be able always to obtain pure hydrogen, to make up for inevitable losses, and lastly to be freed from the fear of losing pure hydrogen, which perhaps might deter us from undertaking some experiments, a permanent arrangement for the purification has been made after the principle laid down in IX. The apparatus for the purification is represented on Pl. IV and is also to be found on Pl. II at ℨ.

The impure hydrogen from 𝔑*hb* is admitted through *Kn* and along a drying tube into a regenerator tube (see Pl. IV) consisting of two tubes enclosing each other concentrically, of which the outer *a* serves for the inflow, the inner *b* for the outlet. Outside the apparatus *a* and *b* are separated as a_0 and b_0, within the apparatus from the point *c* downwards *a* is continued as a_1 and subsequently as the spiral

a_2 to terminate at the top of the separating cylinder *d*, from which the gas escapes through b_1, and the impurities separated from the hydrogen as liquid escape along *e* and *Km* (comp. Pl. II). The liquid air, with which the cooling tube and the separating cylinder are cooled, is admitted along *l* and the cock *m* (and drawn from the vacuum glass $\mathfrak{A}b$, Pl. II); a float *dr* indicates the level of the liquid air. The evaporating air is drawn off by the vacuumpump $\mathfrak{F}$ (Pl. II) along *Kt.* The refrigerator vessel *p* is protected against heat from outside by a double wall *q* of new-silver with capoc *v* packed between, of which the lower end is immersed in a vacuum glass r_1 while the whole is surrounded with a layer of capoc enclosed in a varnished cover of card-board pasted together in the same way as for the hydrogen liquefactor. The glass tube *Y*, opening below mercury, serves among others to read the pressure under which the evaporation takes place.

The cock *Km* is turned so that some more bottles of known capacity are collected of the blown- off gas than, according to the analysis, would be formed by the impurities present in the gas. In this way the purity of the hydrogen is brought to $^1/_{20}\,^0/_0$. It is led along *Kl* to the gasholders, and compressed by $\mathfrak{G}$ and $\mathfrak{H}$ in $\mathfrak{K}hd$.

b. A second purification is effected in the following manner. When we have operated with the liquefactor with pure hydrogen we always, after the experiments are finished, admit a portion of this not yet quite pure gas into the apparatus. After some time, usually after 4 liters of liquid hydrogen are formed, the cock is blocked. As soon as it becomes necessary to move this repeatedly to and fro — TRAVERS and OLSZEWSKI say that this is constantly necessary but I consider it as a sign that the apparatus is about to get more and more disordered — the work is suspended and the cock *M* (Pl. I) closed, after which $\mathfrak{D}_a$ and $\mathfrak{D}_b$ (Pl. II) are blown off to the gasholders along K_a and K_g, and K_c is shut. The liquid hydrogen, after being siphoned, is allowed to evaporate and to pass over into the gasholder for pure hydrogen. The impurities are found when, with *M* and K_c closed, we return to the ordinary temperature and analyze the gas, which in $\mathfrak{D}$ has come to high pressure.

If necessary, the purified hydrogen is once more subjected to this process.

When, after the liquefactor with pure hydrogen has been worked, we go on admitting a quantity of preliminarily purified hydrogen of $^1/_{20}\,^0/_0$ and take care that the impurities are removed, we gradually obtain and maintain without trouble a sufficient quantity of pure hydrogen.

XII. *Cryostat especially for temperatures from — 252° to — 259°.*

§ 1. *The principle.* In X § 1 I have said that we succeeded in pouring into the cryostat of Comm. N°. 94^d VIII a bath of liquid hydrogen, maintaining it there and making measurements in it, but then the vacuum glass cracked. By mere chance it happened that the measuring apparatus which contained the work of several series of measurements came forth uninjured after removal of the sherds and fragments of the vacuum glass. With the arrangement which I am going to describe now we need not be afraid of an adversity as was imminent then. Now the bath of liquid hydrogen is protected against heat from outside by its own vapour. The new apparatus reminds us in many respects of that which I used to obtain a bath of liquid oxygen when the vacuum glasses were not yet known; the case of the cryostat then used has even been sacrificed in order to construct the apparatus described now.

The principal cause of the cracking of vacuum glasses, which I have pointed out in several communications as a danger for placing precious pieces of apparatus into them are the great stresses caused by the great differences in temperature between the inner and the outer wall and which are added to the stresses which exist already in consequence of the vacuum. To the influence of those stresses it was to be ascribed, for instance, that only through the insertion of a metal spring the vacuum tubes (described in Comm. N°. 85, April '05) could resist the cooling with liquid air. It sometimes happens that a vacuum flask used for liquid air cracks without apparent cause and with the same cooling the wide vacuum cylinders are still less trustworthy than the flasks. At the much stronger cooling with liquid hydrogen the danger of cracking increases still. Habit makes us inclined to forget dangers, yet we should rather wonder that a glass as used for the cryostat of Comm. N°. 94^d VIII filled with liquid hydrogen does *not* crack than that it does.

In the new cryostat of Pl. V the cause of the cracking of the vacuum glass has been removed as much as possible and in case it should break in spite of this we have prevented that the measuring apparatus in the bath should be injured. The hydrogen is not poured directly into the vacuum glass B'_{02} but into a glass beaker *Ba*, placed in the vacuum glass (comp. Comm. N°. 23, Jan. '96 at the end of § 4) but separated from it by a new-silver case, which forms, as it were, a lining (see X, *L* Pl. I). Further the evaporated hydrogen is led along the outer wall of the vacuum glass B'_{01}. To be able to work also at reduced pressure and to prevent any admixtures of air from entering into the pure hydrogen used, the whole bath has been placed in a stout cylindrical copper case *Ub*, which can be exhausted.

This cryostat is especially fit for hydrogen, yet may profitably replace those described till now, at least when it is not necessary that we should see what takes place inside the bath. A modified pattern, where this has become possible, in the same way as in the cryostat with liquid oxygen of Comm. N°. 14, Dec. '94, I hope to describe erelong.

In the cryostat now to be described, as in the former, the measuring apparatus, without our changing anything in the mounting of them, will go through the whole range of temperatures from — 23° to — 90° with methyl chloride, from — 103° to — 160° with ethylene, from — 183° to — 217° with oxygen and from — 252° to — 259° with hydrogen (only for the temperatures between — 160° and — 180° we still require methane).

§ 2. *Description.*

a. The new cryostat is represented on Pl. V. The letters, in so far as the parts have the same signification, are the same as for the descriptions of the other cryostats; modified parts are designated by new accents and new parts by analogous letters, so that the explanations of Comms. N°. 83, N°. 94^c and N°. 94^d on the attainment of uniform and constant temperatures, to which I shall refer for the rest, can serve also here. Pl. II shows how the cryostat is inserted into the hydrogen cycle. In chapter X § 7 is described how the liquid hydrogen is led into the cryostat. Especially for the regulation of the temperature this plate should be compared with Pl. VI of Comm. N°. 83, March '03. Instead of *Bu Vac* on the latter plate, the compressor $\mathfrak{G}$ serves as vacuumpump here (see Pl. II of the present paper).

b. The measuring apparatus (as on the plate of Comm. N°. 94^d VIII I have represented here the comparison of a thermoelement with a resistance thermometer) are placed within the protecting cylinder ξ_0 of the stirring apparatus. This is held in its place by 4 glass tubes ξ_{40} fitted with caps of copper tubing ξ_{41} and ξ_{42} at the ends of the rods.

The beaker *Ba*, containing the bath of liquid hydrogen, is supported by a new-silver cylinder Ba_2, in the cylindrical rim Ba_0 of which the glass fits exactly; the beaker is held in its place by 4 flat, thin, new-silver suspension bands running downwards from Ba_0 and uniting below the bottom of *Ba*. The ring Ba_0 is the cylinder Ba_2

continued, with which it is connected by six strengthened supporting ribs Ba_1. At the top it is strengthened by a brass rim Ba_3 with a protruding part, against which presses the upper rim Ua of the case U. On Ba_3 rests the cover N'_{01} in which a stopper is placed carrying the measuring apparatus. The india rubber band effects the closure (comp. also Comm. Nos. 83, 94^c and 94^d).

c. In the case U the vacuumglass B'_0, of which the inner wall B'_{01} is protected by the thin new-silver cup Bb, is suspended by bands L'_6 and supported by the wooden block L'_1. The card-board cover B'_4 forces the evaporated hydrogen, which escapes between the interstices of the supporting ridges, over the paste-board screen B'_{030} with notches B'_{031} along the way indicated by arrows, to escape at T_{12}. The case is lined with felt, covered with nickel paper (comp. Comm. N°. 14, Dec. '94, and Comm. N°. 51, Sept. '99).

d. The keeping of liquid hydrogen within an enclosed space, of which the walls have for a great part a much higher temperature than the critical temperature of hydrogen, involves special safety arrangements. That this was no needless precaution appeared when the vacuum glass cracked unexpectedly (comp. X § 1) and of a quantity of more than 1,5 liter of liquid hydrogen nothing was to be seen after a few seconds. Now this disappearance is equivalent with the sudden formation of some hundreds of liters of gas, which would explode the case if no ample opportunity of escape were offered to the gas as soon as the pressure rises a little above the atmospheric.

In the new cryostat I have avoided this danger in the same way as at the time when I first poured off a bath of liquid oxygen within a closed apparatus (comp. Comm. N°. 14, Dec. '94).

The bottom of the case U is made a safety valve of very large dimensions; as cover W_2 of perforated copper with strengthened ridges it fits into the cylindrical case Ub, which is strengthened with the rim W. Over the external side of this cover (as in the safety tubes for the hydrogen liquefactor) a thin india rubber sheet W_1 — separated from the copper by a sheet of paper — is stretched, which at the least excess of pressure swells and bursts, while moreover the entire vacuum glass or pieces of it, if they should be forced out of the case, push the cover W_2 in front of them without resistance. As the airtight fit of the sheet of india rubber W_1 on the ring W is not trustworthy and diffusion through contact of the india-rubber with the air must be prevented, it is surrounded with hydrogen; this is done by filling the india rubber cylinder Wa, drawn over the supporting ring Ub_4 and the auxiliary cover Wb, with hydrogen along Wc.

The cords *Wd* serve to press the auxiliary cover *Wb* with a certain force against the safety sheet, namely by so much as the excess of pressure amounts to, which for one reason or other we want to admit into the case. To prevent the india rubber from cooling down, for then the arrangement would no longer satisfy the requirements, the lower end of the case is lengthened by the cylindrical piece Ub_2 which between the rim Ub_4 and the principal body of the case is made of new-silver to prevent the cooling of the lower rim. The entire lower part is stuffed with layers of felt and wool while also a copper flange Ub_3 by conduction of heat from outside protects the lower wall from cooling.

e. The hydrogen is admitted through the new-silver tube *a*, on which the siphon tube of a vacuumglass (X § 7) is connected with a piece of india rubber tubing a_2 (which otherwise is closed with a stopper a_4, comp. X § 4 *a*). The new-silver tube is put into the new-silver side piece *Ud*, which is soldered on the case and, being stuffed with capoc held back by a paper tube *Ue*, carries at the end a piece of cork *Uf* for support. When the vacuum glass B_0 with the case *U* are placed round the beaker *Ba*, the tube a_1 is pulled back a little. When subsequently the case is fastened in its position the tube is pushed forward until a ridge on a_1 is checked by a notch in *Ud*, so that its end projects into the beaker *Ba* and the hydrogen can flow into it. The india rubber tube a_2 forms the closure on a_1 and *Ud*.

§ 3. *Remarks on the measurements with the cryostat.*

In chapter X § 7 I have communicated how the preliminary cooling is obtained. In one of the experiments, for instance, 3 liters of liquid air were used for it and the temperature was diminished to —110°. Then hydrogen was very carefully siphoned into the cryostat under constant stirring; a quantity of 5 liters was sufficient to obtain a bath of 1.5 liter. About 0.2 liter per hour evaporated after this. During the reduction of the pressure to about 60 m.m. ± 0.2 liter evaporated, and then the evaporation remained about the same. The temperature could be kept constant to within 0.01° in the way described in the former papers. The temperature curves obtained were no less regular than those of Pl. III in Comm. N°. 83 (Febr. and March '03).

If the pressure is reduced down to 54 m.m. the tapping noise of the valves of the stirring apparatus becomes duller. This is a warning that solid hydrogen begins to deposit.

XIII. *The preparation of liquid air by means of the cascade process.*

§ 1. *Efficiency of the regenerative cascade method.* In none of the communications there was as yet occasion to treat more in detail of the preparation of liquid air by the Leiden cascade process. In the description of the preparation of liquid oxygen (in Comm. N°. 24, Dec. '94) I have said that especially the ethylene refrigerator had been constructed very carefully, and that the principle after which various cycles operating in the *regenerative cascade* can be made was embodied there.

When the new methyl chloride circulation (comp. Comm. N°. 87, March '04) was ready and the inadequate methyl chloride refrigerator was replaced by one constructed after the model of the ethylene boiling vessel with application of the experience gained, it was possible to prepare a much larger quantity of liquid oxygen (10 liters per hour easily) with the same ethylene boiling vessel. This quantity will still increase when the regenerator in the ethylene boiling vessel will be enlarged so much as our experience with the new methyl chloride regenerator has again taught to be desirable and when the exhaust tube of the ethylene boiling vessel will have been replaced by one of greater width than could be used originally. The introduction of a nitrous oxide and of a methane cycle, which in '94 stood foremost on our programme, has dropped into the background especially when, also for other reasons (in order to obtain the temperatures mentioned at the end of XII § 1), it appeared desirable to procure vacuumpumps of greater displacing capacity ('96) and these, being arranged for operations with pure gases (described in Comm. N°. 83, March '03) had become fit to be introduced into the ethylene and the methyl chloride cycles (while in general for the cryostats these two cycles were sufficient, cf. the end of XII § 1). Larger quantities of oxygen could be used in consequence, for which (as mentioned in '94) a Brotherhood compressor was employed (comp. the description of the installation for operations with pure gas in Comm. N°. 51 § 3, Sept. '99). A picture of the cascade method in this stage of development accompanies a description of the cryogenic laboratory by H.H. Francis Hyndman in "Engineering" 4 Mrch '04.

This picture represents how the oxygen cycle is used to maintain the circulation in the nitrogen cycle, described in Comm. N°. 83, March 1903. In the same way as nitrogen we also liquefy air with the oxygen cycle. When it is drawn off the liquid air streams from the tube in a considerable jet; about 9 liters of liquid air are collected per hour, so that in one day we can easily prepare half a hectoliter.

Liquid air has striking advantages above liquid oxygen when we have to store large quantities or when with the gas liquefied in the cryogenic laboratory we must cool instruments in other rooms. Only where constant temperatures are aimed at pure oxygen or nitrogen will be preferred for refrigerating purposes, and even then the liquid air can be the intermediate agent, for we need only lead the gases mentioned through a cooling tube immersed in liquid air in order to liquefy nearly as much of it as the quantity of air evaporated amounts to. And so the permanent stock of liquid air maintained in the Physical Laboratory has gradually increased, so that for several years liquid air has been immediately sent off on application both at home and abroad.

§ 2. *The airliquefactor.* The apparatus for the preparation of liquid air by means of liquid oxygen is in principle identical with that serving for nitrogen, but of larger dimensions (see Pl. VI).

Identical letters designate corresponding parts of the apparatus represented (Comm. N°. 83, Pl. VII) for the liquefaction of nitrogen. To liquefy air the ordinary atmospheric air, after being freed by a solution of sodium hydroxide from carbon dioxide, is compressed to 10 atmospheres in the spiral $RgRf$, Pl. VI fig. 1. This spiral branches off from the tube Rq_{00} in the soldered piece Rg_{01} and carries four branches Rg_1, Rg_2, Rg_3 and Rg_4. Each of these tubes has an internal diameter of 3.5 mm., an external diameter of 5.8 mm., and is 22 M. long. The spiral is wound in 63 layers in the same way as the regenerator spiral of the hydrogen liquefactor (comp. X)and, lined with flannel, it fits the new-silver tube p_0, round which it is drawn in the new silver case p. The four windings are united below to one soldered piece to the spiral Rf, 8 M. long, which is immersed in a bath of liquid oxygen and whence the liquid air flows through Rf_3 into the collecting apparatus (see fig. 2). This is placed by the side of the principal apparatus (see fig. 2) and contains the collecting vessel r_0, where the liquid air is separated and whence it is drawn through the siphon. The collecting glass is fitted with a float dr. During work we can see it rising regularly at a fairly rapid rate.

§ 3. *Further improvements.* The regenerative cascade might still be modified in many points before the principle is fully realized and before one improvement or other, made for one of the cycles, has been introduced also in the others and the efficiency is grown to a maximum; but this problem is rather of a technical nature. We prefer to spend the time at our disposal on other problems, as enough liquid air is

KAMERLINGH ONNES. Methods and apparatus used in the cryogenic laboratory at Leiden.
XIII. The preparation of liquid air by means of the cascade process.

Pl. VI.

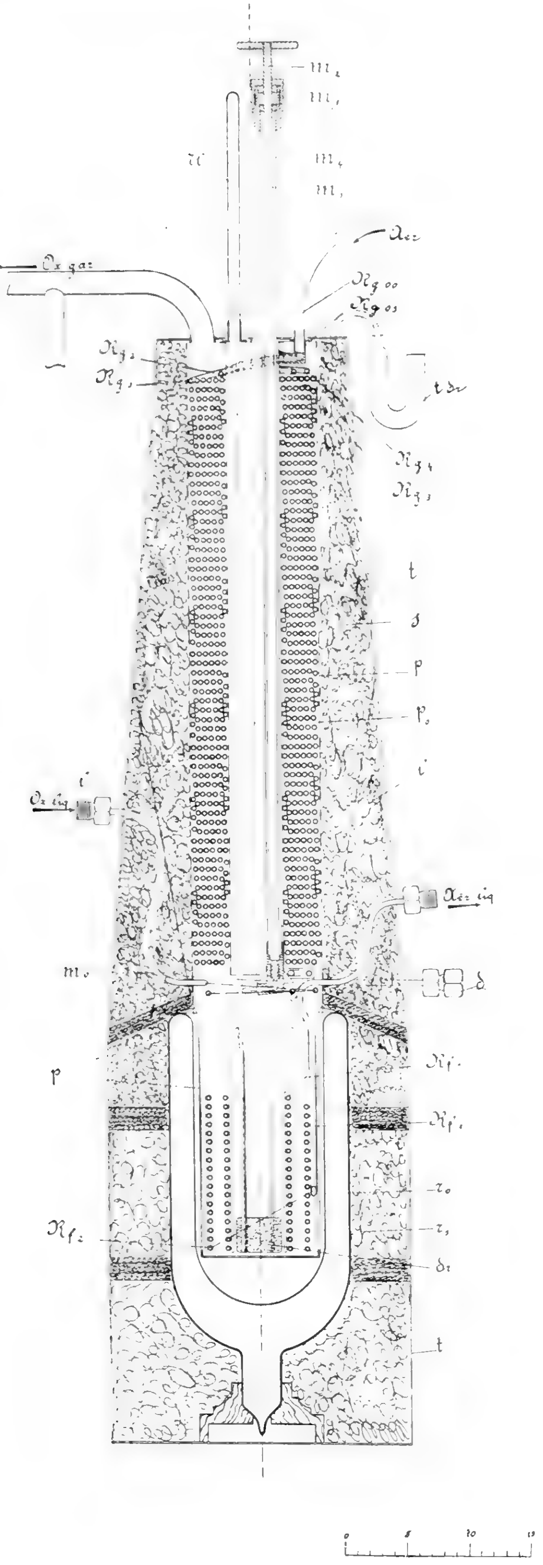

Fig. 1.

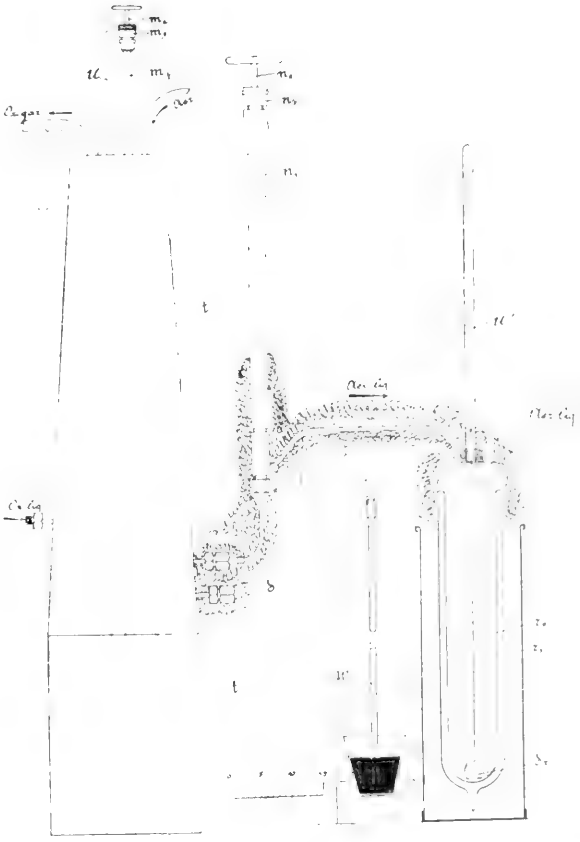

Fig. 2.

produced by the regenerative cascade. Enough but not too much, because for operations with liquid hydrogen (comp. X) and also for other experimentations in the realm of cryogenic work it is very important that we should dispose of such a relatively abundant stock of liquid air as is produced by the Leiden cascade.

XIV. *Preparation of pure hydrogen through distillation of less pure hydrogen.*

It was obvious that we could obtain pure hydrogen for the replenishment of the thermometers and piezometers [1]) when we distil liquid hydrogen at reduced pressure [2]), and then evaporate the very pure liquid thus obtained. Therefore the following apparatus has been constructed (fig. 5).

A vacuum glass A is connected with the liquefactor (see Pl. I and III at N_0) or with a storage bottle, exhausted and filled with liquid hydrogen as indicated in X § 7. Then C (exhausted beforehand) in the vacuum glass B is filled several times out of A, and the vacuum glass B is connected with B_1 to the liquefactor and exhausted like A and also filled with liquid hydrogen and connected with the ordinary airpump at B_2 so that the hydrogen boils in B at 60 m.m. Then hydrogen is distilled over along c_1 into the reservoir C, we

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[1]) In Comm. N^0. 94*e* (June '05) I have mentioned that a purification through compression combined with cooling might be useful in the case of hydrogen even after the latter in the generating apparatus (Comm. N^0. 27, May '96 and N^0. 60, Sept. 1900) had been led over phosphorous pentoxide. I said so especially with a view to the absorption of water vapour as, with due working, the gas — at least to an appreciable vapour tension — cannot contain anything but H_2O and SO_4H_2. How completely the water vapour can be freed in this manner appears from a calculation of Dr. W. H. KEESOM, for which he made use of the formula of SCHEEL (Verh. D. phys. Ges. 7, p. 391, 1905) and from which follows for the pressure of water vapour (above ice) at —180° C. 10^{-18} mm., so that water is entirely held back if the gas remains long enough in the apparatus. This holds for all substances of which the boiling point is higher than that of water (SO_3 vapours, grease-vapours etc.). The operation is therefore also desirable to keep back these substances. As to a gas which is mixed only with water there will remain, when it is led in a stream of 3 liters per hour through a tube of 2 cm. in diameter and 8 cm. in length over phosphorous pentoxide, no more than 1 m.gr. impurity per 40000 liters (MORLEY, Amer. Journ. of Sc. (3) 34 p. 149, 1887). This quantity of 1 m.gr. is probably only for a small part water (MORLEY, Journ. de chim. phys. 3, p. 241, 1905). Therefore the operation mentioned would not be absolutely necessary at least with regard to water vapour when a sufficient contact with the phosphorous pentoxide were ensured. But in this way the uncertainty, which remains on this point, is removed.

[2]) This application follows obviously from what has been suggested by DEWAR, Proc. Chem. Soc. 15, p. 71, 1899.

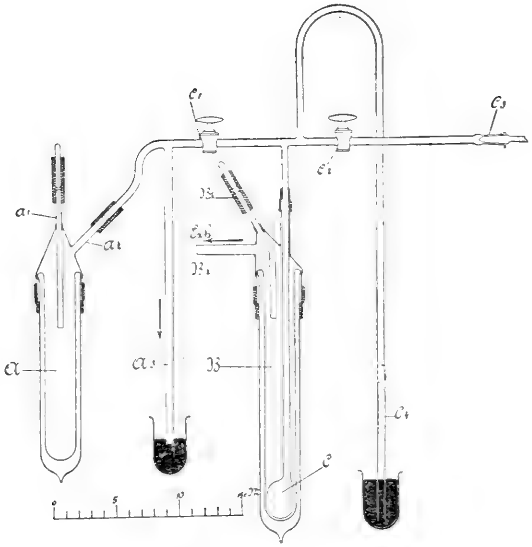

Fig. 5.

shut c_1 and disconnect the india rubber tube at a and remove the whole apparatus to the measuring apparatus which is to be filled with pure hydrogen; to this end the apparatus is connected with the mercury pump, intended for this purpose, at c_3. To take care that the hydrogen in B should evaporate but slowly and the quantity in C should not be lost before we begin to fill the pieces of apparatus, B is placed in a vacuum glass with liquid air.

Physics. — "*On the measurement of very low temperatures.* IX. *Comparison of a thermo-element constantin-steel with the hydrogen thermometer.*" By Prof. H. KAMERLINGH ONNES and C. A. CROMMELIN. Communication N° 95^a from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 30, 1906).

§ 1. *Introduction.* The measurements communicated in this paper form part of a series, which was undertaken long ago with a view to obtain data about the trustworthiness of the determination of low temperatures which are as far as possible independent and intercomparable. Therefore the plan had been made to compare a thermo-element[1]), a gold- and a platinum-resistance thermometer[2])

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[1]) Comp. comms. N°. 27 and 89. (Proc. Roy. Ac. May 1896, June 1896, and Feb. 1904).

[2]) Comp. comms. N°. 77 and 93. (Idem Febr. 1902 and Oct. 1904).

each individually with two gas thermometers and also with each other, while the deviation of the gas thermometer would be determined by means of a differential thermometer [1]). Nitrogen had originally been chosen by the side of hydrogen, afterwards nitrogen has been replaced by helium. Because all these measurements have often been repeated on account of constant improvements, only those figures have been given which refer to the gold- and the platinum-resistance thermometer [2]), and these, for which others will be substituted in Comm. N°. 95^c, are only of interest in so far as they show that the method followed can lead to the desired accuracy. The results obtained with regard to the above-mentioned thermo-element do not yet satisfy our requirements in all respects; yet all the same it appeared desirable to publish them even if it was only because the temperature determinations for some measurements, which will erelong be discussed, have been made with this thermo-element.

§ 2. *Comparisons made by other observers.*

a. Constantin-iron elements have been compared with a hydrogen thermometer only by HOLBORN and WIEN [3]) and LADENBURG and KRÜGEL [4]). The calibration of the two former investigators is based on a comparison at two points viz. in solid carbon dioxide and alcohol (for which — 78°.3 is given) and in liquid air (for which they found — 189°.1). They hold that the temperature can be represented by the formula

$$t = aE + bE^2$$

and record that at an observation for testing purpose in boiling oxygen (— 183°.2 at 760 m.m. mercury pressure) a good harmony was obtained.

LADENBURG and KRÜGEL deem HOLBORN and WIEN's formula unsatisfactory and propose

$$t = aE + bE^2 + cE^3.$$

They compare the thermo-element with the hydrogen thermometer at 3 points, viz. solid carbon dioxide with alcohol, boiling ethylene and liquid air. As a control they have determined the melting point of ether (— 112°) and have found a deviation of 1 deg. With this they rest satisfied.

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[1]) Comp. comm. N°. 94^c. (Idem June 1905).

[2]) Comp. comm. N°. 93. (Idem Oct. 1904).

[3]) Sitz.ber. Ac. Berlin. Bd. 30, p. 673, 1896, and Wied. Ann. Bd. 59, p. 213. 1896.

[4]) Chem. Ber. Bd. 32, p. 1818. 1899.

ROTHE[1]) could only arrive at an indirect comparison with the hydrogen thermometer. He compared his thermo-elements constantin-iron at — 79° with the alcohol thermometer which WIEBE and BÖTTCHER[2]) had connected with the gas thermometer and at — 191° with a platinum-resistance thermometer which at about the same temperature had been compared with the hydrogen thermometer in the Phys. Techn. Reichsanstalt by HOLBORN and DITTENBERGER[3]).

The thermostat left much to be desired; temperature deviations from 0°.4 to 0°.7 occurred within ten minutes (comp. for this § 7). As ROTHE confined himself to two points, he had to rest content with a quadratic formula and he computed the same formula as HOLBORN and WIEN.

From the values communicated for other temperatures we can only derive that the mutual differences between the deviations of the different thermo-elements constantin-iron and constantin-copper from their quadratic formulae could amount to some tenths of a degree. Nothing is revealed with regard to the agreement with the hydrogen thermometer. This investigation has no further relation to the problem considered here.

b. Among the thermo-elements of other composition we mention that of WROBLEWSKI[4]), who compared his new-silver-copper element at + 100° (water), —103° (ethylene boiling under atmospheric pressure) and — 131° (ethylene boiling under reduced pressure) with a hydrogen thermometer and derived thence a cubic formula for t. He tested it by means of a determination of the boiling points of oxygen and nitrogen and found an agreement with the hydrogen thermometer to within 0°.1. As, however, WROBLEWSKI found for the boiling point of pure oxygen at a pressure of 750 m.m. —181°.5, no value can be attached to the agreement given by him.

DEWAR's[5]) investigation of the element platinum-silver was for the time being only intended to find out whether this element was suited for measurements of temperatures at — 250° and lower (where the sensitiveness of the resistance thermometer greatly diminishes), and has been confined to the proof that this really was the case.

c. To our knowledge no investigation has therefore been made as yet, which like that considered in our paper, allows us to judge in

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[1]) Ztschr. für Instrumentenk. Bd. 22 p. 14 and 33. 1902.

[2]) „ „ „ Bd. 10 p. 16. 1890.

[3]) Drude's Ann. Bd. 6 p. 242. 1901.

[4]) Sitzungsber. Ac. Wien Vol. 91. p. 667. 1885.

[5]) Proc. R. S. Vol. 76, p. 317. 1905.

how far thermoelements are suitable for the accurate determination of low temperatures (for instance to within $^1/_{20}{}^\circ$ precise), and also by what formula and with how many points of calibration any temperature in a given range can be determined to within this amount.

§ 3. *Modifications in the thermo-elements and auxiliary apparatus.* We shall consider some modifications and improvements which have not been described in § 1 of Comm. N°. 89. The first two (*a* and *b*) have not yet been applied to the element with which the following measurements are made, but they have afterwards been applied to other elements and so they are mentioned for the sake of completeness.

a. If we consider that the thermo-element in different measurements is not always used under the same circumstances, e.g. is not immersed in the bath to the same depth etc., and that even if this is the case, the time during which this is done at a constant temperature will not always be so long that in either case the same distribution of the temperature will be brought about in the metallic parts of the element, it will prove of the greatest importance that care should be taken, that the temperature of the juncture, given by the electromotive force, differs as little as possible and at any rate very little from that of the surface of the copper protecting block, that is to say that of the bath.

Fig. 1.

The construction of the place of contact shown by fig. 1 is a better warrant for this than that on Pl. I of Comm. N°. 89. The wires *a* and *b* are soldered on the bottoms of small holes *c*, bored in the protecting block and are insulated each by a thin-walled glass tube. If the construction of Pl. I Comm. N°. 89 is not carried out as it should be (whether this has succeeded will appear when we saw through trial pieces) and consequently the juncture is a little removed from the upper surface of the block, it may be easily calculated that, owing to conduction of heat along the wires while the thermo-element is immersed in liquid oxygen a difference in temperature of as much as one degree may exist between the place of contact and the block. When the elements are used under other circumstances, this difference in temperature will have another value and hence an uncertainty will come into the determination of the temperature of the block. Perhaps that also a retardation in the indications of the element will be observed.

Although this construction (fig. 1) (for which a block of greater thickness is required than for that of Comm. N°. 89, Pl. I) has not been applied to the element used, we need not fear uncertainties on this point thanks to the very careful construction of the latter.

b. When temperatures below —253° have to be determined we might fill the apparatus with helium instead of hydrogen as mentioned in § 1 of Comm. N°. 89.

c. The glass tubes of the mercury commutators, described in Comm. N°. 27, are not fixed in corks (see Pl. IV, fig. 4, *k*) but in paraffin, so as to obtain perfect insulation, which, as experience has taught, is not guaranteed by the glass wall. The tubes are continued beyond the sealing places of the platinum wires c_1 c_2 $c_3$and c_4, (as shown by figs. 2 and 3) to avoid breaking of the platinum wires as formerly frequently happened.

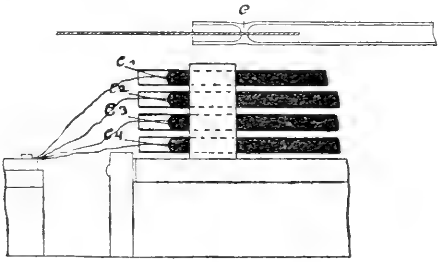

Fig. 2 and 3.

d. The platinum wires of the Weston-elements have been amalgamized by boiling with mercury (which method has since that time been replaced by the method with the electric current [1]). The elements themselves have kept good through all these years.

e. In spite of all the precautions which have been described in Comm. N°. 89, thermo-electromotive forces still remain in the wires, which with the great differences of temperature between various points of one wire must doubtlessly amount to a measurable quantity. When, however, care is taken that the circumstances under which the element is used with respect to the temperature along the wires are about the same as for the calibration, a definite value of the electromotive forces will answer to a definite temperature of the copper block. We do not aim at an accurate determination of the electromotive force of the combination of the metals which at the

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[1] Comp. Jaeger, Die Normalelemente, p. 57.

juncture are in contact with each other, but we only require that a definite electromotive force for a definite temperature of the bath in which the element is immersed should be accurately indicated. (for the rest comp. § 5).

In order to lessen the influence of the conduction of heat along the wire at the juncture we shall for the new elements destined for taking the temperature of a liquid bath make a trial with the insertion into the glass tube at 2 c.m. above the copper rim of the copper block of a copper tube, 5 c.m. long, which is soldered on either side of the glass tube and remains over its whole length immersed in the liquid.

§ 4. *Precautions at the measurements of the electromotive forces.*

a. The apparatus and connections which have been described in § 3 of Comm. N°. 89 have been mounted entirely on paraffin, with which also the enveloping portions of the apparatus are insulated. Only the wires running between the different rooms stretched on porcelain insulators, of which the high insulation-resistance has repeatedly been tested, have no paraffin-insulation. The ice-pots are hanging on porcelain insulators. As a matter of course, all parts of the installation have been carefully examined as to their insulation before they are used.

b. The necessity of continually packing together the ice in the ice-pots has been argued before in Comm. N°. 89.

c. The plug-commutators are of copper. All contacts between different metals in the connection have been carefully protected from variations of temperature by packing of wool or cotton-wool, from which they are insulated by paraffin in card-board boxes. This was only omitted at the contact places of the copper leads with the brass clips of the resistance boxes. To secure to the Weston-elements an invariable temperature, the latter have also been carefully packed. The accumulator is placed in a wooden box.

d. With regard to the testing elements, care has been taken that the steam left the boiling apparatus (comp. Comm. N°. 27, § 8) at a given constant rate.

e. Before a measurement is started we investigate by short-circuiting in the copper commutators in the conductions, leading from the thermo-elements and the Weston-battery to the connections, whether all electromotive forces in the connections are so small and constant (not more than some microvolts), that elimination through the reversal of the several commutators may be considered as perfectly certain.

§ 5. *The control of the thermo-elements.*

It appeared :

a. that when the four places of contact were packed in ice, the electromotive force of the element amounted to less than one microvolt;

b. that the changing of the two places of contact constantin-steel, so that they were alternately placed in the cryostat, indicated only a very small difference in electromotive force. Care is taken, however, that always the same limb is placed into the cryostat;

c. that while the place of contact was moved up and down in the bath no difference could be perceived in the reading (hence the difference of temperature certainly $< 0^\circ.02$).

All this proves that the electromotive forces which are raised in the element outside the places of contact, are exceedingly small.

§ 6. *Corrections and calculations of the determinations of the electromotive forces.*

a. In the following sections R_w R_c R' have the meaning which has been explained in Comm. N°. 89 § 3. E_w, E_c and E' signify the electromotive forces of the observation-element, the comparison-element and the Weston-battery respectively. If we have obtained R_w R_c and R' it follows that :

$$E_w = \frac{R_w}{R_c} E_c \text{ or } E_w = \frac{R_w}{R'} E' .$$

As a test we use :

$$E_c = \frac{E'}{R'} R_c \; .$$

b. In order to find R_w we read on the stops of the resistance box R'_w (in the branch of small resistance), and R''_w (in the branch of great resistance) which are switched in parallel to form R_w.

α. To none of the resistance boxes temperature corrections had to be applied (nor to those given by R_c and R' either).

β. To R'_w we sometimes had to add the connecting resistance of the stops.

γ. To R'_w is added the correction to international ohms according to the calibration table of the Phys. Techn. Reichsanstalt.

δ. To R''_w is added the amount required to render the compensation complete, which amount is derived from the deflections on

TABLE I.

Calibration of the thermo-element P_1, place of contact C in the cryostat.

6 July 1905. Series XV (oxygen boiling under reduced pressure) No. 1. Time: $3^h55'$—$4^h11'$.

Observation-element.

$R'_w = 50+2+1+1.$ $R''_w = 7700.$					$R'_w = 50+2+1+1$ $R''_w = 7200.$		
Rheostat. S. and H. No. 15938.							
Galvanometer deflections.							
Commutators		left	zero	right	left	zero	right
elem.	galv.						
			64.65			65.55	
I	I	64.65			66.60		
			64.81			65.63	
I	II			65.00			64.85
			65.35			65.70	
II	I	65.50			67.25		
			65.42			65.84	
II	II			65.50			64.75
			65.50			66.00	

Comparison-element.
Combination $P_3 + Q_3$.

$R'_c = 50+1.$ $R''_c = 3600.$			$R'_c = 50+1.$ $R''_c = 3800.$		
Rheostat S. and H. No. 15689.					
Galvanometer deflections.					
left	zero	right	left	zero	right
	66.15			66.50	
65.45			64.35		
	66.23			66.54	
		65.65			67.65
	66.35			66.60	
67.80			66.65		
	66.43			66.72	
		63.60			65.55
	66.50			66 80	

Barometerheight 76.14 cm.
(Aneroïd Kipp. 2652)
$t = 19°.4$ (appertaining thermometer)

Weston-elements.

$R'_1 = 8000.$				$R'_1 = 8004.$		
Rheostat No. 17161.						
Galvanometer deflections.						
comm.	left	zero	right	left	zero	right
Galv.						
		66.80			66.90	
I	67.00			65.80		
		66.84			66.96	
II			66.65			68,20
		66.90			67.00	

$t' = 18°.9.$ (Thermometer No. 138)
$t_k = 19°.0.$ (» » 96)
$t_g = 18°.8.$ (» » 149)

the scale of the galvanometer at two values of R''_w (see tables I and IV).

c. In order to find R_c, R'_c and R''_c, which with regard to R_c have a similar meaning as R'_w and R''_w with regard to R_w, are treated like R'_w and R''_w concerning the corrections α, β, γ and δ. The thence derived result R'''_c holds for the temperature at which the water boils in the boiling apparatus at the barometric height B existing there during the observation.

ε. R'''_c is corrected to the value which it would have at a pressure of 760 m.m. mercury at the sealevel in a northern latitude of 45°.

d. To find R' the corrections mentioned sub γ and δ are applied to the invariable resistance R'.

e. E', referring to the temperature t' of the Weston-battery, is derived from JAEGER's table [1]).

§ 7. *Survey of a measurement.* Table I contains all the readings which serve for a measurement of the electromotive force namely for that at — 217° (comp. § 8). We suppose that during the short time required for the different readings (comp. § 3 of comm. N°. 89) the electromotive force of the accumulator (comp. § 4, *c*) remains constant. We further convince ourselves that the temperature in the boiling apparatus of the comparison-element has remained sufficiently constant and that we have succeeded [2]) in keeping the temperature of the bath in the cryostat constant to within 0°.01 [3]) (see table I).

In exactly the same way we have obtained on the same day of observation the values for the electromotive forces which are combined in table III.

From the preceding survey it appears that the measurements can be made with the desired precision even at — 217°. At — 253° the sensitiveness of the element constantin-steel is considerably less than at — 217°. It seems to us of interest to give also for this very low temperature a complete survey of the readings and adjustments so that the reader may judge of what has been attained there (see Table IV).

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[1]) JAEGER, Die Normalelemente 1902. p. 118.

[2]) Comp. Comm. N°. 83, § 5 and Pl. III.

[3]) Together with the readings we have also recorded the temperature of the room (t_k) and of the galvanometer (t_g); these are of interest in case one should later, in connection with the sensitiveness, desire to know the resistance of the galvanometer and the conducting wires during the observation. For the notation of the combination $P_3 + Q_2$ of the comparison-elements we refer to Comm. N°. 89 § 2.

From table I directly follows

TABLE II.

Corrections and results.

Observation-element.	Comparison-element.	Weston-elements.
corr. $\beta\ R'_w = +0.001\ \Omega$	corr. $\beta\ R'_c = +0.001\ \Omega$	
corr. $\gamma\ R'_w = +0.0080\ \Omega$	corr. $\gamma\ R'_c = -0.00015\ \Omega$	corr. $\gamma\ R'_1 = -2.4\ \Omega$
corr. $\delta\ R''_w = +179\ \Omega$	corr. $\delta\ R''_c = +\cdot 149\ \Omega$	corr. $\delta\ R'_1 = +0.654\ \Omega$
	$R'''_c = 50.3163\ \Omega$	
	barom.hght.45°N.B.=76.21cM.	
	corr. $\varepsilon\ R'''_c = -0.0373\ \Omega$	
	Final results.	
$R_w = 53.6404\ \Omega$	$R_c = 50.2787\ \Omega$	$R' = 7998.3\ \Omega$
		$t' = 18°.8$ $E' = 1.0187$ volt.
$E_w = 6.8312$ milliv. 4u 3'	$E_c = 6.4037$ milliv.	

TABLE III.

	E_w	E_c
	6.8312	6.4037
	6.8308	6.4039
	6.8310	6.4038
Mean	6.8310	6.4038

§ 8. *The temperatures.*

a. The thermo-element is placed in a cryostat, as represented on the plate of Comm. N°. 94^d, but there a piezometer takes the place which in our measurements was occupied by a hydrogen thermometer. To promote a uniform distribution of the temperature in the

TABLE IV.

Calibration of the thermo-element P_1, place of contact C in the cryostat.

5 May 1906. Series XXX. (Hydrogen, boiling under atmospheric pressure). No 1. Time: $2^h.19'$—$2^h.28'$.

Observation-element.

$R'_w = 50+5+1+0.5+0.1$ $R''_w = 5200$					$R'_w = 50+5+1+$ $+0.5+0.1$ $R''_u = 5400$		
Rheostat S. and H. No. 15398.							
Galvanometer deflections.							
Commutators elem.	galv	left	zero	right	left	zero	right
			39.89			40.32	
I	I	39.15			40.83		
			39.94			40.38	
I	II			39.87			39.16
			40.05			40.45	
II	I	39.85			41.50		
			40.17			40.65	
II	II			39.70			39.18
			40.32			40.90	

Comparison-element.
Combination $P_3 + Q_2$.

Commutators elem.	galv	$R_c' = 50+0.5+$ $+0.2+0.1+$ $+0.1$ $R''_c = 5500$			$R'_c = 50+0.5+$ $+0.2+0.1+$ $+0.1$ $R''_c = 5300$		
		Rheostat S. and H. No. 15689.					
		Galvanometer deflections.					
		left	zero	right	left	zero	right
			41.08			41.63	
I	I	38.82			38.45		
			41.22			41.81	
I	II			39.84			41.50
			41.35			42.02	
II	I	42.37			41.80		
			41.49			42.15	
II	II			36.80			38.65
			41.63			42.20	

Barometer 76.77 cm.
(Aneroïd Kipp. No. 2652)
$t = 18°.0$ (appertaining thermometer)

Weston-elements.

	$R'_1 = 8000$			$R'_1 = 8004$		
	Rheostat S. and H. No. 17161.					
	Galvanometer deflections.					
comm. Galv.	left	zero	right	left	zero	right
		43.10			43.55	
I	42.90			45.20		
		43.34			43.66	
II			43.84			42.28
		43.55			43.78	

$t' = 18°.7$ (Thermometer No. 138).
$t_k = 19°.6$ (〃 No. 96).
$t_g = 19°.2$ (〃 No. 149).

TABLE V.

Corrections and results.

Observation-element.	Comparison-element.	Weston-elements.
corr. β. $R'_w = +0.001\ \Omega$	corr. β. $R'_c = +0.001\ \Omega$	
corr. γ. $R'_w = +0.00537\ \Omega$	corr. γ. $R'_c = +0.0084\ \Omega$	corr. γ. $R'_1 = -2.4\ \Omega$
corr. δ. $R''_w = +20\ \Omega$.	corr. δ. $R''_c = -209\ \Omega$	corr. δ. $R'_1 = +0.8\ \Omega$
	$R'''_c = 50.4133\ \Omega$	
	Bar.hght. 45° N.B. = 76.82 cM. corr. ε $R'''_c = -0.1459\ \Omega$	
	Final results.	
$R_w = 55.9981\ \Omega$	$R_c = 50.2644\ \Omega$	$R' = 7998.4\ \Omega$
		$t' = 18°.5$ $E' = 1.0187$ volt.
$E_w = 7.1321$ milliv. 2h24′	$E_c = 6.4075$ milliv.	

bath a tube is mounted symmetrically with the thermo-element, and has the same shape and dimensions as the latter. Comp. also Comm. N°. 94^c § 1. For the attainment of a constant and uniform temperature with this cryostat we refer to Comm. N°. 94^d and the Comms. quoted there. The temperature was regulated by means of a resistance thermometer. For the two measurements in liquid hydrogen we have made use of the cryostat described in Comm. N°. 94^f.

b. With a bath of liquid methyl chloride we have obtained the temperatures —30°, —59° and —88°; with ethylene —103°, —140° and —159°; with oxygen —183°, —195°, —205° —213° and —217°; with hydrogen —253° and —259°.

c. The temperatures are read on the scale of the hydrogen thermometer described in Comms. N°. 27 and N°. 60. On the measurements with this apparatus at low temperatures another communication will erelong be published.

§ 9. *Results.*

Column I of the following table VI contains the numbers of the measurements, column II the dates, column III the temperatures measured directly with the hydrogen thermometer, column IV the electromotive forces $-E_w$ in millivolts, column V the number of observations, column VI the greatest deviations in the different determinations of E_w of which the appertaining E_w is the mean, column VII the same reduced to degrees.

TABLE VI.

CALIBRATION OF THE THERMO-ELEMENT CONSTANTIN-STEEL.

I	II	III	IV	V	VI	VII
20	27 Oct. 05	— 58°.753	2.3995	3	0.0006	0°.016
21	30 Oct. 05	— 88.140	3.4825	3	29	81
17	8 July 05	— 103.833	4.0229	3	56	168
16	7 July 05	— 139.851	5.1469	3	6	21
18	26 Oct. 05	— 139.873	5.1469	4	12	41
19	26 Oct. 05	— 158.831	5.6645	3	15	59
11	27 June 05	—[182.692]	6.2297	3	10	46
28	2 Mrch. 06	— 195.178	6.4717	4	28	150
12	29 June 05	—[204.535]	6.6382	3	31	186
27	2 Mrch. 06	— 204.694	6.6361	4	26	156
14	30 June 05	—[212.832]	6.7683	3	8	56
13	6 July 05	— 212.868	6.7668	3	15	106
29	3 Mrch. 06	— 217.411	6.8221	3	14	112
15	6 July 05	— 217.416	6.8310	3	4	32
30	5 May 06	— 252.93	7.1315	4	17	39
31	5 May 06	— 259.24	7.1585	1	—	—

The observations 11, 12 and 14 are uncertain because in those cases the hydrogen thermometer had a very narrow capillary tube so that the equilibrium was not sufficiently secured. According to other simultaneous observations (Comm. N°. 95^c at this meeting), which have later been repeated, the correction for N°. 11 is probably — 0°.058. The two other ones have been used unaltered.

The mean deviation of E_c for the different days from the mean value, and also the mean largest deviation of the values of E_c found on one day amounts to 3 microvolts, which amount shows that in the observation of the comparison-element the necessary care has not been bestowed on one or other detail, which has not been explained as yet. We must come to this conclusion because the observation-element yields for this mean only 1,8 microvolt.

§ 10. *Indirect determinations.*

In order to arrive at the most suitable representation of E_w as a function of t, it was desirable not only to make use of the observations communicated in § 9 but also to avail ourselves of a large number of indirect measurements, obtained through simultaneous observations of the thermo-element and a platinum-resistance thermometer, the latter having been directly compared with the hydrogen thermometer (comp. Comm. N°. 95^b, this meeting).

These numbers have been combined in table VII where the columns contain the same items as in the preceding table, except that here the temperatures are derived from resistance measurements.

TABLE VII.

INDIRECT CALIBRATION OF THE THERMO-ELEMENT CONSTANTIN-STEEL.

I	II	III	IV	V	VI	VII
22	13 Dec. 05	— 29°.825	1.2523	3	0.0005	0°.012
24	14 Dec. 05	— 58.748	2.3980	4	6	16
23	13 Dec. 05	— 88.161	3.4802	3	6	17
1	23 Jan. 05	— 103.576	4.0100	5	9	27
3	30 Jan. 05	[— 182.604]	6.2270	4	32	147
5	16 Mrch. 05	[— 182.828]	6.2340	3	13	60
4	2 Febr. 05	— 195.135	6.4730	3	20	107
6	17 Mrch. 05	— 195.261	6.4814	5	10	53
7	30 Mrch. 05	— 204.895	6.6397	3	55	330
26	26 Jan. 06	— 212.765	6.7637	4	33	233
8	3 April 05	— 212.940	6.7686	4	15	106
25	25 Jan. 06	— 217.832	6.8276	4	29	232

§ 11. *Representation of the observations by a formula.*

a. It was obvious that the formula of AVENARIUS:

$$E = a\frac{t}{100} + b\left(\frac{t}{100}\right)^2$$

can give a sufficient agreement for a very limited range only. If, for instance, the parabola is drawn through 0°, —140° and —253°, we find:

$$a = + 4.7448$$
$$b = + 0.76117.$$

In this case the deviation at —204° amounts to no less than 7°. If we confine ourselves to a smaller range and draw the parabola through 0°, —88° and —183°, we find:

$$a = + 4.4501$$
$$b = + 0.57008,$$

while at —140° the deviation still amounts to 1°.3.

Such a representation is therefore entirely unsatisfactory.

b. With a cubic formula of the form

$$E = a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3$$

we can naturally attain a better agreement. If, for instance, we draw this cubic parabola through 0°, —88°, —159° and —253°, we find:

$$a = + 4.2069$$
$$b = + 0.158$$
$$c = - 0.1544$$

and the deviation at —204° is 0°.94. A cubic formula confined to the range from 0° to —183°, gave at —148° a deviation of 0°.34. [1]) A cubic formula for t, expressed in E (comp. § 2), gives much larger deviations. [2])

c. A formula, proposed by STANSFIELD [3]) for temperatures above 0°, of the form

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[1]) As we are going to press we become acquainted with the observations of HUNTER (Journ. of phys. chem. Vol. 10, p. 319, 1906) who supposes that, by means of a quadratic formula determined by the points —79° and —183°, he can determine temperatures at —122° to within 0°.1. How this result can be made to agree with ours remains as yet unexplained.

[2]) After the publication of the original Dutch paper we have taken to hand the calculation after the method exposed in § 12 of a formula of the following form:

$$E = a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + e\left(\frac{t}{100}\right)^4.$$

We hope to give the results at the next meeting.

[3]) Phil. Mag. Ser. 5, Vol. 46, p. 73, 1898.

$$E = aT + b \log T + c,$$

where T represents the absolute temperature, proved absolutely useless.

d. We have tried to obtain a better agreement with the observations by means of a formula of five terms with respect to powers of t. To this end we have tried two forms:

$$E = a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + e\left(\frac{t}{100}\right)^5 + f\left(\frac{t}{100}\right)^7 \quad . \quad . \quad . \quad (A)$$

and

$$E = a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + e\left(\frac{t}{100}\right)^4 + f\left(\frac{t}{100}\right)^6 \quad . \quad . \quad . \quad (B)$$

First the constants of the two equations are determined so that the equations satisfy the temperatures —59°, —140°, —159°, —183° and — 213°. (A) indicated at — 253° a deviation of 113.1 microvolts, (B) a deviation of 91.8 microvolts. We have preferred the equation (B) and then have sought an equation (BIV) which would represent as well as possible the temperature range from 0° to — 217°, two equations (BI and BIII) which would moreover show a not too large deviation at — 253°, for one of which (BIII) a large deviation was allowed at — 217°, while for the other (BI) the deviations are distributed more equally over all temperatures, and lastly an equation (BII) which, besides —253°, would also include —259°.

§ 12. *Calculation of the coefficients in the formula of five terms.* The coefficients have first been derived from 5 temperatures distributed as equally as possible over the range of temperatures, and then corrected with respect to all the others without a rigorous application, however, of the method of least squares.

In order to facilitate this adjustment we have made use of a method indicated by Dr. E. F. VAN DE SANDE BAKHUYZEN in which instead of the 5 unknown coefficients 5 other unknown values are introduced which depend linearly on the former [1]). For these are chosen the exact values of E for the five observations used originally, or rather the differences between these values and their values found to the first approximation.

Five auxiliary calculations reveal to us the influence of small variations of the new unknown value on the representation of the other observations and by means of these an approximate adjustment

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[1]) Also when we rigorously apply the method of least squares this substitution will probably facilitate the calculation.

may be much more easily brought about than by operating directly with the variations of the original coefficients [1]).

After the first preliminary formula was calculated all the 28 observations have subsequently been represented. The values thus found are designated by R_0. The deviations of the observed values from those derived from this first formula are given in column III of table VIII under the heading $W-R_0$. The deviations from the temperatures in the immediate neighbourhood of each other have been averaged to normal differences and are combined in column IV under the heading $(W-R_0)$.

These deviations have served as a basis for an adjustment undertaken according to the principles discussed above.

It yielded the following results:
leaving — 253° and — 259° out of consideration we find as coefficients of the equation (B) (comp. § 11):

$$\left.\begin{array}{ll} a_4 = +\ 4.32044 & e_4 = +\ 0,011197 \\ b_4 = +\ 0,388466 & f_4 = -\ 0,0044638 \\ c_4 = -\ 0.024019 & \end{array}\right\} \quad . \ . \ . \ . \quad (BIV)$$

If we only leave out of consideration — 259° we find for the coefficients of equation (B) the two following sets (comp. § 11):

$$\left.\begin{array}{ll} a_3 = +\ 4.33049 & e_3 = +\ 0,053261 \\ b_3 = +\ 0.436676 & f_3 = +\ 0,003898 \\ c_3 = +\ 0,048091 & \end{array}\right\} \quad . \ . \ . \quad (BIII)$$

and

$$\left.\begin{array}{ll} a_1 = +\ 4.35603 & e_1 = +\ 0,103459 \\ b_1 = +\ 0,531588 & f_1 = +\ 0,0118632 \\ c_1 = +\ 0,157678 & \end{array}\right\} \quad . \ . \ . \ . \ . \quad (BI)$$

If we include in the equation all the temperatures, also that of the liquid hydrogen boiling under reduced pressure, we find for the coefficients of the equation (B)

$$\left.\begin{array}{ll} a_2 = +\ 4.35905 & e_2 = +\ 0,111619 \\ b_2 = +\ 0,542848 & f_2 = +\ 0,0132130 \\ c_2 = +\ 0,172014 & \end{array}\right\} \quad . \ . \ . \quad (BII)$$

The deviations from the observations shown by these different equations are found under $(W-R_1)$ $(W-R_2)$ $(W-R_3)$ and $(W-R_4)$ in columns V, VI, VII and VIII of table VIII.

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[1]) When the polynomial used contains successive powers of the variable beginning with the first power, that influence is determined by the interpolation-coefficients of LAGRANGE.

TABLE VIII.

DEVIATIONS OF THE CALIBRATION-FORMULAE FOR THE THERMO-ELEMENT CONSTANTIN-STEEL.

I	II	III	IV	V	VI	VII	VIII
No.	t	$W-R_0$	$(W-R_0)$	$(W-R_1)$	$(W-R_2)$	$(W-R_3)$	$(W-R_4)$
22	— 29°.825	—0.0080	—0.0080	—0 0030	—0 0032	—0.0013	—0.0011
24	— 58.748	— 13	— 6	+ 26	+ 26	+ 16	+ 11
20	— 58.753	0					
21	— 88.140	+ 44	+ 29	+ 31	+ 32	+ 8	+ 7
23	— 88.161	+ 14					
1	—103.576	0	+ 14	+ 4	+ 4	— 16	— 11
17	—103.833	+ 43					
16	—139.851	+ 5	+ 1	— 20	— 20	— 18	+ 4
18	—139.873	— 2					
19	—158.831	0	0	— 20	- 20	— 10	— 5
3	[—182.604]	+ 41	+ 47	+ 31	+ 33	+ 38	+ 31
11	[—182.750]	+ 36					
5	[—182.828]	+ 63					
4	—195.135	+ 15	+ 28	+ 13	+ 17	+ 12	+ 4
28	—195.178	— 6					
6	—195.261	+ 76					
12	[—204 535]	+ 34	+ 5	— 10	— 5	— 20	— 20
27	—204.694	— 17					
7	—204 895	— 11					
26	—212.765	+ 21	+ 40	+ 25	+ 29	+ 8	+ 22
14	[—212.832]	+ 58					
13	—212.868	+ 38					
8	—212.940	+ 45					
29	—217.411	— 36	— 7	— 23	— 19	— 45	— 18^5
15	—217.416	+ 52					
25	—217.832	— 36					
30	—252.93	0	0	— 20	— 40	— 20	+ 280
31	—259.24	+ 87	+ 87	+ 68	+ 37	+ 90	+ 490

To observation 11 of this table we have applied the correction mentioned at table VI. To the observations 17 and 7 we have accorded half the weight on account of the large deviation from the single determinations mutually (comp. tables VI and VII) [1].

§ 13. *Conclusion.* For the mean error of the final result for one temperature (when this is taken equal for all temperatures) we find by comparison with the formula found:

	microv.
R_1	± 2.8
R_2	± 3.2
R_3	± 2.6 (2.1 when leaving also out of account — 217°)
R_4	± 1.8

The mean error of the result of one day, according to the mutual agreement of the partial results, is:

± 2.9 microvolts,

whence we derive for the mean error of one temperature, supposing that on an average two daily results are averaged to one final result:

± 2.0 microvolts.

(2 microvolts agree at — 29° with 0°.05, at — 217° with 0°.16).

Hence it seems that we may represent the electromotive force of the thermo-element constantin-steel between 0° and — 217° by the five-terms formula to within 2 microvolts. For the calibration to — 217° we therefore require measurements at at least 5 temperatures [2].

The representation including the temperatures of liquid hydrogen is much less satisfactory; for the mean error would be found according to this representation ± 3.2 microvolts, agreeing with 0°.075 at — 29° and 0°.74 at — 252° and — 259°.

In order to include the hydrogen temperatures into the formula a 6th term will therefore probably be required.

But for measurements at the very lowest temperatures the element constantin-steel is hardly suitable (comp. § 7).

In conclusion we wish to express hearty thanks to Miss T. C. Jolles and Messrs. C. Braak and J. Clay for their assistance in this investigation.

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[1] In the calculations for observations 3, 11 and 5 are used temperatures 0°,081 lower than the observed ones. A repetition of the calculation with the true values has not been undertaken, as it would affect only slightly the results, the more because the observations are uncertain.

[2] If the four term formula (comp. footnote 2 § 11) should prove for this interval as sufficient as the five term formula, this number would be reduced to four.

Physics. — *On the measurement of very low temperatures. X. Coefficient of expansion of Jena glass and of platinum between + 16° and — 182°.*" By Prof. H. Kamerlingh Onnes and J. Clay. Communication N°. 95^b from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 30, 1906).

§ 1. *Introduction.*

The difference between the coefficients a and b in the expansion formula for the linear expansion $l = l_0 \left[1 + \left\{a \frac{t}{100} + b\left(\frac{t}{100}\right)^2\right\} 10^{-6}\right]$ and k_1 and k_2 in the formula for the cubic expansion

$$v_t = v_0 \left[1 + \left\{k_1 \frac{t}{100} + k_2 \left(\frac{t}{100}\right)^2\right\} 10^{-6}\right]$$

between 0° and — 182° found by Kamerlingh Onnes and Heuse (comp. Comm. N°. 85, June '03, see Proceedings of April '05) and those found by Wiebe and Böttcher and Thiesen and Scheel for temperatures above 0° made it desirable that the strong increase of b at low temperatures should be rendered indubitable by more accurate measurements [1]).

In the first place we have made use of more accurate determinations of the variation of the resistance of platinum wires with the temperature (comp. Comm. N°. 95^c, this meeting) in order to substitute more accurate temperatures for those given in Comm. N°. 85, which served only for the calculation of a preliminary formula, and then to calculate by means of them new values for a and b which better represent the results of the measurements than those given in Comm. N°. 85.

By means of the formula

$$W_t = W_0 (1 + 0{,}00390972\, t - 0{,}0_6 9861\, t^2),$$

which holds for the kind of platinum wire used in Comm. N°. 85, we have arrived at the following corrections:

in table IV read — 87°,14 instead of — 87°,87
and —181°,42 „ „ —182°,99
in table V read — 86°,98 „ „ — 87°,71
and —181°,22 „ „ —182°,79

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[1]) That the coefficient of expansion becomes smaller at lower temperatures is shown by J. Zakrzewski by measurements down to — 103°. This agrees with the fact that the expansion of most substances above 0° is represented by a quadratic formula with a positive value of b. Our investigation refers to the question whether b itself will increase with lower temperatures.

Thence follows

Jena glass 16^{III}	$a = 781$	$b = 90$	1903.
	$k_1 = 2343$	$k_2 = 272.$	
Thüringer glass (n°. 50)	$a = 920$	$b = 120$	
	$k_1 = 2761$	$k_2 = 362.$	

Secondly it remained uncertain whether the mean temperatures of the ends were exactly identical with those found after the method laid down in § 4 of that Comm. The execution of the control-determination as described in Comm. N°. 85 § 4 (comp. § 4 of this paper) proved that in this respect the method left nothing to be desired.

Moreover, availing ourselves of the experience acquired at former determinations, we have once more measured the expansion of the same rod of Jena glass and have reached about the same results which, owing to the greater care bestowed on them, are even more reliable.

Lastly it was of importance to decide whether the great increase of b at low temperatures also occurred with other solid substances and might therefore be considered as a property of the solid state of several amorphous substances. Therefore and because it was desirable also for other reasons to know the expansion of platinum we have measured the expansion of a platinum rod in the same way as that of the glass rod. Also with platinum we have found the same strong increase of b, when this is calculated for the same interval at lower temperatures, so that cubic equations for the lengths of both substances must be used when we want to represent the expansion as far as — 182°.

After these measurements were finished SCHEEL (Zeitschr. f. Instr. April 1906 p. 119) published his result that the expansion of platinum from — 190° to 0° is smaller than follows from the quadratic formula for the expansion above 100°. For the expansion from + 16° to — 190° SCHEEL finds — 1641 μ per meter, while — 1687 μ would follow from our measurements. But he thinks that with a small modification in the coefficients of the quadratic formula his observations can be made to harmonize with those above 100°. Our result, however, points evidently at a larger value of b below 0°.

The necessity of adopting a cubic formula with a negative coefficient of t^3 may be considered as being in harmony with the negative expansion of amorphous quartz found by SCHEEL (l. c.) between — 190° and 16° when we consider the values of a and b in a quadratic formula for the expansion of this substance between 0° and + 250°.

A more detailed investigation of these questions ought to be made of course with more accurate means. It lies at hand to use the method of FIZEAU. Many years ago one of us (K. O.), during a visit at Jena, discussed with Prof. PULFRICH the possibility of placing a dilatometer of ABBE into the Leiden cryostat, but the means of procuring the apparatus are lacking as yet. Meanwhile the investigation following this method has been taken in hand at the Reichsanstalt [1]). A cryostat like the Leiden one, which allows of keeping a temperature constant to 0,01° for a considerable time, would probably prove a very suitable apparatus for this investigation.

TRAVERS, SENTER and JAQUEROD [2]) give for the coefficient of expansion of a not further determined kind of glass between 0° and — 190° the value 0,0000218. From the mean coefficient of expansion from 0° to 100° we conclude that this glass probably is identical with our Thüringer glass.

The mean coefficient of expansion between 0° and — 190° for Thüringer glass found at Leiden in 1903 is 0,00002074.

§ 2. *Measurement of the coefficient of expansion of Jena glass and of platinum between* 0° *and* — 182°.

The rod of Jena glass used was the same as that of Comm. N°. 85.

At the extremities of the platinum tube of 85 c.m. length glass ends were soldered of the same kind as the Jena rod. For the determination of the mean temperature of the ends thin platinum wire was wound round these extremities which wire at either end passed over into two platinum conducting wires and was enveloped in layers of paper in order to diminish as much as possible the exterior conduction of heat.

The temperature of the middle portion of the Jena rod was also determined by means of a platinum wire wound round it as in Comm. N°. 85. The rod was further enveloped in thin paper pasted together with fishglue, and to test the insulation the resistance was measured on purpose before and after the pasting. The temperature of the bath was determined halfway the height of the bath by means of the thermo-element constantin-steel (comp. Comm. N°. 95*a*, this meeting).

This temperature was adopted as the mean temperature of the platinum tube, which was entirely surrounded with the liquid gas and was only at its extremities in contact with the much less

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[1]) HENNING, afterwards SCHEEL, Zeitschr. f. Instrk. April 1905, p. 104 and April 1906, p. 118. RANDALL, Phys. Review 20, p. 10, 1905 has constructed a similar apparatus.

[2]) TRAVERS, SENTER and JAQUEROD, Phil. Trans. A 200.

conducting pieces of glass, which partly projected out of the bath.

The scale (comp. Comm. N°. 85) was wrapped round with a thick layer of wool enclosed in card-board of which the seams had been pasted together as much as possible. The temperature of the room was kept as constant as possible by artificial heating and cooling with melting ice, so that the temperatures of the scale vary only slightly.

They were read on three thermometers at the bottom, in the middle and at the top.

The scale and the points of the glass rods were illuminated by mirrors reflecting daylight or arc-light, which had been reflected by paper and thus rendered diffuse.

The vacuum tube (comp. Comm. N°. 85) has been replaced by a new one during the measurements. The evacuation with the latter had succeeded better. So much liquid gas was economized. For the measurement with liquid oxygen we required with the first tube $1^1/_4$ liter per hour and $^1/_4$ liter with the second. Of N_2O we used with the first only $^1/_4$ liter per $1^1/_4$ hour.

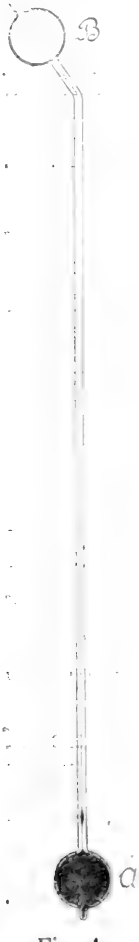

Fig. 1.

In order to prevent as much as possible irregularities in the mean temperature the bath has been filled as high as possible, while dry air was continually blown against the projecting points. They were just kept free from ice. In two extreme cases which had been chosen on purpose — the bath replenished with oxygen as high as possible and the points covered with ice, and the bath with the float at its lowest point and the point entirely free from ice — the difference of the mean temperature of the ends was 10 degrees, corresponding to a difference in length of 4 microns. The greatest difference which has occurred in the observations has certainly been smaller and hence the entire uncertainty of the length cannot have surpassed 2 microns.

At the lower extremities the difference is still smaller.

All this holds with regard to oxygen, in nitrous oxide such variations in the distribution of the temperature can be entirely neglected.

With some measurements we have observed that the length of the rods, when they had regained their ordinary temperature after cooling, first exceeded the original length, but after two days it decreased again to that value.

The cause of those deviations has not been explained. In a case where a particularly large deviation had been stated which did not altogether return to zero, it appeared, when the points were unwrapped, that a rift had come into the glass.

To see whether a thermical hysteresis had come into play a thermometerbulb (see fig. 1) with a fine capillary tube was filled with mercury. First the level of the mercury was compared with an accurate thermometer at the temperature of the room in a water-bath in a vacuum glass. Then the apparatus was turned upside down so that the mercury passed into the reservoir B, which is a little greater than A. Subsequently A and also a part of the stem was cooled down during 3 hours in liquid air in a sloping position so that thanks to the capillary being bent near B no mercury could flow back

TABLE I. — JENA GLASS 16^{III}.

Date	Time	Temp. scale	L_t	L_{16°	W_t	W_o	ϑ	λ
16 Dec.	2*h*.35	15.7	1026.285	1026.280	40.620		15.9	
1904	3*h* 50	16.0	.286	.279	40.786		17.0	
	4*h*.22	16.3	.292	.290	40.845		17.4	
20 Dec	1*h*.50	15.3	1025.571	1025.559	*s.* 3.503	5.021		$\lambda_s=$ 40.6
	2*h* 10	15.4	.560	.550	*m.*25.029	38.28	- 86.78	
	2*h*.30	15.4	.571	.561	*i.* 6.300	7.191		$\lambda_i=22.1$
21 Dec.	3*h*.15	14.6	1026.308	1026.291	*m.*40.523		15.1	
	3*h*.45	14.7	.299	.284			15.1	
	4*h*.15	14.7	.308	.289	*m* 40.583		15.6	
22 Dec.	10*h* 50	15.0	1025.108	1025.091	*s.* 2.105	5.021		$\lambda_s=30.8$
	12*h*.15	15.0	.112	.095	*m.* 9.880	38.28	—181.48	
	12*h*.50	15.0	.115	.098	*i* 5.005	7.191		$\lambda_i=18.0$
23 Dec.	12*h*.30	15.8	1026.341	1026.341	*m.*40.606		15.6	
	3*h*.	15.6	.339	.339			15.2	
	3*h*.30	15.6	.335	.336	*m.*40.537		15.2	
11 Jan.	3*h*.40	15.4	1026.288	1026.278	40.634		15.9	
1905	4*h*.30	15.5	.291	.280	40.703		16.4	

to *A*. When *A* had regained the temperature of the room the mercury was passed again from *B* into *A* and the apparatus replaced into the same waterbath as before. The deviation of the level of the mercury was of the same order as the reading error of the thermometer, about 0.003°. A perceptible thermical hysteresis therefore we do not find.

TABLE II. — PLATINUM.

Date	Time	Temp. scale	L_t	$L_{16°}$	W_t	W_o	ϑ	λ
16 Dec.	5*h* 50	16.5	1027.460	1027.461			17.0	
1904		16.4	1027.461	1027.459			17.0	
17 Dec.[1]	1*h* 45	16.6	1026.620	1026.630				
	9*h* 45	16.3	1026.618	622				
	10*h* 5	16.3	613	617				
19 Dec.	8*h*	14.8	1027.459	1027.442			15.5	
	8*h* 30	14.8	457	1027.440			15.5	
20 Dec.	3*h*	15.5	1026.627	1026.630	s 3.475	4.993		$\lambda_s = 40.2$
	3*h* 30	15.5	630	633	m		−86.32	
	3*h* 55	15.4	631	635	i 7.575	8.653		$\lambda_i = 31.5$
21 Dec.	4*h* 40	14.7	1027.460	1027.441			15.5	
	5*h* 10	14.9	459	444			15.5	
	6*h*	14.8	459	442			15.5	
22 Dec.	10*h* 40	15.3	1025.963	1025.951	s 2.140	4.993		$\lambda_s = 28.9$
	11*h* 10	15.3	1025.973	961	m		−182.6	
	1*h* 45	14.9	1025.964	947	i 5.649	8.653		$\lambda_i = 18.5$
23 Dec.	11*h* 25	15.7	1027.434	1027.436			15.0	
		15.6	440	441			15.0	
		15.7	440	442			15.2	
3 Febr.	2*h*	15.4	1027.463	1027.459			15.2	
		15.4	459	455			15.2	

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[1] Journ. Chem. Soc. 63. p. 135. 1893.

In table II (p. 204) the temperatures are used which are found with the thermo-element. A control-measurement with the thermo-element placed in the same vacuum tube without rod gave for the temperature in nitrous oxide — 87°,3 instead of — 86°,32.

The mean value of the two determinations is used for the calculation.

Another reason for the measurement of the temperature of the bath with a thermo-element as a control was the large difference between the mean temperature found by us and the boiling point of nitrous oxide — 89° given by RAMSAY and SHIELDS [1]).

As we are going to press we find that HUNTER [2]) has given — 86°.2 for that temperature.

§ 3. *Results.*

Jena glass 16 III	**a**	**835**	**b**	**117**	**1905**
	k_1	**2505**	**k_2**	**353.**	
Platinum	**a**	**905,3**	**b**	**49,4**	
	k_1	**2716**	**k_2**	**148,4.**	

As regards platinum:

BENOIT finds	from 0° to 80°	*a* 890,1	*b* 12,1
SCHEEL	from 20° to 100°	*a* 880,6	*b* 19,5
HOLBORN and DAY	from 0° to 1000°	*a* 886,8	*b* 13,24

As to the differences between the values obtained now and those of Comm. N°. 85 (comp. § 1), we must remark that these are almost entirely due to the differences in the determinations of temperature. The uncertainties of the latter, however, do not influence in the least the conclusion about *b* and the necessity of a cubic formula.

There is every reason to try to combine our determinations on Jena glass above and below 0° in such a cubic formula. Taking into account also the previous determination 242.10^{-6} as the mean cubic coefficient from 0° to 100° (Comm. N°. 60, Sept. 1900, § 20) we find in the formula for the linear expansion below 0° and in the corresponding one for the cubic expansion

$$l_t = l_0\left[1+\left\{a'\frac{t}{100}+b'\left(\frac{t}{100}\right)^2+c'\left(\frac{t}{100}\right)^3\right\}10^{-6}\right]$$

Jena glass 16 III	**a'**	**789,4**	**k'_1**	**2368,1**
	b'	**39,5**	**k'_2**	**120,2**
	c'	**— 28,8**	**k'_3**	**86,2**

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[1]) With this measurement in N_2O we have not obtained a temperature determination with the thermo-element. This determination is not included in the calculation. It is mentioned here on account of the agreement with the determination of 20 Dec., which for the rest has been made under the same circumstances.

[2]) Journ. Phys. Chem. May 1906, p. 356.

§ 4. *Control-experiment.*

The ends of the Jena glass rod were subsequently cut off and sealed together with a short intermediate rod. This short stick was placed in a glass of the same width as the vacuum tube with the same stopper and so short that the points projected in the same

TABLE III. — JENA GLASS ENDS.

Date	Temp. scale	L_t	L_{16°	W_t	W_0	ϑ	λ
12 April 1905							
10*h* 15	15.4	227.684	227 683			15.4	
11*h*		.686	.685			15.4	
11*h* 43	15.4	227.684	227.682			15.5	
	15.4	.681	.679			15.5	
N_2O							
3*h* 50	15.4	227.533	227 536	*s* 3.473	5.021		$\lambda_s =$ 42.3
4*h* 24	15.4	.543	.541				
4*h* 52	15.4	.550	.548	*i* 5.490	7.191		$\lambda_i =$ 32.3
13 April	17.4	227.677	227.681			17.1	
14 April	16.2	227.675	227.676			15.9	
10*h* 10							
O_2							
2*h* 50	18.4	227.474	227.482	*s* 1.941	5.021		$\lambda_s =$ 35.5
4*h*22	18.9	.482	.494	*i* 4.683	7.191		$\lambda_i =$ 8.9
15 April	16.6	227.725	227 727			15.7	
11*h* 1	16.6	.724	.726			16.0	
4*h* 20	16.4	227.706	.708			15.8	
4*h* 46	16.4	.711	.713			16.0	
16 April	14.1	227.706	227.702			13.6	
17 April	14.2	227.682	227.678			14.0	
		.685	.681				

manner as those of the rods in the vacuum glass. Now we have taken only a double glass filled with wool, enveloped in a card-board funnel and tube for letting out the cold vapours.

The measurements are given in table III.

The λ's found in the experiment are of the same order of magnitude as those found with the long rods. The calculation with the coefficients a and b found in § 2 yields:

$L_{N_2O} = 227{,}547$ while we have found $L_{N_2O} = 227{,}544$
$L_{O_2} = 227.487$ „ „ „ „ $L_{O_2} = 227{,}488$.

In conclusion we wish to express hearty thanks to Miss T. C. Jolles and Miss A. Sillevis for their assistance in this investigation.

Physics. — "*On the measurement of very low temperatures. XI. A comparison of the platinum resistance thermometer with the hydrogen thermometer.*" By Prof. H. Kamerlingh Onnes and J. Clay. Communication N°. 95^c from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 30, 1906).

§ 1. *Introduction.* The following investigation has been started in Comms. N°. 77 and N°. 93 VII of B. Meilink as a part of the more extensive investigation on the thermometry at low temperatures spoken of in Comm. N°. 95^a. In those communications the part of the investigation bearing on the electrical measurements was chiefly considered.

The hydrogen thermometer was then (comp. Comm. N°. 93 § 10) and has also this time been arranged in the same way as in Comm. N°. 60. Afterwards it appeared, however, that at the time the thermometer did not contain pure hydrogen, but that it was contaminated by air. The modifications which are consequently required in tables V and VI of Comm. N°. 93 and which particularly relate to the very lowest temperatures, will be dealt with in a separate communication.

Here we shall discuss a new comparison for which also the filling with hydrogen has been performed with better observance of all the precautions mentioned in Comm. N°. 60.

We have particularly tried to prove the existence of the *point of inflection* which may be expected in the curve (comp. § 6) representing the resistance as a function of the temperature, especially with regard to the supposition that the resistance reaches a *minimum* at very low temperatures, increases again at still lower temperatures and even becomes infinite at the absolute temperature 0 (comp.

Suppl. N°. 9, Febr. '04). And this has been done especially because temperature measurements with the resistance thermometer are so accurate and so simple.

From the point of view of thermometry it is important to know what formula represents with a given accuracy the resistance of a platinum wire for a certain range, and how many points must be chosen for the calibration in this range.

In Comm. N°. 93 § 10 the conclusion has been drawn that between 0° and — 180° a quadratic formula cannot represent the observations more accurately than to 0°.15, and that if for that range a higher degree of accuracy is required, we want a comparison with the hydrogen thermometer at more than two points, and that for temperatures below — 197° a separate investigation is required. In the investigation considered here the temperatures below — 180° are particularly studied; the investigation also embraces the temperatures which can be reached with liquid hydrogen.

It is of great importance to know whether the thermometer when it has been used during a longer time at low temperatures would retain the same resistance. We hope to be able later to return to this question. Here we may remark that with a view to this question the wire was annealed before the calibration. Also the differences between the platinum wires, which were furnished at different times by Heraeus, will be considered in a following paper.

§ 2. *Investigations by others.* Since the appearance of Comm. N°. 93 there has still been published on this subject the investigation of Travers and Gwyer [1]. They have determined two points. They had not at their disposal sufficient cryostats such as we had for keeping the temperatures constant. About the question just mentioned: how to obtain a resistance thermometer which to a certain degree of accuracy indicates all temperatures in a given range, their paper contains no data.

§ 3. *Modification in the arrangement of the resistances.* The variation of the zero of the gold wire, mentioned in Comm. N°. 93 VIII, made us doubt whether the plates of mica between the metallic parts secured a complete insulation, and also the movability of one of the glass cylinders made us decide upon a modification in the construction of the resistances, which proved highly satisfactory and of which we

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[1] Travers and Gwyer. Z. f. Phys. Chem. LII, 4, 1905. The wire of which the calibration is given by Olszewski, 1905, Drude's Ann. Bd. 17, p. 990, is apparently according to himself no platinum wire. (Comp. also § 6, note 1).

have availed ourselves already in the regulation of the temperatures in the investigation mentioned in Comm. N°. 94^d.

A difficulty adheres to this arrangement which we cannot pass by unnoticed. Owing to the manner in which this thermometer has been mounted it cannot be immersed in acid. Therefore an apparatus consisting entirely of platinum and glass remains desirable. A similar installation has indeed been realized. A description of it will later be given. The figures given here exclusively refer to the thermometer described in Comm. N°. 94^d (p. 210).

Care has been taken that the two pairs of conducting wires were identical. Thus the measurement of the resistance is performed in a much shorter time so that both for the regulation of the temperature in the cryostat and, under favourable circumstances, for the measurement the very same resistance thermometer can be used.

§ 4. *The temperatures.*

The temperatures were obtained in the cryostat, described in Comm. N°. 94^d, by means of liquid methyl chloride —39°, —59°, —88°, of liquid ethylene — 103°, — 140°, — 159°, of liquid oxygen — 182°, — 195°, — 205°, — 212°, — 217°, by means of liquid hydrogen — 252° and — 259°. The measurements were made with the hydrogen thermometer as mentioned in § 1.

§ 5. *Results for the platinum wire.*

These results are laid down in table I (p. 210).

The observations marked with [ ] are uncertain on account of the cause mentioned in Comm. N°. 95^a § 10 and are not used in the derivation and the adjustment of the formulae. For the meaning of $W—R_{A_I}$ in the column "remarks" I refer to § 6.

§ 6. *Representation by a formula.*

a. We have said in § 1 that the quadratic formula ¹) was insufficient even for the range from 0° to —180°.

If a quadratic formula is laid through — 103° and — 182°, we find :

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¹) The correction of CALLENDAR, used at low temperatures by TRAVERS and GWYER, Z. f. Phys. Chem. LII, 4, 1905 comes also to a quadratic formula. DICKSON's quadratic formula, Phil. Mag. June 1898, is of a different nature but did not prove satisfactory either; comp. DEWAR Proc. R. Soc. 64, p. 227, 1898.

The calibration of a platinum thermometer through two fixed points is still often applied when no hydrogen thermometer is available (for instance BESTELMEYER Drude's Ann. 13, p. 968, '04).

TABLE I.

COMPARISON BETWEEN THE PLATINUM RESISTANCE THERMOMETER AND THE HYDROGEN THERMOMETER.

Date		Temperature hydrogentherm.	Resistance measured	Remarks
0°		0°	137 884 Ω	mean of 5 measurements.
27 Oct. '05	5 h. 0	— 29.80	121.587	
	2 h. 50	— 58.75	105.640	
30 Oct. '05	3 h. 50	— 88.14	89.277	
8 July '05	10 h. 12	— 103.83	80.448	
26 Oct. '05	5 h. 20	— 139.87	59.914	
7 July '05	4 h. 25	— 139.85	59.920	
26 Oct. '05	3 h. 16	— 158.83	48.929	
27 June '05	1 h. 40	[— 182.69]	34.861	$W-R_{A_I}=-0.061$
30 June '06	11 h. 0	— 182.75	34 858	
27 June '05	3 h. 50	[— 195.30]	27.598	$W-R_{A_I}=+0.082$
2 March '06	3 h. 35	— 195.18	27.595	
29 June '05	11 h. 6	[— 204.53]	22.016	$W-R_{A_I}=-0.110$
2 March '06	1 h. 30	— 204.69	22.018	
30 June '05	3 h. 0	[— 212.83]	17.255	$W-R_{A_I}=-0.082$
5 July '05	5 h. 53	— 212.87	17 290	
5 July '05	3 h. 20	— 217.41	14.763	
3 March '05	10 h. 0	— 217.41	14.770	
5 May '06	3 h. 0	— 252.93	1.963	
5 May '06	5 h. 7	— 259.24	1.444	

$$W_t = W_0 \left\{ 1 + 0{,}39097 \left(\frac{t}{100}\right) - 0{,}009862 \left(\frac{t}{100}\right)^2 \right\}.$$

For instance at — 139° it gives $W-R$: + 0,084. A straight line may be drawn through — 182°, — 195°, — 204° and — 212° and then — 217° deviates from it by 0°,25 towards the side opposite to — 158°. Hence the existence of *a point of inflection* is certain (comp. sub *d*). Therefore it is evident that a quadratic formula will not be sufficient for lower temperatures.

b. But also a cubic formula, even when we leave out of account the hydrogen temperatures, appears to be of no use.

For the cubic formula through the points —88°,14, —158°,83, —204°,69, we obtain:

$$W_t = W_0 \left\{ 1 + 0{,}393008 \frac{t}{100} - 0{,}0_2 73677 \left(\frac{t}{100}\right)^2 + 0{,}0_3 58386 \left(\frac{t}{100}\right)^3 \right\}.$$

It gives for instance at — 182° a deviation of — 0,110, at — 217° a deviation of + 0,322 [1]).

c. In consequence of difficulties experienced with formulae in ascending powers of *t*, we have used formulae with reciprocal powers of the absolute temperatures (comp. the supposition mentioned in § 1 that the resistance becomes infinite at the absolute zero).

Three of these have been investigated:

$$\frac{W_t}{W_0} = 1 + a \frac{t}{100} + b \left(\frac{t}{100}\right)^2 + c \left(\frac{t}{100}\right)^3 + d \left(\frac{10^2}{T} - \frac{10^2}{273{,}09}\right) \quad . \quad . \quad (A)$$

$$\frac{W_t}{W_0} = 1 + a \frac{t}{100} + b \left(\frac{t}{100}\right)^2 + c \left(\frac{t}{100}\right)^3 + d \left(\frac{10^2}{T} - \frac{10^2}{273{,}09}\right) + e \left[\frac{10^4}{T^2} - \frac{10^4}{(273{,}09)^2}\right] \quad . \ (B)$$

$$\frac{W_t}{W_0} = 1 + a \frac{t}{100} + b \left(\frac{t}{100}\right)^2 + c \left(\frac{t}{100}\right)^3 + d \left(\frac{10^2}{T} - \frac{10^2}{273{,}09}\right) + e \left(\frac{10^6}{T^3} - \frac{10^6}{(273{,}09)^3}\right) \quad . \ (C)$$

We shall also try a formula with a term $\frac{e}{T^4}$ instead of $\frac{e}{T^3}$.

For the first we have sought a preliminary set of constants which was subsequently corrected after the approximate method indicated by Dr. E. F. VAN DE SANDE BAKHUYZEN (comp. Comm. N°. 95*a*) in two different ways. First we have obtained a set of constants A_I with which a satisfactory accurate agreement was reached down to — 217°, a rather large deviation at — 252° and a moderate deviation at — 259°. Column $W-R_{AI}$ of table II contains the deviations. Secondly we have obtained a set of constants which yielded a fairly

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[1]) These values deviate slightly from those communicated in the original.

accurate agreement including — 252°, but a large deviation at — 259°. These are given in table II under the heading $W—R_{AII}$.

Lastly we have obtained a preliminary solution B which fairly represents all temperatures including — 252° and — 259° and from which the deviations are given in table II under $W—R_B$, and a solution of the form C which agrees only to — 252° and to which $W—R_C$ relates.

The constants of the formulae under consideration are:

	A_I	A_{II}	B	C
a	+ 0.399625	+ 0.400966	+ 0.412793	+0.40082
b	— 0.0002575	+ 0.001159	+ 0.013812	+0.001557
c	+ 0.0049412	+ 0.0062417	+ 0.012683	+0.00557
d	+ 0.019380	+ 0.026458	+ 0.056221	+0.01975
e			— 0.0033963	—0.16501

TABLE II.

COMPARISON BETWEEN THE PLATINUM RESISTANCE THERMOMETER AND THE HYDROGEN THERMOMETER.

Temperature observed with the hydrogen thermometer.	Number of observations with the hydrogen therm.	Resistance observed in Ω	$W-R_{AI}$	$W-R_{AII}$	$W—R_B$	$W—R_C$
0°		137.884	0	0	0	0
— 29.80	3	121.587	+ 0.025	+ 0.066	+ 0.210	+ 0.063
— 58.75	3	105.640	+ 0.014	— 0.011	+ 0.153	+ 0.048
— 88.14	4	89.277	— 0 012	— 0.050	— 0.001	+ 0.008
— 103.83	3	80.448	— 0.023	— 0.061	— 0.075	— 0.015
— 139.87	3*	59.911	+ 0.004	— 0.005	— 0.082	— 0.005
— 158.83	3	48.929	+ 0.023	+ 0.044	0	+ 0.008
— 182.75	2	34.858	— 0.029	+ 0.027	+ 0.083	— 0.035
— 195.18	2	27.595	+ 0.009	+ 0.061	+ 0.148	+ 0 007
— 204.69	1	22.018	— 0.014	+ 0.012	+ 0.100	— 0.014
— 212.87	3	17.290	— 0.024	— 0.065	— 0.001	— 0.031
— 217.41	4*	14.766	+ 0.028	— 0.048	+ 0.270	+ 0.007
— 252.93	2	1.963	+ 2.422	+ 0.057	— 0.001	0
— 259.24	1	1.444	+ 0.199	— 4.201	0	

In those cases where the $W—R$ have been derived from two determinations the values in the 2nd column are marked with an * 1)).

If we derive from the differences between the observed and the computed values as far as —217° the mean error of an observation by means of A_I, this mean error is expressed in resistance ± 0,025 Ω, in temperature ± 0°,044.

The mean error of an observation of the hydrogen thermometer, as to the accidental errors, amounts to 0°,02 corresponding in resistance to ± 0,010 Ω, while that of the determination of the resistance may be left out of consideration. We cannot decide as yet in how far the greater value of the differences between the observations and the formula is due to half systematic errors or to the formula.

For the point of inflection in the curve representing the resistance as a function of the temperature we find according to B — 180° 2)).

In conclusion we wish to express hearty thanks to Miss T. C. JOLLES and Mr. C. BRAAK for their assistance in this investigation.

Physics. — "*On the measurement of very low temperatures. XII. Comparison of the platinum resistance thermometer with the gold resistance thermometer.* By Prof. H. KAMERLINGH ONNES and J. CLAY. Communication N°. 95^d from the Physical laboratory at Leiden.

(Communicated in the meeting of June 30, 1906).

§ 1. *Introduction.* From the investigation of Comm. N°. 93, Oct. '04, VIII it was derived that as a metal for resistance thermometers at low temperatures gold would be preferable to platinum on account of the shape of the curve which indicates the relation between the resistance and the temperature.

Pure gold seems also better suited because, owing to the signification of this metal as a minting material, the utmost care has been bestowed on it for reaching the highest degree of purity and the quantity of admixtures in not perfectly pure gold can be exactly determined. The continuation to low temperatures of the measurements described in Comm. N°. 93 VIII — which had to be repeated because, although MEILINK's investigation just mentioned had proved the usefulness of the method, a different value for the resistance

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1) The deviations of the last two lines differ a little from the original Dutch paper.

2) Owing to e being negative (B) gives no minimum; a term like that with e does not contradict, however, the supposition $w = \infty$ at $T = 0$ (§ 1) as the formula holds only as far as —259°.

had been found before and after the exposure of the wire to low temperatures — acquired a special value through this peculiarity of gold.

As will appear from what follows, the *point of inflection* of the resistance as a function of the temperature must lie much lower for gold than for platinum. Our favourable opinion about gold as a thermometric substance was confirmed with regard to temperatures to a little below —217°. With respect to the lower temperatures our opinion is still uncertain. A *minimum of resistance* seems not to be far off at —259°.

§ 2. *The apparatus and the measurements.* About the measurements we can only remark that they are performed entirely according to the methods discussed in Comm. N°. 93.

The pure gold was furnished through the friendly care of Dr. C. Hoitsema. It has been drawn to a wire of 0,1 mm. in diameter by Heraeus.

The gold wire was wound upon 2 cylinders, it was about 18 m. in length and its resistance at 0° was 51,915 Ohms. The temperatures were reached in the cryostat of Comm. N°. 94^d as in the investigation in Comm. N°. 95^c.

The determinations of temperature were made by means of the resistance of the platinum wire of Comm. N°. 95^c. The zero determinations before and after the measurements at low temperatures agreed to perfection (this agreement had left something to be desired in the measurements dealt with in Comm. N°. 93).

The measurements were made partly directly by means of the differential galvanometer, partly indirectly by comparing the gold resistance with a platinum resistance, which itself had been compared with the originally calibrated platinum resistance (comp. Comm. N°. 95^c).

§ 3. *The Results,* obtained after the direct and the indirect method are given in column 3 of table III and indicated by *d* and *i* respectively.

For the observations the cryostat was brought to the desired temperature by regulating it so that the resistance of the platinum wire had a value corresponding to this temperature, and by keeping this temperature of the bath constant during the measurements of the resistance of the gold wire. The temperatures given in table III are the temperatures on the hydrogen thermometer according to the observations of Comm. N°. 95^c belonging to the resistance of the platinum thermometer.

TABLE III.

CALIBRATION OF THE GOLD RESISTANCE THERMOMETER.

Date.	Temperature resistance.	Observed gold resistance.	$W-R_{A}$	$W-R_{B\,I}$	$W-R_{B\,II}$
1906	0	51.915 *d*	0	0	0
1 Febr. 5 h. 57	— 28°.96	46 137 *i*	— 0.002	— 0.018	+ 0.029
» 3 h. 40	— 58.58	40 326 *i*	+ 22	+ 12	+ 46
» 12 h. 25	— 87.43	34.640 *i*	— 27	— 3	— 2
12 June 2 h. 20	— 103.82	31.432 *d*	— 24	+ 15	+ 4
» 11 h.	— 139.86	24.284 *d*	— 28	+ 16	+ 10
17 Jan. 3 h. 20	— 159.11	20.394 *i*	— 28	— 1	+ 14
1 June 11 h. 50	— 182.75	15.559 *d*	+ 6	+ 4	+ 39
» 5 h. 8	— 195.18	12.980 *d*	+ 30	+ 19	+ 40
» 4 h.	— 204.69	10.966 *d*	+ 24	+ 18	+ 1
» 3 h.	— 212.87	9.203 *d*	— 2	0	— 76
12 Jan. 11 h.	— 216.25	8.460 *i*	— 30	— 17	— 128
18 May 4 h. 10	— 252.88	2.364 *d*	+ 1.059	+ 2	— 6
» 6 h.	— 259.18	2.047 *d*	+ 1.334	— 3.277	— 6

In order to agree with Dewar, we ought to have found for the resistance of the gold wire at the boiling point of hydrogen 1.708 Ω instead of 2.364 Ω. Also the further decrease of the resistance found by Dewar [1]) in hydrogen evaporating under a pressure of 30 mM. is greater than that was found by us. We may remark that this latter decrease of the resistance according to him would belong to a decrease of 4 degrees on the gas thermometer, and that we in accordance with Travers, Senter and Jaquerod [2]) found a difference in temperature of 6,°3 between the boiling point of hydrogen at a pressure of 760 m.m. and of 60 m.m. (preliminary measurements).

§ 4. *Representation of the variation of the gold resistance by a formula.* As to this we refer to what has been said in Comm.

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[1]) Dewar, Proc. Roy. Soc. Vol. 68 p. 360. 1901.

[2]) Travers, Senter and Jaquerod, Phil. Transact. A. 200.
Proc. Roy. Soc. Vol. 68, p. 361, 1901.

N°. 95^c, XII. § 6. The resistance of the gold wire can be represented fairly well as far as — 217° as a function of the temperature by a formula of the form A.

$$\frac{W_t}{W_o} = 1 + 0{,}39070 \frac{t}{100} + 0.017936 \left(\frac{t}{100}\right)^2 + $$
$$+ 0{,}0085684 \left(\frac{t}{100}\right)^3 + 0.0080999 \left(\frac{T}{100} - \frac{100}{273.09}\right) . \quad (A)$$

This formula A is not fit to include the hydrogen temperatures. For the deviations $W - R_A$ comp. table III.

We have therefore made use of a formula B, and

$$\left.\begin{aligned} \frac{W_t}{W_o} = 1 &+ 0{,}382404 \left(\frac{t}{100}\right) + 0{,}0102335 \left(\frac{t}{100}\right)^2 + \\ &+ 0{,}0035218 \left(\frac{t}{100}\right)^3 - 0{,}0268911 \left(\frac{100}{T} - \frac{100}{273{,}09}\right) + \\ &+ 0{,}0052211 \left\{\left(\frac{100}{T}\right)^2 - \left(\frac{100}{273{,}09}\right)^2\right\} \end{aligned}\right\} (B\,I)$$

is in good harmony down to — 253°, while

$$\left.\begin{aligned} \frac{W_t}{W_o} = 1 &+ 0{,}394548 \left(\frac{t}{100}\right) + 0{,}0200118 \left(\frac{t}{100}\right)^2 + \\ &+ 0{,}0102889 \left(\frac{t}{100}\right)^3 + 0{,}0229106 \left(\frac{100}{T} - \frac{100}{273{,}09}\right) \\ &- 0{,}00094614 \left\{\left(\frac{100}{T}\right)^2 - \left(\frac{100}{273{,}09}\right)^2\right\} \end{aligned}\right\} (B\,II)$$

gives a fair harmony also at — 259° [1]).

The deviations are given under the headings $W - R_{B\,I}$ and $W - R_{B\,II}$ in columns 5 and 6 of table III. The mean error of an observation with respect to the comparison with formula $B\,I$ is ± 0,017 Ω in resistance and ± 0°,09 in temperature. Formula $B\,I$ gives for the point of inflection of the gold resistance — 220°.

Mathematics. — "*Quadratic complexes of revolution.*" By Prof. Jan de Vries.

§ 1. When the rays of a complex can be arranged in reguli of hyperboloids of revolution with the same axis, then the complex can bear revolving about that axis. If such a complex of revolution Ω contains also the second regulus of each of the indicated hyperboloids, then it is symmetric with respect to each plane through its axis

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[1]) The coefficients of the formulae and the values of the deviations, found at a renewed calculation, differ slightly from those given in the original Dutch paper.

and it can be distinguished as a *symmetric complex of revolution*. This is the case with the complexes of tangents of surfaces of revolution.

We determine the general equation of the quadratic complexes of revolution with axis OZ in the coordinates of rays

$$p_1 = x - x' \quad , \quad p_2 = y - y' \quad , \quad p_3 = z - z',$$
$$p_4 = yz' - zy' \quad , \quad p_5 = zx' - xz' \quad , \quad p_6 = xy' - yx'.$$

By substitution of

$$p_1 = \alpha\bar{p}_1 - \beta\bar{p}_2 \quad , \quad p_2 = \beta\bar{p}_1 + \alpha\bar{p}_2 \quad , \quad p_3 = \bar{p}_3,$$
$$p_4 = \alpha\bar{p}_4 - \beta\bar{p}_5 \quad , \quad p_5 = \beta\bar{p}_4 + \alpha\bar{p}_5 \quad , \quad p_6 = \bar{p}_6,$$

(where $\alpha^2 + \beta^2 = 1$) in the general quadratic equation we easily find that the equation of an Ω can contain terms only with

$$(p_1^2 + p_2^2),\ (p_4^2 + p_5^2),\ p_3,\ p_6,\ (p_1 p_5 - p_2 p_4) \text{ and } (p_1 p_4 + p_2 p_5).$$

As the latter combination can be replaced by $- p_3 p_6$ in consequence of a wellknown identity we find for Ω the equation

$$A(p_1^2+p_2^2)+Bp_3^2+2Cp_3p_6+Dp_6^2+E(p_4^2+p_5^2)+2F(p_1p_5-p_2p_4)=0. \quad (1)$$

If $C=0$, equation (1) does not change when x is replaced by $-x$; so it represents a *symmetrical* complex.

The coordinates of rays

$$q_1 = u - u' \quad , \quad q_2 = v - v' \quad , \quad q_3 = w - w' \quad ,$$
$$q_4 = vw' - wv' \quad , \quad q_5 = wu' - uw' \quad , \quad q_6 = uv' - vu' \quad ,$$

where u, v and w represent the coordinates of planes are connected with the coordinates p by the wellknown relations

$$p_1 : q_4 = p_2 : q_5 = p_3 : q_6 = p_4 : q_1 = p_5 : q_2 = p_6 : q_3.$$

So Ω can also be represented by

$$E(q_1^2+q_2^2)+Dq_3^2+2Cq_3q_6+Bq_6^2+A(q_4^2+q_5^2)+2F(q_2q_4-q_1q_5)=0 \ . \ . \quad (2)$$

This equation is found out of (1) by exchanging p_k and q_k, and of A, B, C, D, E, F and $E, D, C, B, A, -F$.

§ 2. The cone of the complex of the point (x', y', z') has as equation:

$$A(x-x')^2+A(y-y')^2+B(z-z')^2+2C(y'x-x'y)(z-z')+D(y'x-x'y)^2+$$
$$+E(z'y-y'z)^2+E(z'x-x'z)^2+2F(x-x')(x'z-z'x)+2F(y-y')(y'z-z'y)=0. \quad (3)$$

In order to find the equation of the singular surface we regard the cones of the complex whose vertices lie in XOZ and note the condition expressing that the section of such a cone and XOY breaks up into two right lines. After suppression of the factor z^2 which is to be rejected and substitution of $x^2 + y^2 = r^2$ for x^2, we find the equation

$$D(AE-F^2)r^4+(AE+BD-C^2-F^2)r^2(Ez^2-2Fz+A)+ \\ +B(Ez^2-2Fz+A)^2=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As this can be decomposed into two factors of the form $Lr^2+M(Ez^2-2Fz+A)$, *the singular surface* Σ *consists of two quadratic surfaces of revolution.*

These touch each other in the cyclic points I_1 and I_2 of the plane XOY and in the points B_1 and B_2 on OZ determined by

$$Ez^2-2Fz+A=0.$$

The two surfaces cut each other according to the four isotropic right lines indicated by the equations

$$x^2+y^2=0 \text{ and } Ez^2-2Fz+A=0 \quad . \quad . \quad . \quad . \quad (5)$$

If Ω is symmetric ($C=0$) the two parts of the singular surface have as equations

$$(AE-F^2)(x^2+y^2)+B(Ez^2-2Fz+A)=0, \quad . \quad . \quad (6)$$

$$D(x^2+y^2)+Ez^2-2Fz+A=0. \quad . \quad . \quad . \quad . \quad (7)$$

If we find $B=0$ and $D=0$, then Σ breaks up into the four planes (5) and Ω is a particular *tetraedal complex.*

Out of (3) it is easy to find that the cones of the complex of the points B_1, B_2, I_1 and I_2 break up into pencils of rays to be counted double.

These points shall be called *bisingular.*

§ 3. The rays of the complex resting on a straight line l touch a surface which is the locus of the vertices of the cones of the complex touched by l. This *axial surface* is in general of order four and of class four and possesses eight nodes. [1])

We shall determine the axial surface of OZ. The points of intersection $(0, 0, z')$ of an arbitrary cone of the complex with OZ are indicated by the equation

$$[E(x^2+y^2)+B]z'^2-2[F(x^2+y^2)+Bz]z'+[A(x^2+y^2)+Bz^2]=0.$$

This has two equal roots if

$$\{(AE-F^2)(x^2+y^2)+B(Ez^2-2Fz+A)\}(x^2+y^2)=0 \quad . \quad (8)$$

So the axial surface of OZ consists of the two isotropic planes through the axis and a quadratic surface of revolution which might be called the *meridian surface.* If Ω is symmetrical, it forms part of the singular surface as is proved out of (6).

Also the axial surface of the right line l_∞ lying at infinity in XOY breaks up into two planes, and a quadratic surface. Its

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[1]) Sturm, *Liniengeometrie* III, p. 3 and 6.

equation is found most easily by regarding the rays of the complex normal to XOZ. From $x = x'$, $z = z'$ ensues $p_1 = 0$, $p_3 = 0$, $p_4 = zp_2$, $p_5 = 0$, $p_6 = -xp_2$. By substitution in (1) we find

$$(A + Dx^2 + Ez^2 - 2\,Fz)\,p_2^{\,2} = 0,$$

and from this for the indicated surface

$$D\,(x^2 + y^2) + Ez^2 - 2\,Fz + A = 0 \quad . \; . \; . \; . \quad (9)$$

For the symmetrical complex this *parallel surface* is according to (7) the second sheet of the singular surface.

The planes of the pencils of rays of the bisingular points B_1, B_2 form the lacking part of the axial surface of l_∞. We can show this by determining the equation of the axial surface of the right line $z' = 0$, $y' = b$, and by putting in it $b = \infty$. We then find

$$(Ez^2 - 2\,Fz + A)\,\{D\,(x^2 + y^2) + Ez^2 - 2\,Fz + A\} = 0 \quad . \quad (10)$$

The *meridian surface*, the *parallel surface*, and the two parts of the singular surface belong to a selfsame pencil, having the skew quadilateral $B_1I_1B_2I_2$ as basis.

If in the equation of the cone of the complex the sum of the coefficients of x^2, y^2 and z^2 is equal to zero, then the edges form ∞^1 triplets of mutually perpendicular rays. The vertices of the *triorthogonal* (equilateral) *cones of the complex* belonging to Ω form the surface of revolution

$$(D + E)\,(x^2 + y^2) + 2Ez^2 - 4Fz + (2A + B) = 0 \quad . \; . \quad (11)$$

It has two circles in common with each of the parts of Σ. These contain the vertices of the cones of the complex which break up into *two perpendicular planes*.

§ 4. The distance l_0 from a right line to OZ is determined by

$$l_0^{\,2} = \frac{p_6^{\,2}}{p_1^{\,2} + p_2^{\,2}}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

the angle λ between a ray and XOY by

$$tg^2\lambda = \frac{p_3^{\,2}}{p_1^{\,2} + p_2^{\,2}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

So the condition $l_0\,tang\,\lambda = a$ furnishes the complex

$$p_3p_6 = a\,(p_1^{\,2} + p_2^{\,2}) \quad . \; . \; . \; . \; . \; . \; . \quad (14)$$

Here we have a simple example of a *symmetrical complex of revolution.*

The equation

$$p_3^{\,2} = a\,(p_1^{\,2} + p_2^{\,2}) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

determines a complex Ω whose rays form with the axis a constant angle, so they cut a circle lying at infinity.

The equation

$$a^2 p_3^2 = p_4^2 + p_5^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

furnishes a complex Ω, whose rays cut the circle $x^2 + y^2 = a^2$. For XOY cuts each cone of the complex according to this circle.

If l represents the distance from a ray O then

$$l^2 = \frac{p_4^2 + p_5^2 + p_6^2}{p_1^2 + p_2^2 + p_3^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If XOY is displaced along a distance c in its normal direction, p_4 and p_5 pass into $(p_4 - cp_2)$ and $(p_5 + cp_1)$. So for the distance l_1 from a ray to the point $(0, 0, c)$ we have

$$l_1^2 = \frac{(p_4^2 + p_5^2 + p_6^2) + 2c(p_1p_5 - p_2p_4) + c^2(p_1^2 + p_2^2)}{p_1^2 + p_2^2 + p_3^2}. \quad (18)$$

If in this equation we substitute $-c$ for c we shall find a relation for the distance l_2 from the ray to point $(0, 0, -c)$.

The equation

$$\alpha_1 l_1^2 + \alpha_2 l_2^2 = \beta$$

furnishes a complex Ω with the equation

$$\{(\alpha_1 + \alpha_2)c^2 - \beta\}(p_1^2 + p_2^2) - \beta p_3^2 + (\alpha_1 + \alpha_2)(p_4^2 + p_5^2 + p_6^2) + \\ + 2(\alpha_1 - \alpha_2)c(p_1 p_5 - p_2 p_4) = 0. \quad . \quad . \quad . \quad . \quad . \quad (19)$$

This symmetrical complex is very extensively and elementarily treated by J. NEUBERG (*Wiskundige Opgaven*, IX, p. 334—341, and *Annaes da Academia Polytechnica do Porto*, I, p. 137—150). The special case $\alpha_1 l_1 + \alpha_2 l_2 = 0$ was treated by F. CORIN (*Mathesis*, IV, p. 177—179, 241—243).

For $l_1 = l_2$ we find simply

$$p_1 p_5 - p_2 p_4 = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This complex contains the rays at equal distances from two fixed points. As c does not occur in the equation the fixed points may be replaced by any couple of points on the axis having O as centre [1]).

§ 5. When there is a displacement in the direction of OZ the coordinates of rays p_1, p_2, p_3 and p_6, do not change whilst we obtain

$$p_4 = \overline{p}_4 + h\overline{p}_2 \quad \text{and} \quad p_5 = \overline{p}_5 - h\overline{p}_1,$$

so

$$p_1 p_4 + p_2 p_5 = \overline{p}_1 \overline{p}_4 + \overline{p}_2 \overline{p}_5.$$

The forms $(p_4^2 + p_5^2)$ and $(p_1 p_5 - p_2 p_4)$ are now *not* invariant.

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[1]) This complex is tetraedral. See STURM, *Liniengeometrie*, I, p. 364.

When in equation (1) of the complex Ω the coefficients E and F are zero, the complex Ω is displaced in itself by each helicoidal movement with axis OZ. This complex can be called *helicoidal.*

The singular surface has as equation

$$(BD - C^2)(x^2 + y^2) + AB = 0; \quad \ldots \ldots \quad (21)$$

so it consists of a cylinder of revolution and the double laid plane at infinity.

§ 6. By *homographic* transformation the complex Ω can be changed into a quadratic complex with *four real bisingular points.*

If we take these as vertices of a tetrahedron of coordinates $O_1 O_2 O_3 O_4$, it is not difficult to show that the equation of such a complex has the form

$$A p^2_{12} + B p^2_{34} + 2\, C p_{12} p_{34} + 2\, D p_{13} p_{42} + 2\, E p_{14} p_{23} = 0. \quad (22)$$

If we again introduce the condition that the section of the cone of the complex with one of the coordinate planes consists of two right lines we find after some reduction for the *singular surface*

$$A(D-E)y_1^2 y_2^2 + 2\{AB-(C-D)(C-E)\}y_1 y_2 y_3 y_4 + B(D-E)y_3^2 y_4^2 = 0 \ . \ (23)$$

So this consists of two quadratic surfaces, which have the four right lines O_1O_3, O_1O_4, O_2O_3 and O_2O_4 in common.

For $A = 0$, $B = 0$ the complex proves to be tetraedral.

For $D = E$ the equation is reducible to

$$A p^2_{12} + B p^2_{34} + 2\,(C - D)\, p_{12} p_{34} = 0,$$

and indicates two linear complexes.

For the axial surfaces of the edges O_1O_2 and O_3O_4 we find

$$x_3 x_4 \{ 2A\, x_1 x_2 + (D - E)\, x_3 x_4 \} = 0 \quad \ldots \ldots \quad (24)$$

and

$$x_1 x_2 \{ 2B\, x_3 x_4 + (D - E)\, x_1 x_2 \} = 0 \quad \ldots \ldots \quad (25)$$

For a point $(0, y_2, 0, y_4)$ of the edge O_2O_4 the cone of the complex is represented by

$$A\, y_2^2 x_1^2 + 2\,(C - E)\, y_2 y_4 x_1 x_3 + B\, y_4^2 x_3^2 = 0; \ . \ . \ . \quad (26)$$

so it consists of two planes through O_2O_4.

This proves that the edges O_1O_3, O_1O_4, O_2O_3, O_2O_4 are *double rays* of the complex [1]).

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[1]) See STURM, *Liniengeometrie* III, pp. 416 and 417.

Physiology. — *"A few remarks concerning the method of the true and false cases."* By Prof. J. K. A. Wertheim Salomonson. (Communicated by Prof. C. Winkler.)

The method of the true and false cases was indicated by Fechner and used in his psychophysical investigations. He applied this method in different ways: first to determine the measure of precision (Präcisionsmasz) when observing difference-thresholds, afterwards to determine these difference-thresholds.

Already in the course of his first experiences arose the difficulty that not only correct and incorrect answers were obtained, corresponding with the "true" and "false" cases, but that also dubious cases occurred, in which the observer could not make sure as to the kind of difference existing between two stimuli, or whether there did exist any difference at all. Fechner himself, and many other investigators after him, have tried in different ways to find a solution to this difficulty. What ought to be done with these dubious cases?

Fechner has indicated several methods, which he subjected to an elaborate criticism. Finally he concluded that the method to be preferred to all others was that one, in which the dubious cases were distributed equally amongst the false and the true cases. If e. g. he found w true cases, v false cases and t dubious cases, he calculated his measure of precision as if there had been $w + \frac{1}{2} t$ true cases and $\frac{1}{2} t + v$ false cases.

Furthermore he showed that a method, employed especially by American experimental physiologists, in which the reagent is urged always to state a result, even if he remains in doubt, practically means the same thing as an equal distribution of the t cases amongst the true and the false cases.

Fechner still worked out another method, by means of which the threshold value was first calculated from the true cases, then from both the true and dubious cases, whilst the final result was obtained with the aid of both threshold values.

A most elegant method to calculate the results of the method of the false and true cases has been pointed out by G. E. Müller, starting from this view, that as a matter of necessity the three groups of cases must be present, and that they have equal claims to exist; that the number of cases belonging to each of these groups in any case, are equally governed by the well-known law of errors. From the figures for the true false and dubious cases the thresholdvalue may afterwards be calculated.

I need not mention some other methods, e.g. that of Foucault, that of Jastrow, because the method of Foucault is certainly incorrect (as has been demonstrated among others by G. E. Müller), whilst that of Jastrow is not quite free of arbitrariness.

Against all these different ways of using the method of the false and true cases, I must raise a fundamental objection, which I will try to elucidate here.

Whenever two stimuli of different physical intensity are brought to act on one of the organs of the senses, either the reagent will be able to give some information as to the difference between these stimuli, or he will not be able to do so. If he cannot give any information, then we have before us a dubious case, if on the contrary he is able to give some information, this information may either be correct, — this constituting a true case — or it may be incorrect, when we shall have a false case.

If the experiment is repeated a sufficient number of times, we shall have obtained at last a certain number of true cases w, of false cases v and of dubious cases t.

Generally it is admitted that the reagent has indeed perceived correctly w times, that he has been mistaken v times, that he was in doubt t times. If this premiss were correct, Fechner's or G. E. Müller's views might be correct too. This however is not the case. An error has already slipped into the premiss, as will become evident furtheron.

No difference of opinion exists as to the dubious cases. To this category belong first those cases, where the reagent got the impression of positive equality, and next those cases, where he did not perceive any difference, and consequently was in doubt. Together they embrace such cases only, in which a greater or lesser or even infinitesimal physical difference was not perceived.

Neither need any difference of opinion exist as regards the false cases. In these cases a stimulus has been acting on the organs of the senses, and information was given about the effect, but on account of a series of circumstances, independent of the will of the reagent, his judgment was not in accordance with the physical cause. The physical cause therefore has not been perceived, but accidental circumstances led the reagent to believe that he was able to emit a judgment, though this judgment, accidentally, was an incorrect one.

And now we are approaching the gist of the argument. If it be possible, that amongst a series of experiments a certain number occur, in which the reagent really does not perceive the physical cause, but is yet induced by chance to emit a judgment which proves to be an *incorrect* one, then there ought to be also a number of cases, in which likewise the physical cause is not perceived, in which however by chance a judgment is emitted, though this time a *correct* one. These facts being dependent on circumstances beyond our will, the chances are equal that either a wrong or a right judgment may be given. If therefore we had v false cases, we may reasonably admit the existence of v cases, in which practically the physical cause has not been perceived, and where yet a judgment, this time a correct one, has been given. These v cases however have been recorded amongst the true cases, though they cannot be admitted as cases of correct perception: it is only in $w—v$ cases that we may suppose the physical cause to have been really and correctly perceived; in all other cases, in $2v + t$ cases therefore, there has been no perception of the real difference of the stimuli.

In this way we have only to consider two possibilities, constituting the *perceived* and *non-perceived* cases, the number of which I will indicate by ξ and χ. The supposition that we may apply the principles of the calculus of probability to them, is justified a priori.

This supposition is changed into a certainty, if we apply the mathematical relations, stated by FECHNER to exist between the numbers of true and false cases.

As is well known, FECHNER added to the number of true cases, obtained by the experiment, one half of the dubious cases: he used therefore in his calculation a rectified number of true cases $w' = w + \frac{1}{2}t$. In the same manner he corrected the number of false cases by adding to them likewise one half of the dubious cases: $v' = v + \frac{1}{2}t$.

In calculating the number of my perceived cases, I get $\xi = w—v$, whilst the number of non-perceived cases is represented by $\chi = t + 2v$. Evidently I may also express the number of perceived cases by

$$\xi = w^1 - v^1.$$

As FECHNER has given for the relative value of the corrected number of true cases the expression:

$$\frac{w^{1'}}{w+t+v} = \frac{w+\frac{1}{2}t}{n} = \tfrac{1}{2} + \frac{1}{\sqrt{\pi}} \int_0^{Dh} \varepsilon^{-t^2} dt$$

and for the corrected relative number of false cases the expression:

$$\frac{x'}{w+t+v} = \frac{v+\frac{1}{2}t}{n} = \tfrac{1}{2} - \frac{1}{\sqrt{\pi}} \int_0^{Dh} \varepsilon^{-t^2} dt$$

we obtain from these immediately for ξ and χ the two relations:

$$\xi = \frac{2}{\sqrt{\pi}} \int_0^{Dh} \varepsilon^{-t^2}\, dt$$

and

$$\chi = 1 - \frac{2}{\sqrt{\pi}} \int_0^{Dh} \varepsilon^{-t^2}\, dt.$$

We find therefore that the way of dealing with the true, dubious and false cases as proposed by me, allows us to use FECHNER's well-known tables.

I wish to lay some stress here on the fact, that G. E. MÜLLER's formulae give the same result, saving only the well-known difference in the integral-limits: these latter being 0 and $(S_u \pm D)\, h_u$.

I need scarcely add that my remarks do not touch in the least the question about "thresholdvalue" between FECHNER and G. E. MÜLLER.

It is evident, that the result of the calculation of a sufficiently extensive series of experiments according to the principles, given in my remarks should give numbers, closely related to those either of FECHNER or of G. E. MÜLLER — depending on the limits of integration. Still I wish to draw special attention to the fact that the formulae of G. E. MÜLLER about the true, false and dubious cases are rather the statistical representation of a series of nearly identical psychological processes, whilst the opinion professed by me on the method of the false and true cases, represents a pure physiological view.

Finally my remarks show, that CATTELL and FULLERTON's way of applying the method of the true and false cases is less arbitrary than it seems to be at first sight. They take for the thresholdvalue the difference of stimuli with which the corrected number of true cases attains 75 %. Such being the case, ξ and χ are both = 50 %. They consider therefore the thresholdvalue to be a difference between two stimuli such, that there is an equal chance of this difference being perceived or not.

Chemistry. — *"The shape of the spinodal and plaitpoint curves for binary mixtures of normal substances."* (Fourth communication: *The longitudinal plait.*) By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

1. In order to facilitate the survey of what has been discussed by me up to now, I shall shortly resume what has been communicated on this subject in four papers in These Proceedings and in two papers in the Arch. Teyler.

a. In the *first* paper in These Proceedings (22 April 1905) the equation:

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

was derived for the *spinodal* lines for mixtures of *normal* substances, on the supposition that a and b are independent of v and T, and that $a_{12} = \sqrt{a_1 a_2}$, while

$$(av-\beta\sqrt{a})^3\,[(1-2x)\,v-3x\,(1-x)\beta] +$$
$$+ \sqrt{a}\,(v-b)^2\left[3(av-\beta\sqrt{a})\,(av-2\beta\sqrt{a}) + \frac{a(v-b)\,(v-3b)}{x(1-x)}\right] = 0 \quad (2)$$

was found for the v,x-projection of the *plaitpoint line,* when $\alpha = \sqrt{a_2} - \sqrt{a_1}$ and $\beta = b_2 - b_1$.

b. In the *second* paper in These Proceedings (27 May 1905) the shape of these lines for different cases was subjected to a closer examination. For the simplification of the calculations $\beta = 0$, i.e. $b_1 = b_2$, was assumed, so that then the proportion θ of the critical temperatures of the two components is equal to the proportion π of the two critical pressures. If we then put $\frac{\sqrt{a_1}}{\alpha} = \varphi$, $\frac{b}{v} = \omega$, $\frac{T}{T_0} = \tau$ (where T_0 is the "third" critical temperature, i. e. the plaitpoint temperature for $v = b$), the two preceding equations become:

$$\tau = 4\omega\,[x(1-x) + (\varphi + x)^2\,(1-\omega)^2] \quad . \quad . \quad . \quad . \quad (1a)$$

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

It now appeared that the plaitpoint curve has a *double point,* when $\varphi = 1{,}43$, i.e. $\theta = \pi = 2{,}89$. If $\theta > 2{,}89$, the (abnormal) case of fig. 1 (loc. cit.) presents itself (construed for $\varphi = 1$, $\theta = (1 + {}^1/_\varphi)^2 = 4$); if on the other hand $\theta < 2{,}89$, we find the (normal) case of fig. 2 (loc. cit.) (construed for $\varphi = 2$, $\theta = 2{}^1/_4$).

At the same time the possibility was pointed out of the appearance of a third case (fig. 3, loc. cit.), in which the branch of the plaitpoint line running from C_1 to C_2 was *twice* touched by a spinodal line. Here also the branch C_0A is touched by a spinodal line [in the first two cases this took place only once, either (in fig. 1, loc. cit.) on the branch C_1A (A is the point $x=0$, $v=b$), or (in fig. 2 loc. cit.) on the branch C_0A (C'_0 is the before-mentioned third critical point)].

So it appeared that *all* the abnormal cases found by KUENEN may already appear for mixtures of *perfectly normal* substances.

It is certainly of importance for the theory of the critical phenomena that the existence of *two different branches* of the plaitpoint curve has been ascertained, because now numerous phenomena, also in connection with different "critical mixing points" may be easily explained.

c. In the *third* paper in These Proceedings (June 24, 1905)[1]) the equation:

$$\Delta=\frac{1}{T_1}\left(\frac{dT}{dx}\right)_0=\theta\sqrt{\frac{1}{\pi}}\left[\theta\sqrt{\frac{1}{\pi}}\left({}^3/_2-{}^1/_2\sqrt{\frac{1}{\pi}}\right)^2-1\right) \quad . . (3)$$

was derived for the *molecular increase* of the lower critical temperature for the *quite general* case $a_2 \lessgtr a_1$, $b_2 \lessgtr b_1$, which equation is reduced to the very simple expression

$$\Delta=\theta\,(\theta-1) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3^a)$$

for the case $\pi=1\,(p_2=p_1)$.

This formula was confirmed by some observations of CENTNERSZWER and BÜCHNER.

d. The *fourth* paper appeared in the Archives Teyler of Nov. 1905. Now the restricting supposition $\beta=0$ (see *b*) was relinquished for the determination of the *double point* of the plaitpoint line, and the quite general case $a_2 \lessgtr a_1$, $b_2 \lessgtr b_1$ was considered. This gave rise to very intricate calculations, but finally expressions were derived from which for every value of $\theta=\frac{T_2}{T_1}$ the corresponding value of $\pi=\frac{p_2}{p_1}$, and also the values of x and v in the double point can be calculated.

Besides the special case $\theta=\pi$ (see *b*) also the case $\pi=1$ was examined, and it was found that then the double point exists for $\theta=9{,}90$. This point lies then on the line $v=b$.

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[1]) The three papers mentioned have together been published in the Arch. Néerl. of Nov. 1905.

e. The *fifth* paper (These Proceedings, Dec. 30, 1905) [1]) contained the condition for a *minimum critical* (*plaitpoint*) *temperature,* and that for a *maximum vapour pressure* at higher temperatures (i. e. when at lower temperatures the three-phase-pressure is greater than the vapour pressures of the components). For the first condition was found:

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

for the second:

$$\theta < \frac{\pi}{2\sqrt{\pi}-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which conditions, therefore, do not always include each other [2]).

After this the connodal relations for the three principal types were discussed in connection with what had already been written before by KORTEWEG (Arch. Néerl. 1891) and later by VAN DER WAALS (These Proceedings, March 25, 1905). The successive transformations of main and branch plait were now thrown into relief *in connection with the shape of the plaitpoint line, and its splitting up into two branches as examined by me.*

f. In the *sixth* paper (Arch. Teyler of May 1906) the connodal relations mentioned were first treated somewhat more fully, in which also the p, x-diagrams were given. There it was proved, that the points R_1, R_2 and R'_2, where the spinodal lines touch the plaitpoint line, are *cusps* in the p, T-diagram.

Then a graphical representation was plotted of the corresponding values of θ and π for the double point in the plaitpoint line, in connection with the calculations mentioned under *d.*

Both the graphical representation and the corresponding table are here reproduced. The results are of sufficient importance to justify a short discussion.

We can, namely, characterize all possible pairs of substances by the values of θ and π, and finally it will only depend on these values, which of the three main types will appear. To understand this better, it is of importance to examine for what combination (π, θ) one type passes into another. As to the transition of type I to II (III), it is exactly those combinations for which the plaitpoint line has a double point. In fig. 1 (see the plate) every point of the

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[1]) Inserted in the Arch. Néerl. of May 1906.

[2]) These results were afterwards confirmed by VERSCHAFFELT (These Proceedings March 31, 1906; cf. also the footnote on p. 749 of the English translation).

plane denotes a combination (θ, π), to which every time a certain pair of substances will answer.

$\theta = \frac{T_2}{T_1}$	$\pi = \frac{p_2}{p_1}$	x	$v/_b$
1,00	7,50 en 0,13	0,96 en 0,040	2,57 en 2,57
1,19	7,21 » 0,13	0,94 » 0,036	2,49 » 2,60
1,71	6,26 » 0,13	0,84 » 0,025	2,26 » 2,68
1,88	5,76 » 0,13	0,78 » 0,021	2,18 » 2,71
2,04	5,42 » 0,12	0,72 » 0,018	2,11 » 2,74
2,22	4,94 » 0,12	0,63 » 0,014	2,02 » 2,79
2,89	2,89 » 0,12	0,24 » 0,003	1,73 » 2,87
9,90	1,00 » 0,11	0,01 » 0,001	1,00 » 2,95
∞	— » 0,11	— » 0,000	— » 3,00

In the said figure the line $C'APB$ denotes the corresponding values of θ and π from $\theta = 0$ to $\theta = 9{,}9$. For C' $\theta = 0$, $\pi = 9$, for A $\theta = 1$, $\pi = 7{,}5$; with $\theta = 2{,}22$ corresponds $\pi = 4{,}94$. (Case $\pi = \theta^2$ or $a_2 = a_1$); for P $\pi = \theta = 2{,}89$ (Case $\pi = \theta$ or $b_2 = b_1$); for B $\theta = 9{,}9$, $\pi = 1$. For values of $\theta > 9{,}9$ the double point would lie on the side of the line $v = b$, where $v < b$. It appears from the figs. 23, 24 and 25 of the said paper, that then the line BD $(\pi = 1)$ forms the line of demarcation between type I and II (III). For starting from a point, where $\pi < 1$ (however little) and θ is comparatively low, where therefore we are undoubtedly in region II (III), we see clearly that we cannot leave this region, when with this value of π that of θ is made to increase. For we can never pass to type I, when not for realizable values of v (so $< b$) a double point is reached, and now a simple consideration (see the paper cited) teaches, that for $\pi < 1$ a double point would always answer to a value of $v < b$.

Now it is clear that $\theta = 0, \pi = 9$ is the same as $\theta = \infty, \pi = {}^1/_9$; that $\theta = \pi = 2{,}89$ is identical with $\theta = \pi = {}^1/_{2,89} = 0{,}35$; etc., etc. (the two components have simply been interchanged), so that the line CA' will correspond with the line $C'A$, while $A'B'$ corresponds with AB. If we now consider only values of θ which are > 1, if in other words we always assume $T_2 > T_1$, we may say that the region of the normal type II (III) is practically bounded by the lines ABD, AA' and $A'C$. On the right of ABD we have the abnormal type I ($C_2H_6 + CH_3OH$, ether $+ H_2O$); on the left of $A'C$ we have also the type I. But whereas in the first region of I the branches of the plaitpoint line are C_2C_0 and C_1A, they are C_1C_0 and C'_2B (see figs. 23—25 loc. cit.) in the second region. It is namely easy to show, (loc. cit.), that for $\pi > 1$ the branches of the plaitpoint line are either C_1C_2 and C_0A (type II and III), or C_1A and C_0C_2 (type I), while for $\pi < 1$ these branches are C_1C_2 and C_0B (type II and III) or C_2B and C_0C_1 (type I). The line $\pi = 1$ divides therefore the region of type II (III) into two portions, where we shall resp. find the shape of the plaitpoint line branches mentioned (viz. for $\theta > 1$). But in practice it will most likely never happen, that with $\theta > 1$ a value of π corresponds which is much smaller than 1, for a higher critical pressure goes generally together with a higher critical temperature. We may therefore say that with a given value of π the abnormal type I is found when θ is *comparatively large* [larger than the double point (of the plaitpoint line) value of θ], whereas the normal type II (or III) appears when θ is *comparatively small* (smaller than the said double point value).

It is now of the greatest importance to examine, when type II passes into III, where the plaitpoint line C_1C_2 is twice touched by a spinodal line (in R_1 and R_2'). This investigation forms the conclusion of the last paper in the Arch. Teyler.

The calculations get, however, so exceedingly intricate, that they proved practically unfeasible for the general case $a_2 \gtrless a_1$, $b_2 \gtrless b_1$. Only the special cases $\beta = 0$ ($b_2 = b_1$ or $\pi = \theta$) and $\pi = 1$ admitted of calculation, though even then the latter was still pretty complicated.

Then it appeared, that for $\beta = 0$ the region of type III is exactly $= 0$, that it simultaneously appears and disappears in the double point P, where $\pi = \theta = 2{,}89$. But in the case $\pi = 1$ the region lies between $\theta = 4{,}44$ and $\theta = 9{,}9$ (the double point). This is therefore QB in fig. 1; i. e. for values of $\theta > 1$ and $< 4{,}44$ we find type II (see fig. 2^a); for $\theta = 4{,}44$ (in Q) the plaitpoint line gets a point of inflection (see fig. 2^b), whereas from $\theta = 4{,}44$ to $\theta = 9{,}9$ we meet with type III (fig. 2^c) with two points R_1 and R_2', where the spinodal lines touches the plaitpoint line. This type disappears in the double point P, where $\theta = 9{,}9$ and R_2 and R_2' coincide in P (fig. 2^d), and passes for values of $\theta > 9{,}9$ into type I (fig. 2^e). We point out, that the figs. 2^a—2^c represent an intermediate case (i. e. between $\pi = \theta$ and $\pi = 1$, see fig. 1), for in the case of

$\pi = 1$ the branch AR_2C_0 would coincide with AB ($v = b$). Therefore the special value 4,44 has been replaced by θ_q (the value of θ in Q) and the value 9,9 by θ_p (the value of θ in P).

Of the curve which separates type II from type III we know as yet only the points P and Q (see fig. 1) and the further course of this line is still quite unknown, for which reason we have denoted it by a dotted line.

In any case the investigations, described in the Arch. Teyler have *proved*, that this very abnormal type III *is possible for mixtures of normal substances.* If the critical pressures of the two components are the same ($\pi = 1$), then we meet with this type when θ lies between 4,4 and 9,9. The critical temperatures must therefore lie far apart, but not so far (see fig. 1) as would be necessary for the appearance of type I.

We shall once more emphatically point out that the *numeric* results of our investigation will naturally be modified, when b is not assumed to be independent of v and T, or when one of the two components should be associating substances. This will cause the types III and I to make their appearance *earlier* than has been derived above (i. e. with lower values of θ with for the rest equal values of π), but that *qualitatively* everything will remain unchanged. This appears already from the fact that the substitution of the quite general assumption $b_1 \lesseqgtr b_2$ for the simplified assumption $b_1 = b_2$ (in the first paper in the Arch. Teyler) has made no change is the existence of a double point in the plaitpoint line with certain corresponding values of θ and π, and that also the calculations for the limits of type III (in the second paper in the Arch. Teyler) may be carried out for the quite general case $b_1 \lesseqgtr b_2$. So the phenomena remain qualitatively the same for very different pairs of values of b_1 and b_2, and will therefore not change *essentially* either, when one definite pair of values, holding e. g. for the critical circumstances of one of the components, is subjected to changes, whether by association, or by other causes, when v or T change — no more as e. g. the critical phenomena for a simple substance will *essentially* change when b is no longer constant, but is supposed to be dependent of v and T, or when that substance forms complex molecules.

The longitudinal Plait.

2. In former papers it has been demonstrated that in the neighbourhood of C_0 a minimum plaitpoint temperature makes its appearance

both with type I in the line C_0C_2 and with type II in the line C_0A, and that therefore with decrease of temperature a *separate plait* begins to detach itself starting from C_0 at a definite temperature T_0 (the plaitpoint temperature in C_0), which plait will merge into the main plait (or its branch plait) later on in an homogeneous double point. The consequence of this is, that with type I e. g. at lower temperatures the main plait will always be *open* towards the side of the small volumes, so that increase of pressure will never cause the two split phases to coincide.

Let us however specially consider the case of type II. Here the usual course, inter alia described in the last cited paper in the Proceedings of Dec. 30, 1905, is this. At a certain temperature, passing from higher to lower temperatures, a spinodal curve touches the branch of the plaitpoint line AC_0 in R_2. In the well-known way a closed connodal curve begins to form within the connodal line proper, which closed curve gets outside the original connodal curve at lower temperatures, and gives rise to a new (branch) plait, and at the same time to a three phase equilibrium (figs. 3^a and 3^b). In many cases this branch plait has already appeared before the plait which starts from C_0, begins to develop at somewhat lower temperature. Later on the two branches coincide (at the minimum temperature in D), and then form again a continued branch plait (fig. 3^c). [1]).

Now for the special case $b_2 = b_1$ the point D lies always very near C_0 (see the paper in these Proceedings referred to under b. in § 1). If then e. g. $T_2/T_1 = 2^1/_4$, then $T_m/T_0 = 0{,}96$, when T_m represents the temperature in the minimum at D. The real longitudinal plait round C_0 exists then only at very high pressures (fig. 3^b), while the open plait of fig. 3^c can hardly be called a longitudinal plait, but is much sooner to be considered as the branch plait of the transverse plait which has joined the original longitudinal plait. Increase of pressure makes here always the two coexisting liquid phases approach each other, unless with very high pressures, when these phases diverge again.

The calculation proves that in the quite general case $b_1 \lessgtr b_2$ the point D may get much nearer in the neighbourhood of R_2, and also that the temperature in the plaitpoint C_0 may be comparatively high, so that in opposition to what has been represented in fig. 3^a the longitudinal plait has already long existed round C_0 before a three phase equilibrium has formed at M (fig. 4^a and 4^b). The meeting

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[1]) In this and some other figures the spinodal curves seem to touch in the homogeneous double point D, instead of to intersect, as they should.

of this longitudinal plait, which has then already greatly extended, with the branch plait takes place much more in the neighbourhood of the line 1, 2 of the three phase triangle, so that after the meeting the plait assumes the shape drawn in fig. 4^c, which makes it for the greater part retain its proper character of longitudinal plait. So at first increase of pressure makes the phases approach each other (this portion may be exceedingly small, but as a rule it will exist); then further increase of pressure makes the phases 1 and 2 again diverge, till x_1 and x_2 approach to limiting values at $p = \infty$, without the longitudinal plait ever closing again — as was formerly considered possible [cf. inter alia VAN DER WAALS, Cont. II, p. 190 (1900)]. For in consequence of the minimum at D the longitudinal plait always encloses the point C_0. Only at temperatures higher than T_0, at which the longitudinal plait does not yet exist, there can be question of homogeneity till the highest pressures. But then the plaitpoint P belongs to the *branch plait* of the *transverse plait,* and *not* to the longitudinal plait. This is indicated among others by fig. 3^a, *after* the closed connodal curve in M has broken through the connodal curve proper of the transverse plait; or by fig. 3^b, *before* a longitudinal plait has developed round C_0.

Of course we may also meet with the case, that the plait round C_0 coincides with the branch plait at the moment that the latter with its plaitpoint just leaves the transverse plait, as shown in fig. 5^a, but this involves necessarily a *relation* between θ and π, and is therefore always a *very special case.* Then the branch plait happens to leave the transverse plait exactly in the minimum at D. After the meeting the plait shows the shape as traced in fig. 5^b. Now increase of pressure causes the two phases 1 and 2 to diverge *from the beginning.*

But the longitudinal plait round C_0 may also meet the connodal line of the transverse plait, *before* the closed connodal line has got outside the transverse plait (fig. 6^a). Then the three phase equilibrium does not develop, as in fig. 4^a, at the transverse plait (from which a branch plait issues), but at the *longitudinal plait* round C_0. The latter penetrates then further into the transverse plait, till its meets the isolated closed connodal curve in D (fig. 6^b), after which the confluence with it takes place in the unrealizable region (fig. 6^c).

This plait is then the *longitudinal plait proper,* of which there is generally question with mixtures of substances which are not miscible in all proportions. But we should bear in mind that just as well the above treated case of fig. 4 may present itself, with that of fig. 5 as transition case.

The calculation teaches that the transition case presents itself when the proportion θ of the critical temperatures of the two components is in the neighbourhood of 1, and the proportion π of the critical pressures is at the same time pretty large.

A clear representation of these different relations is also given by the two p, T-diagrams of fig. 7 and fig. 7^a. (The temperature of C_0 is there assumed to be lower than that of R_2, but it may just as well be higher). The plaitpoints p' on the part R_2A below the cusp are the unrealizable plaitpoints (see also figs. 3—6); the plaitpoints p on the part R_2M before M also (then the isolated closed connodal curve has not yet got outside the main plait); the plaitpoints P beyond M are all realizable.

So after the above we arrive at the conclusion that in all cases in which a distinct longitudinal plait appears of the shape as in figs. 4^c or 6^c (so when the minimum D lies near R_2), the critical mixing point M of the three phases need not always lie on the longitudinal plait (see fig. 4^a), and also that the longitudinal plait with its plaitpoint P will not always coincide with the transverse plait itself, but it can also coincide with the branch plait of the transverse plait, so that at that moment no three phase equilibrium, i. e. no vapour phase is found (see fig. 4^c). The two liquid phases 1 and 2, however, coincide in this case.

The case drawn in figs. 5^a and 5^b remains of course an exception, and the conditions for its occurrence may be calculated (see above). But this calculation, as well as that which in general indicates the situation of the points R_2, D and M, will be published elsewhere (in the Arch. Teyler). It is, however, self-evident that the above general considerations are by no means dependent on these special calculations.

It is perhaps not superfluous to call attention to the fact that the concentration x_3 of the vapour phase is neither in fig. 4^a, nor in fig. 5^a or 6^a, the same as the concentration of the two coinciding liquid phases $x_{1,2}$, as VAN DER LEE wrongly believes to have shown in his Thesis for the doctorate (1898), [see p. 66—69, 73—74 and Thesis III; also VAN DER WAALS, Cont. II, p. 181 (1900)]. Now we know namely, that when x_3 lies between x_1 and x_2 at lower temperatures, this need not continue to be so till x_1 and x_2 have coincided. The latter would be quite accidental; in general one of the maxima, e. g. in the p,x-line, which lie in the unstable region between x_1 and x_2, will get outside the plait before x_1 and x_2 have coincided. Cf. the figs. 12^a to 12^f in my Paper in These Proceedings of March 25 1905 and § 8 p. 669—670, and also the footnote on p. 665.

Already in a previous paper (These Proceedings June 27 1903) I had elaborately demonstrated this, and somewhat later (These Proceedings 31 Oct. 1903) KUENEN arrived at the same opinion independently of me.[1]) And in 1900 SCHREINEMAKERS (Z. f. Ph. Ch. **35**, p. 462—470) had experimentally demonstrated that one maximum leaves the longitudinal plait for exactly the same mixture (phenol and water), for which VAN DER LEE thought he could theoretically prove, that $x_3 = x_{1,2}$.[2])

Finally I shall just point out that in the peculiar shape of the p,T-diagram of the plaitpoint line (fig. 7) in the neighbourhood of the point D, and in the fact that the two critical moments represented by figs. 4^a and 4^c (as D and M in general do *not* coincide) do *not* coincide, the clue may be found for the explanation of a highly puzzling and as yet unexplained phenomenon, which has been observed as well by GUTHRIE as by ROTHMUND [Z. f. Ph. Ch. **26**, p. 446 (1898)][3]) in their experiments, viz. the appearance and disappearance of a distinct cloudiness when the mixture is heated above the "critical temperature of mixing", which cloudiness often continued to exist up to 10° above this temperature.

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[1]) C. f. also KUENEN: Theorie der Verdampfung und Verflüssigung von Gemischen. Leipzig 1906, p. 170, note.

[2]) For the rest the assumption $x_3 = x_{1,2}$ at the point M leads, as the calculations teach, not only to strange, but to highly absurd conclusions.

[3]) C. f. also FRIEDLÄNDER, Ueber merkwürdige Erscheinungen in der Umgebung des kritischen Punktes. Z. f. Ph. Ch. **38**, p. 385 (1901).

(October 25, 1906).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday October 27, 1906.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 27 October 1906, Dl. XV).

CONTENTS.

Mathematics. — *"The force field of the non-Euclidean spaces with positive curvature"* by Mr. L. E. J. Brouwer. (Communicated by Prof. D. J. Korteweg).

(Communicated in the meeting of September 29, 1906).

D[1]. *The spherical Sp_2.*

I. The theorems under C § I and II hold invariably for the spherical and elliptical Sp_n's. But on account of the finiteness of these spaces we need not postulate a limiting field property for the following developments. We shall first consider the spherical spaces.

Firstly we remark for the general linevector distribution of the spherical Sp_n that the total sum of the divergency is 0; for the outgoing vectorcurrents out of the different space-elements destroy each other. This proves already that as elementary ${}_0^1X$ we can but take the field of a double point.

Schering (Göttinger Nachrichten 1873), and Killing (Crelle's Journal, 1885) give as elementary gradient field the derivative of the potential function $\int_r^{\frac{1}{2}\pi} \frac{dr}{sin^{n-1} r} \equiv v_n(r)$. [2]

But the derivative of this field consists of two equal and opposite divergencies in two opposite points; and it is clear that an arbitrary integral of such fields always keeps equal and opposite divergencies in the opposite points, so it cannot furnish the general divergency-distribution limited only to a total divergency sum $= 0$.

II. If we apply for a spherical Sp_n the theorem of Green to the whole space (i. e. to the two halves, in which it is divided by an arbitrary closed Sp_{n-1}, together), doing this particularly for a scalar function φ which we presuppose to have nowhere divergency and a scalar function having only in two arbitrary points P_1 and P_2 equal and opposite divergencies and nowhere else (such functions we shall deduce in the following), we then find

$$\varphi_{P_1} - \varphi_{P_2} = 0,$$

i. o. w. φ is a constant, the points P_1 and P_2 being taken arbitrarily.

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[1] A, B and C refer to: "The force field of the non-Euclidean spaces with negative curvature". (See these Proceedings, June 30, 1906).

[2] We put the space constant $= 1$, just as we did in the hyperbolic spaces.

So there is no ${}_0^1X$ possible with nowhere divergency, thus no ${}^1X$ having nowhere rotation and nowhere divergency, and from this ensues:

A linevector distribution in a spherical Sp_n is determined uniformly by its rotation and its divergency.

III. The general vector distribution in a spherical Sp_n must thus be obtainable again as an arbitrary integral of:

1. fields E_1, whose second derivative consists of two equal and opposite scalar values close to each other.

2. fields E_2, whose first derivative consists of planivectors distributed regularly in the points of a small ${}^{n-2}$sphere and perpendicular to that ${}^{n-2}$sphere.

At finite distance from their origin the fields E_1 and E_2 have an identical structure.

IV. For the spherical Sp_2 there exists a simple way to find the field E_1 namely conform representation by stereographic projection of a Euclidean plane with a doublepoint potential, which double point is situated in the tangential point of the sphere and the plane. If we introduce on both surfaces as coordinates the distance to the double point and the angle of the radiusvector with the doublepoint-axis — in the plane ϱ and φ, on the sphere r and φ — we have:

$$\tfrac{1}{2}\,\varrho = \tan \tfrac{1}{2}\, r.$$

The potential in the plane: $\dfrac{\cos\varphi}{\varrho}$ becomes on the sphere:

$$\tfrac{1}{2} \cos\varphi \cot \tfrac{1}{2}\, r.$$

This potential shows nothing particular in the centre of projection on the sphere, so it is really the potential to be found of a single double point, the field E_1. (If we place in the opposite point of the double point an other double point in such a way that the unequal poles correspond as opposite points, we find as potential $\tfrac{1}{2}\cos\varphi\,(\cot\tfrac{1}{2}\,r + \tan\tfrac{1}{2}\,r) = \dfrac{\cos\varphi}{\sin r}$, which is the Schering potential of a double point).

V. Here too we can meanwhile break up the field of a double point into two fictitious "fields of a single agens point"; for this we have but to take $\displaystyle\int_r^{\pi} \tfrac{1}{2}\cot\tfrac{1}{2}\,r\,dr = -\,l\sin\tfrac{1}{2}\,r \equiv F(r)$; so that for an arbitrary gradient distribution holds

$$ {}^{1}_{0}X = \overline{\nabla}_{1} \int \frac{\overline{\nabla}_{2}\, {}^{1}_{0}X}{2\pi} F(r)\, d\tau \; . \; . \; . \; . \; . \; . \; . \qquad (I) $$

The "field of a single agens point" has however divergencies everywhere on the sphere.

VI. Out of the field E_1 we deduce in an analogous way as under B § VI the field E_2 of a rotation double point normal to the agens-doublepoint of the field E_1. As scalar value of the planivector potential we find there:

$$ \tfrac{1}{2} \sin \varphi \cot \tfrac{1}{2} r, $$

as we had to expect, completely dual to the scalar potential of the field E_1.

As fictitious force field of a unity-rotationelement we deduce out of this (in the manner of B § VI):

$$ \tfrac{1}{2} \cot \tfrac{1}{2} r, $$

directed normally to the radiusvector. For the rest this force field has rotation everywhere in Sp_2.

VII. Out of this we find (comp. under *B* § VII) for the scalar value of the planivector potential of a rotation-element:

$$ \int_{r}^{\pi} \tfrac{1}{2} \cot \tfrac{1}{2} r \, dr \equiv F(r), $$

so that for an arbitrary ${}^{1}_{2}X$:

$$ {}^{1}_{2}X = \overline{\nabla}_{2} \int \frac{\overline{\nabla}_{1}\, {}^{1}_{2}X}{2\pi} F(r)\, d\tau. \; . \; . \; . \; . \; . \qquad (II) $$

And an arbitrary vectorfield is the ∇ of a potential:

$$ \int \frac{\nabla X}{2\pi} F(r)\, d\tau. $$

E. The spherical Sp_3.

I. The purpose is in the first place to find E_1; we shall compose it of some singular potential functions with simple divergency distributions, and which are easy to construct.

Let us suppose a principal ^{2}sphere B with poles P_1 and P_2, and on B a principal circle C with poles Q_1 and Q_2 determining on B meridian circles M cutting C in points H.

We can construct in the first place out of the SCHERING potential the potential of two double points, in P_1 and P_2, the positive poles of which are both directed towards Q_1 (so that in opposite points unequal poles correspond). Let us determine a point S of the hypersphere by the distance $PS = r$ and $\angle QPS = \varphi$ (where for P and Q the index 1 or 2 must be taken according to S lying with P_1 or with P_2 on the same side of B), then this potential (α) becomes

$$\pm \frac{\cos\varphi}{\sin^2 r},$$

where the sign $+$ ($-$) must be taken for the half hyperspheres between P_1 (P_2) and B.

This field has no other divergency but that of the double points P_1 and P_2.

If we now reverse the sign of the potential in the half hypersphere on the side of P_2, we obtain the potential (β):

$$\frac{\cos\varphi}{\sin^2 r}.$$

The divergency of this consists in the first place of two double points, *one* directed in P_1 towards Q_1 and *one* directed in P_2 towards Q_2 (so that now in two opposite points equal poles correspond); and then of a magnetic scale (indeed a potential discontinuity) in sphere B varying in intensity according to $\cos\varphi$.

II. By the side of this we wish to find a potential, the divergency of which consists of only such a magnetic scale in sphere B with an intensity proportional to $\cos\varphi$. Now a field of a magnetic scale in B with an intensity varying according to an other zonal spherical harmonic, is easy to find. Let us namely take in each "meridian sphere" PQH as potential of a point S the angle $PHS = \frac{1}{2}\pi - \angle QHS$ (P and Q to be provided with indices in the way indicated above according to the place of S) $= \tan^{-1}\{\cos\varphi \tan r\}$, then we have such a potential: in the hypersphere it is a zonal spherical harmonic about PQ as axis; on the sphere B it has its only divergency in the shape of a magnetic scale, the intensity of which varies according to a zonal spherical harmonic with pole Q.

Let us now take in turns all the points of the sphere B as pole Q' of such a potential function, and let us integrate all those potentials over the solid angle about P each potential being multiplied by $\cos Q'Q$, then according to a wellknown theorem on spherical harmonics the integral is a zonal harmonic of form $\cos\varphi\, f(r)$, where $f(r) = \int \cos\varphi \,.\, \tan^{-1}\{\cos\varphi \tan r\}\, d\omega$, ($d\omega$ representing the element of the solid angle about P), whilst this integral field has as only divergency a magnetic scale in B with intensity proportional to $\cos\varphi$.

Effecting the integration we obtain:

$$f(r) = 2\pi \int_0^\pi \sin\varphi \cos\varphi \tan^{-1}\{\cos\varphi \tan r\}\, d\varphi.$$

$$f(r) = 2\pi \left\{ -\cot r + \frac{r}{\sin^2 r} \right\},$$

and for the corresponding potential function (γ) we find:

$$2\pi \cos\varphi \left\{ -\cot r + \frac{r}{\sin^2 r} \right\}.$$

III. If we take the difference of the field (β) multiplied by $\frac{1}{2}$ and the field (γ) multiplied by $\frac{1}{2\pi^2}$ the magnetic scale in B disappears and we have left the field (δ):

$$\frac{\cos\varphi}{\pi} \left\{ \frac{\frac{\pi}{2} - r}{\sin^2 r} + \cot r \right\},$$

which field has as only divergency two double points in P_1 and P_2 of which in the opposite points equal poles correspond.

The sum of this field (δ) and the field (α) multiplied by $\frac{1}{2}$ must now give a field having as divergency a single double point with unity-moment in P_1, i. o. w. the field E_1.

We therefore find on the half hypersphere between P_1 and B:

$$\frac{1}{\pi} \cos\varphi \left\{ \frac{\pi - r}{\sin^2 r} + \cot r \right\}$$

and on the half hypersphere between P_2 and B:

$$\frac{1}{\pi} \cos\varphi \left\{ \frac{-r}{\sin^2 r} + \cot r \right\},$$

or if we define on both halves the coordinates r and φ according to P_1 and $P_1\,Q_1$ we obtain the following expression holding for both halves:

$$\frac{1}{\pi} \cos\varphi \left\{ \frac{\pi - r}{\sin^2 r} + \cot r \right\} \equiv \psi(r) \cos\varphi.$$

IV. To break up this field into two fictitious "fields of a single agens point" (having however divergency along the whole hypersphere) we take for the latter $\int_r^\pi \psi(r)\, dr \equiv F_1(r)$.

Then for an arbitrary gradient distribution holds:

$${}^1_0X = \overline{\nabla}^{1} \int \frac{\overline{\nabla}^{2}\, {}^1_0X}{4\pi} F_1(r)\, d\tau \dots, \dots \qquad (I)$$

V. The field E_1 of a circular current according to the equator plane in the origin, is identical outside the origin to the above field E_1; but now each force line is closed, and has a line integral of 4π along itself.

According to the method of A § IX we find of this field E_2 the planivector potential H in the meridian plane and independent of the azimuth.

We find when writing $\pi - r = \beta$:

$$\Sigma = \frac{1}{\pi} \sin^2\varphi\, (1 + \beta \cot r)\, d\vartheta.$$

So

$$H = \frac{1}{\pi} \sin\varphi \frac{1 + \beta \cot r}{\sin r},$$

vanishing along all principal circles in the opposite point.

From which we deduce for the force of an element of current with unity-intensity in the origin directed according to the axis of the spherical system of coordinates:

$$\frac{1}{\pi} \sin\varphi \frac{1 + \beta \cot r}{\sin r},$$

directed normally to the meridianplane.

VI. From this we deduce as in A § XI a vector potential V of an element of current parallel to that element of current and a function of r only. For the scalar value U of that vector potential we have the differential equation:

$$-\frac{\partial}{\partial r}\left\{ U \sin\varphi \sin r\, d\varphi \right\} dr - \frac{\partial}{\partial \varphi}\left\{ U \cos\varphi\, dr \right\} d\varphi =$$

$$= \frac{1}{\pi} \sin\varphi \frac{1 + \beta \cot r}{\sin r} \,.\, dr \,.\, \sin r\, d\varphi.$$

Or:

$$U - \frac{\partial}{\partial r}\left\{ U \sin r \right\} = \frac{1}{\pi}(1 + \beta \cot r),$$

of which the solution is

$$U = \frac{c}{\cos^2 \frac{1}{2} r} + \frac{1}{\pi}\left\{ \frac{\frac{1}{4}\beta^2}{\cos^2 \frac{1}{2} r} - \frac{\beta}{\sin r} \right\}.$$

We choose $c = 0$, and we find as vector potential V of a unity-element of current:

$$\frac{1}{\pi}\left\{\frac{\frac{1}{4}\beta^2}{\cos^2\frac{1}{2}r} - \frac{\beta}{\sin r}\right\} = F_2(r),$$

directed parallel to the element of current. The function $F_2(r)$ vanishes in the opposite point.

For an arbitrary flux now holds:

$$\overset{1}{_2}X = \overline{\overset{2}{\nabla}} \int \frac{\overline{\overset{1}{\nabla}}\; \overset{1}{_2}X}{4\pi} F_2(r)\, d\tau. \quad \ldots\ldots \quad (II)$$

And finally the arbitrary vector field X is the ∇ of the potential:

$$\int \frac{\overline{\overset{2}{\nabla}} X}{4\pi} F_1(r)\, d\tau + \int \frac{\overline{\overset{1}{\nabla}} X}{4\pi} F_2(r)\, d\tau.$$

F. *The spherical Sp_n.*

I. To find the field E_1 we set to work in an analogous way as for the spherical Sp_3. The principal sphere B becomes here a $^{n-1}$sphere B; the principal circle C of the points H a principal $^{n-2}$sphere C of the points H.

For the potential (α) is found:

$$\pm \frac{\cos\varphi}{\sin^{n-1} r};$$

for the potential (β):

$$\frac{\cos\varphi}{\sin^{n-1} r};$$

this field (β) has in the sphere B a magnetic $^{n-1}$scale.

The potential (γ) is integrated out of fields $\tan^{-1}\{\cos\varphi \tan r\}$ according to $\cos\varphi$, the first zonal $^{n-1}$spherical harmonic on B. This integration furnishes when dw represents the element of the n-dimensional solid angle about P:

$$\cos\varphi\, f(r),$$

where:

$$f(r) = \int \cos\varphi \tan^{-1}\left\{\cos\varphi \tan r\right\} dw = k_{n-1}\int_0^{\pi} \sin^{n-2}\varphi \cos\varphi \tan^{-1}\left\{\cos\varphi \tan r\right\} d\varphi =$$

$$= \frac{k_{n-1}}{n-1}\int_0^{\pi} \sin^n\varphi \frac{\tan r\, d\varphi}{1 + \tan^2 r \cos^2\varphi}$$

(k_n defined as under C § III).

Putting under the sign of the integral a factor $\sin^2\varphi \tan^2 r$ outside the brackets and, by regarding that factor as $\frac{1}{\cos^2 r} - (1+\cos^2\varphi \tan^2 r)$, writing the integral as sum of two integrals to the former of which the same division in two is applied, etc., we find, if we write

$$\int_0^\pi \sin^h r \, dr = S_h :$$

$$\frac{(n-1)f(r)}{k_{n-1}} \sin^{n-1} r = -\sin^{n-2} r \cos r \, S_{n-2} - \sin^{n-4} r \cos r \, S_{n-4} \ldots\ldots - \sin^2 r \cos r \, S_2 + \pi (1 - \cos r)$$

(for n even)

$$= -\sin^{n-2} r \cos r \, S_{n-2} - \sin^{n-4} r \cos r \, S_{n-4} \ldots\ldots - \sin r \cos r \, S_1 + 2\, r$$

(for n odd)

$$= \pi \, . \frac{(n-1)(n-3)\ldots\ldots}{(n-2)(n-4)\ldots\ldots} \int_0^r \sin^{n-1} r \, dr = (n-1)\, S_{n-2} \int_0^r \sin^{n-1} r \, dr,$$

(for n even)

$$= 2 \, . \frac{(n-1)(n-3)\ldots\ldots}{(n-2)(n-4)\ldots\ldots} \int_0^r \sin^{n-1} r \, dr = (n-1)\, S_{n-2} \int_0^r \sin^{n-1} r \, dr.$$

(for n odd)

If we write ξ_n for $2 \, . \, \pi \, . \, 2 \, . \, \pi \, . \, 2 \ldots.$, to n factors, we have

$$k_n = \frac{\xi_n}{(n-2)(n-4)\ldots\ldots}, \quad \text{and} \quad \frac{k_{n+1}}{k_n} = S_{n-1}.$$

Therefore :

$$f(r) \sin^{n-1} r = k_n \int_0^r \sin^{n-1} r \, dr ,$$

and the potential (γ) becomes :

$$k_n \frac{\cos\varphi}{\sin^{n-1} r} \int_0^r \sin^{n-1} r \, dr.$$

II. We find the field (δ) by taking difference of field (β) multiplied by $\frac{1}{2}$ and field (γ) by $\frac{1}{k_n S_{n-1}} = \frac{1}{k_{n+1}}$, i. e.

$$\frac{\cos\varphi}{\sin^{n-1}r}\cdot\frac{\frac{1}{2}S_{n-1}-\int_0^r \sin^{n-1}r\,dr}{S_{n-1}}=\frac{\cos\varphi}{\sin^{n-1}r}\cdot\frac{\int_r^{\frac{1}{2}\pi}\sin^{n-1}r\,dr}{S_{n-1}}.$$

This field has as only divergency two double points, in P_1 and P_2, of which equal poles correspond in the opposite points. The field E_1 is then obtained by adding to it the field (a) multiplied by $\frac{1}{2}$. We find on the half ^{n}sphere between P_1 and B:

$$\frac{1}{S_{n-1}}\cdot\frac{\cos\varphi}{\sin^{n-1}r}\int_r^{\pi}\sin^{n-1}r\,dr.$$

On the half ^{n}sphere between P_2 and B:

$$-\frac{1}{S_{n-1}}\cdot\frac{\cos\varphi}{\sin^{n-1}r}\int_0^{r}\sin^{n-1}r\,dr.$$

Or, if we define on both halves the coordinates r and φ according to P_1 and P_1Q_1, we arrive at the expression holding for both halves:

$$\frac{1}{S_{n-1}}\cdot\frac{\cos\varphi}{\sin^{n-1}r}\cdot\int_r^{\pi}\sin^{n-1}r\,dr=\psi_n(r\,.)\cos\varphi.$$

III. For the potential of the fictitious "field of a single agens point" we find:

$$\int_r^{\pi}\psi_n(r)\,dr=F_1(r).$$

And for the arbitrary gradient distribution holds:

$$ {}^1_0X=\overline{\nabla^{1}}\int\frac{\overline{\nabla^{2}}\,{}^1_0X}{k_n}F_1(r)\,d\tau \quad . \quad . \quad . \quad . \qquad . \quad . \quad (I)$$

Of the divergency distribution of $F_1(r)$ in points of a general position we know that, taken for two completely arbitrary centra (fictitious agens points) with opposite sign and then summed up, it furnishes 0: so on one side that distribution is independent of the position of the centre and on the other side it lies geometrically equivalent with respect to all points; so it is a constant. But if the function $F_1(r)$ has constant divergency in points of general position it satisfies a differential equation putting the divergency constant. In this is therefore a second means to determine the function F_1 and out of this the field E_1.

The differential equation becomes:

$$\frac{d}{dr}\left\{\sin^{n-1} r \, . \, \frac{dF_1}{dr}\right\} = c \sin^{n-1} r \, . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

$$\sin^{n-1} r \, . \, \frac{dF_1}{dr} = c \int \sin^{n-1} r \, dr.$$

$$\frac{dF_1}{dr} = c \, . \, \frac{\int \sin^{n-1} r \, dr}{\sin^{n-1} r}.$$

If the field E_1 is to be composed out of the function $F_1(r)$ then the opposite point of the centre may not have a finite outgoing vector current; we therefore put $\int \sin^{n-1} r \, dr = 0$, so that we get

$$\frac{dF_1}{dr} = - \frac{c}{\sin^{n-1} r} \int_r^\pi \sin^{n-1} r \, dr,$$

which corresponds to the above result.

IV. The field E_2 of a small vortex ${}^{n-2}$sphere according to Sp_{n-1}, perpendicular to the axis of the just considered double point, is identical to that field E_1 outside the origin; but now each force line is closed and has a line integral k_n along itself.

According to the method of C § VII we shall find of this field E_2 the planivector potential H, lying in the meridian plane and dependent only on r and φ ;so that it is a ${}^{2}_{1}X$. We find :

$$dh = c\varepsilon \sin^{n-2} r \sin^{n-2} \varphi.$$

Force in r-direction :

$$(n-1) \cos \varphi \left\{ \frac{1}{(n-1) S_{n-1}} + \frac{\cot r}{S_{n-1}} \, . \, \frac{\int_r^\pi \sin^{n-1} r \, dr}{\sin^{n-1} r} \right\} \equiv (n-1) \cos \varphi \, . \, \omega_n (r.)$$

$$\Sigma = \int_0^\varphi (n-1) \cos \varphi \, \omega_n (r) \, . \, c\varepsilon \sin^{n-2} r \sin^{n-2} \varphi \, . \, \sin r \, d\varphi =$$

$$= \omega_n r \, . \, c\varepsilon \sin^{n-1} r \sin^{n-1} \varphi.$$

$$H = \frac{\Sigma}{dh} = \omega_n (r) \sin r \sin \varphi \equiv \chi_n (r) \sin \varphi.$$

From this ensues for the force of a plane vortex element with unity-intensity in the origin :

$$\chi_n (r) \sin \varphi,$$

directed parallel to the acting vortex element and projecting itself on that plane according to the tangent to a concentric circle; whilst φ is the angle of the radiusvector with the Sp_{n-2} perpendicular to the vortex element.

V. In the same way as in C § IX we deduce from this the planivector potential V of a vortex element directed everywhere parallel to the vortex element and of which the scalar value is a function of r only. That scalar value U of that vector potential is here determined by the differential equation:

$$-\frac{\partial}{\partial\varphi}\left\{U\cos\varphi\,.\,dr\,.\,c\varepsilon\sin^{n-3}r\cos^{n-3}\varphi\right\}d\varphi\,-$$

$$-\frac{\partial}{\partial r}\left\{U\sin\varphi\,.\,\sin r\,d\varphi\,.\,c\varepsilon\sin^{n-3}r\cos^{n-3}\varphi\right\}dr=$$

$$=\chi_n(r)\sin\varphi\,.\,\sin r\,d\varphi\,.\,dr\,.\,c\varepsilon\sin^{n-3}r\cos^{n-3}\varphi.$$

$$(n-2)\,U-\frac{dU}{dr}\sin r-(n-2)\,U\cos r=\chi_n(r)\sin r.$$

$$\frac{dU}{dr}-(n-2)\,U\,tg\,\tfrac{1}{2}r=-\chi_n(r).$$

$$U=\frac{1}{\cos^{2(n-2)}\frac{1}{2}r}\,.\int_r^{\pi}\cos^{2(n-2)}\tfrac{1}{2}r\,.\,\chi_n(r)\,dr,$$

a function vanishing in the opposite point, which we put $\equiv F_2(r)$. We then find for an arbitrary flux:

$$\tfrac{1}{2}X=\overline{\nabla}^{2}\int\frac{\overline{\nabla}^{1}\,\tfrac{1}{2}X}{k_n}F_2(r)\,d\tau\quad.\;.\;.\;.\;.\;.\quad(II)$$

And taking an arbitrary vector field to be caused by its two derivatives (the magnets and the vortex systems) propagating themselves through space as a potential according to a function of the distance vanishing in the opposite point, we find:

$$X=\nabla\left\{\int\frac{\overline{\nabla}^{2}X}{k_n}F_1(r)\,d\tau+\int\frac{\overline{\nabla}^{1}X}{k_n}F_2(r)\,d\tau\right\}.$$

G. *The Elliptic Sp_n.*

Also for the elliptic Sp_n the derivative of an arbitrary linevector distribution is an integral of elementary vortex systems Vo_y and Vo_z, which are respectively the first and the second derivative of an isolated line vector. For elementary $\overset{1}{_0X}$ we shall thus have to put the field of a divergency double point.

The Schering elementary potential $\int_r^{1/2\pi} \frac{dr}{\sin^{n-1} r} \equiv v_n(r)$ is here a plurivalent function (comp. KLEIN, Vorlesungen über Nicht-Euklidische Geometrie II, p. 208, 209); it must thus be regarded as senseless.

II. The unilateral elliptic Sp_n is enclosed by a plane Sp_{n-1}, regarded twice with opposite normal direction, as a bilateral singly connected Sp_n-segment by a bilateral closed Sp_{n-1}. If we apply to the Sp_n enclosed in this way the theorem of GREEN for a scalar function φ having nowhere divergency, and for one having in two arbitrary points P_1 and P_2 equal and opposite divergencies and fartheron nowhere (such a function will prove to exist in the following), we shall find:

$$\varphi_{P_2} - \varphi_{P_1} = 0,$$

i. o. w. φ is a constant, the points P_1 and P_2 being arbitrarily chosen.

So no $\overset{1}{_0X}$ is possible having nowhere divergency, so no ^1X having nowhere rotation and nowhere divergency; and from this ensues:

A linevector distribution in an elliptical Sp_n is uniformly determined by its rotation and its divergency.

III. So we consider:

1. the field E_1, with as second derivative two equal and opposite scalar values quite close together.

2. the field E_2 with as first derivative planivectors regularly distributed in the points of a small $^{n-2}$sphere and perpendicular to that small $^{n-2}$sphere.

At finite distance from their origin the fields E_1 and E_2 are of identical structure.

IV. To find the potential of the field E_1 we shall represent it uni-bivalently on the spherical Sp_n; the representation will have as divergency two doublepoints in opposite points, where equal poles correspond as opposite points; it will thus be the field (d), deduced under F § II, multiplied by 2:

$$\frac{\cos \varphi}{\sin^{n-1} r} \cdot \frac{\int_r^{1/2\pi} \sin^{n-1} r \, dr}{\frac{1}{2} S_{n-1}} = \lambda_n (r) \cos \varphi .$$

In the field corresponding to this in the elliptic space, all force lines move from the positive to the negative pole of the double point; a part cuts the pole Sp_{n-1} of the origin: these force lines are unilateral in the meridian plane; the remaining do not cut it; these are bilateral in the meridian plane.

The two boundary force lines forming together a double point in the pole Sp_{n-1}, have the equation:

$$\sin^{n-1} \varphi \left\{ \sin^{n-1} r + (n-1) \cot r \int_r^{1/2\pi} \sin^{n-1} r \, dr \right\} = \pm 1 .$$

The Sp_{n-1} of zero potential consists of the pole Sp_{n-1} and the equator Sp_{n-1} of the double point; its line of intersection with the meridian plane has a double point in the force lines doublepoint. All potential curves in the meridian plane are bilateral.

V. For the fictitious "field of a single agens point" the potential is $\int \lambda_n (r) \, dr$. It is rational to let it become 0 in the pole Sp_{n-1}; so we find:

$$\int_r^{1/2\pi} \lambda_n (r) \, dr = F_1 (r),$$

and for the arbitrary gradient distribution holds:

$$ {}^1_0X = \overline{\nabla}^1 \int \frac{\overline{\nabla}^2 \, {}^1_0X}{k_n} F_1 (r) \, d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

We could also have found $F_1 (r)$ out of the differential equation (H) of F § III, which it must satisfy on the same grounds as have been asserted there. For the elliptic Sp_n also we find:

$$\frac{dF_1}{dr} = c \, . \, \frac{\int \sin^{n-1} r \, dr}{\sin^{n-1} r} .$$

But here in the pole Sp_{n-1}, lying symmetrically with respect to the centre of the field, the force, thus $\int \sin^{n-1} r \, dr$ must be 0; so that we find:

$$\frac{dF_1}{dr} = - \frac{c}{\sin^{n-1} r} \int_r^{\frac{1}{2}\pi} \sin^{n-1} r \, dr.$$

VI. In the usual way we deduce the ${}_1^2X$, which is planivector potential of the field E_2.

$$dh = c\varepsilon \sin^{n-2} r \sin^{n-2} \varphi.$$

Force in r-direction:

$$(n-1) \cos \varphi \left\{ \frac{2}{(n-1) S_{n-1}} + \frac{2 \cot r}{S_{n-1}} \cdot \frac{\int_r^{\frac{1}{2}\pi} \sin^{n-1} r \, dr}{\sin^{n-1} r} \right\} \equiv (n-1) \cos \varphi \cdot \mu_n (r).$$

$$\Sigma = \int_0^{\varphi} (n-1) \cos \varphi \cdot \mu_n (r) \cdot c\varepsilon \sin^{n-2} r \sin^{n-2} \varphi \cdot \sin r \, d\varphi =$$

$$= \mu_n (r) \cdot c\varepsilon \sin^{n-1} r \sin^{n-1} \varphi.$$

$$H = \frac{\Sigma}{dh} = \mu_n (r) \sin r \sin \varphi \equiv \varkappa_n (r) \sin \varphi.$$

From which ensues for the force of a plane vortex element with unity-intensity in the origin:

$$\varkappa_n (r) \sin \varphi,$$

directed parallel to the acting vortex element and projecting itself on its plane according to the tangent to a concentric circle; φ is here the angle of the radiusvector with the Sp_{n-2} perpendicular to the vortex element.

VII. Here too a planivector potential of a vortex element can be deduced, but we cannot speak of a direction propagated parallel to itself, that direction not being uniformly determined in elliptic space; after a circuit along a straight line it is transferred into the symmetrical position with respect to the normal plane on the straight line.

But we can obtain a vector potential determined uniformly, by taking that of two antipodic vortex elements in the spherical Sp_n (in their ^{2}sphere the two indicatrices are then oppositely directed).

The vector potential in a point of the elliptic Sp_n then lies in the space through that point and the vortex element; if we regard the plane of the element as equator plane in that space then the planivector potential V is normal to the meridian plane: it consists of:

1. a component U_1 normal to the radiusvector, according to the formula:

$$\frac{U_1}{\cos \varphi} = \frac{1}{\cos^{2(n-2)} \frac{1}{2} r} \int_{r}^{\pi} \cos^{2(n-2)} \tfrac{1}{2} r \, \chi_n(r) \, dr +$$

$$+ \frac{1}{\sin^{2(n-2)} \frac{1}{2} r} \int_{\pi - r}^{\pi} \cos^{2(n-2)} \tfrac{1}{2} r \, . \, \chi_n(r) \, dr.$$

2. a component U_2 through the radiusvector, according to the formula:

$$\frac{U_2}{\sin \varphi} = \frac{1}{\cos^{2(n-2)} \frac{1}{2} r} \int_{r}^{\pi} \cos^{2(n-2)} \tfrac{1}{2} r \, \chi_n(r) \, dr -$$

$$- \frac{1}{\sin^{2(n-2)} \frac{1}{2} r} \int_{\pi - r}^{\pi} \cos^{2(n-2)} \tfrac{1}{2} r \, . \, \chi_n(r) \, dr .$$

If we regard this planivector potential as function of the vortex element and the coordinates with respect to the vortex element and represent that function by G_2, then

$$\tfrac{1}{2}X = \overline{\nabla^{2}} \int \frac{G_2 \left\{ \overline{\nabla^{1}} \, \tfrac{1}{2}X, r, \varphi \right\}}{k_n} \, d\tau. \quad . \quad . \quad . \quad . \quad (II)$$

holds for an arbitrary flux in the elliptic Sp_n.

And regarding an arbitrary vector field as caused by the two derivatives (the magnets and the vortex systems) propagating themselves through the space to a potential, we write:

$$X = \nabla \int \frac{\overline{\nabla^{2}} \, X \, . \, F_1(r) + G_2 \left(\overline{\nabla^{1}} \, X, r, \varphi \right)}{k_n} \, d\tau.$$

VIII. In particular for the elliptic Sp_3 the results are:

Potential of an agens double point:

$$\frac{\cos \varphi}{\sin^2 r} \cdot \frac{\int_{r}^{\frac{1}{2}\pi} \sin^2 r \, dr}{\frac{1}{2} S_2} = \frac{2 \cos \varphi}{\pi} \cdot \left\{ \frac{\left(\frac{1}{2}\pi - r\right)}{\sin^2 r} + \cot r \right\},$$

or if we put $\frac{1}{2}\pi - r = \gamma$:

$$\frac{2 \cos \varphi}{\pi} \cdot \left\{ \frac{\gamma}{\sin^2 r} + \cot r \right\}.$$

Equation of the boundary lines of force:

$$\sin^2\varphi\,(1+\gamma\cot r)=\pm 1.$$

Potential of a single agens point:

$$\frac{2}{\pi}\,.\,\gamma\,.\,\cot r.$$

Vector potential of an elementary circular current:

$$\frac{2}{\pi}\sin\varphi\,.\,\frac{1+\gamma\cot r}{\sin r}.$$

So also force of an element of current:

$$\frac{2}{\pi}\sin\varphi\,.\,\frac{1+\gamma\cot r}{\sin r}.$$

Linevector potential of an element of current:

according to the radiusvector: $\dfrac{\cos\varphi}{\pi}\left\{\dfrac{\frac{1}{4}\beta^2}{\cos^2\frac{1}{2}r}-\dfrac{\pi}{\sin r}+\dfrac{\frac{1}{4}r^2}{\sin^2\frac{1}{2}r}\right\}.$

normal to the radiusvector: $\dfrac{\sin\varphi}{\pi}\left\{\dfrac{\frac{1}{4}\beta^2}{\cos^2\frac{1}{2}r}+\dfrac{2r-\pi}{\sin r}-\dfrac{\frac{1}{4}r^2}{\sin^2\frac{1}{2}r}\right\}.$

IX. For the elliptic plane we find:

Potential of an agens double point:

$$\cos\varphi\cot r.$$

Equation of the boundary lines of force:

$$\sin\varphi=\pm\sin r,\quad\text{or}\quad\varphi=\left\{\begin{matrix}r\\ \pi-r\end{matrix}\right..$$

Potential of a single agens point:

$$-\,l\sin r.$$

Scalar value of the planivector potential of a double point of rotation:

$$\frac{\sin\varphi}{\sin r}.$$

Thus also force of a rotation element:

$$\frac{\sin\varphi}{\sin r}.$$

Planivector potential of a rotation element:

$$l\cot\tfrac{1}{2}r.$$

We notice that the duality of both potentials and both derivatives existing for the spherical Sp_2, has disappeared again in these results. The reason of this is that for the representation on the sphere a divergency in the elliptic plane becomes two equal divergencies in opposite points with equal signs; a rotation two equal rotations in opposite points with different signs; for the latter we do not find the analogous potential as for the former; the latter can be found here according to the Schering potential formula.

With this is connected immediately that in the elliptic plane the field of a single rotation (in contrast to that of a single divergency) has as such possibility of existence, so it can be regarded as unity of field. That field consists of forces touching concentric circles and great $\frac{1}{\sin r}$.

Postscript. In the formula for vector fields in hyperbolic spaces:

$$Pot.\ X = \int \frac{\overset{2}{\nabla} X}{k_n} F_1(r)\, d\tau + \int \frac{\overset{1}{\nabla} X}{k_n} F_2(r)\, d\tau$$

nothing for the moment results from the deduction but that to $\overset{2}{\nabla} X$ and $\overset{1}{\nabla} X$ also must be counted the contributions furnished by infinity. From the field property ensues, however, immediately that the effect of these contributions disappears in finite, so that under the integral sign we have but to read $\overset{2}{\nabla} X$ and $\overset{1}{\nabla} X$ in finite.

For the $\overset{1}{\nabla}$ at infinity pro surface-unity of the infinitely great sphere is $<$ order e^{-r}; the potential-effect of this in finite becomes $<$ order $re^{-(n-2)r} \times e^{-r} = re^{-(n-1)r}$; so the force-effect $<$ order $e^{-(n-1)r}$; so the force-effect of the entire infinitely great spherical surface is infinitesimal.

And the $\overset{2}{\nabla}$ at infinity pro surface-unity is $<$ order $\frac{1}{r}$; it furnishes a potential-effect in finite $<$ order $e^{-(n-1)r} . \frac{1}{r}$, thus a force-effect $<$ order $e^{-(n-1)r} . \frac{1}{r^2}$; so the force-effect, caused by the infinite, remains $<$ order $\frac{1}{r^2}$.

The reasoning does not hold for the force field of the hyperbolical Sp_2 in the second interpretation (see under B § VIII), but it is in the nature of that interpretation itself that the derivatives at infinity are indicated as such, therefore also counted.

Meteorology. — *"On Magnetic Disturbances as recorded at Batavia."*

By Dr. W. van Bemmelen.

(Communicated in the meeting of September 29, 1906).

Some months ago Mr. Maunder of the Greenwich-Observatory addressed a request to the Batavia Observatory to provide him with a list of magnetic storms recorded at Batavia with a view of testing his results as to the influence of the synodic rotation of the sun to the occurrence of disturbances.

Mr. Maunder concludes from an inspection of the disturbances recorded at Greenwich (and also at Toronto) that they show a tendency to recur after a synodic rotation of the sun and that sometimes even two and more returns occur. His conclusion is:

"Our magnetic disturbances have their origin in the sun. The solar "action which gives rise to them does not act equally in all directions, "but along narrow, well defined streams, not necessarily truly radial. "These streams arise from active areas of limited extent. These active "areas are not only the source of our magnetic disturbances, but "are also the seats of the formation of sun-spots."

As soon as I could find the necessary leisure I prepared a list for the period 1880—1899, containing 1149 disturbances and immediately after made some statistical calculations based on them.

A discussion of such statistical results is always better made by the author of the list, than by another person for whom it is impossible to consult the original sheets.

Though intending to publish the list, statistics and some reproductions in full, I wish to give a preliminary account of my results, because these questions are now of actual importance.

Rules followed in preparing the list.

An exact definition of what is understood by the expression "magnetic storm" has never been given; certain features however are characteristic to it, viz:

1. The sudden commencement.
2. The postturbation.
3. The increased agitation.

Concerning the second, which I called the postturbation [1]), the well known fact may be remarked, that during a storm the *mean* level of the components of the force changes, till a maximum digression is reached, and afterwards returns slowly to its old value.

In 1895 I called attention to this phenomenon and investigated its distribution over the earth.

This research enabled me to give the following description of the postturbation.

During a magnetic storm a force appears contrary to the earth's ordinary magnetic force, with this difference, that its horizontal component is directed along the meridians of the regular part of the earth's magnetism, consequently not pointing to the magnetic pole, but to the mean magnetic axis of the earth.

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[1]) Cf. Meteorologische Zeitschrift 1895, p. 321. Terrestrisch Magnetisme I p. 95, II 115, V 123, VIII 153.

In accordance with this description, during the earlier part of a storm the horizontal force diminishes, the vertical force increases, and during the latter part these forces resume slowly their original values. The characteristic features sub 1 and 2 either do not necessarily attend every storm, or if so, they do not show themselves clearly enough to enable us to decide definitely whether a succession of waves in a curve must be considered as a storm or not.

On the contrary the increased agitation is an essential feature and has therefore been adopted by me as a criterion.

Unfortunately it is impossible to establish the lowest level above which the never absent agitation may be called a storm, because the agitation is not only determined by the amplitude of the waves, but also by their steepness and frequency.

To eliminate as much as possible the bad consequences which necessarily attend a personal judgment, the list has been prepared:

1. by one person;
2. in as short a time as possible;
3. from the aspect of the curves for one component only (in casu the horizontal intensity, which in Batavia is most liable to disturbance);
4. for a period with nearly constant scale-value of the curves (1 mm. = ± 0,00005 C.G.S.);

For each storm has been noted:

1. the hour of commencement;
2. ,, ,, ,, expiration;
3. ,, ,, ,, maximum;
4. the intensity.

Mr. MAUNDER calls a storm with a sudden start an S-storm; analogously I will call one with a gradual beginning a G-storm. In the case of a sudden impulse the time of beginning is given to the tenth of an hour; in that of gradual increase of agitation only by entire hours.

The hour of beginning of a G-storm is not easy to fix. I have chosen for it the time of the very beginning of the increased agitation, and not the moment in which the agitation begins to show an unmistakable disturbance character.

Afterwards it became clear I had shown a decided preference for the even hours, which may be accounted for by the fact that only the even hours are marked on the diagrams.

To eliminate this discordance I have added the numbers of G-storms commencing at the odd hours for one half to the preceding and for the other half to the following hour.

Because a storm as a rule expires gradually, it is often impossible to give the exact moment it is past. If doubtful I have always taken the longest time for its duration; hence many days following a great storm are reckoned as being disturbed, which otherwise would have passed as undisturbed.

For the time of the maximum I have taken the moment of maximum agitation, which does not always correspond with the hour of maximum postturbation.

I believe the hour at which the mean H-force reaches its lowest level is a better time-measure for the storm-maximum, but to determine it a large amount of measuring and calculating is required, the change in level being often entirely hidden by the ordinary solar-diurnal variation.

The intensity of the storm has been given after a scale of four degrees: 1 = small; 2 = moderate; 3 = active; 4 = very active.

It is not possible to give a definition of this scale of intensity in words, the reproduction of typical cases would be required for this.

Hourly distribution of the beginning of storms.

It is a known fact, that the starting impulse is felt simultaneously all over the earth. The Greenwich and Batavia lists furnished me with 53 cases of corresponding impulses, which, if the simultaneity is perfect, must enable us to derive the difference in longitude of the two observatories.

I find in 6 cases 7^h12^m
„ 19 „ $7\ \ 0$
„ 28 „ $7\ \ 6$
Mean $7^h\ 7^m15^s$

True difference $7^h7^m19^s$.

It it very remarkable indeed to derive so large a difference of longitude with an error of 4 seconds only, from 53 cases measured roughly to 0.1 hour.

The simultaneity should involve an equal hourly distribution if every *S*-impulse were felt over the whole earth. As this is not the case, which is proved by the lists of Greenwich and Batavia, it is easy to understand that the Batavia-impulses show indeed an unequal hourly distribution. We find them more frequent at 6^h and 10^h a. m. and 7^h p. m.

Hourly distribution of *S*-impulses.

Hour	Number in %	Hour	Number in %
0 a. m.	4.1	noon 12	4.7
1	2.5	13	5.0
2	3.0	14	3.3
3	2.2	15	3.9
4	4.1	16	4.4
5	3.9	17	3.6
6	6.3	18	4.1
7	4.5	19	5.5
8	5.1	20	3.6
9	5.8	21	3.9
10	6.1	22	3.6
11	5.0	23	3.3

This same distribution we find again in the case of the *G*-storms, but much more pronounced; a principal maximum at about 8ʰ a. m., and a secondary one at 6ʰ p. m.

Accordingly the hour of commencement of the *G*-disturbances is dependent upon the position of the station with respect to the sun, and it seems, that the hours most appropriate for the development of a *G*-disturbance also favour the development of an *S*-impulse.

Hourly distribution of the commencement of G-storms (in %).

Hour	0	2	4	6	8	10	noon 12	14	16	18	20	22
Intensity: 1	6.0	6.0	5.1	6.7	18.7	17.9	7.4	4.7	6.0	8.0	6.5	7.1
» 2	4.5	4.9	4.2	5.7	20.8	16.4	7.3	5.6	5.4	9.2	8.4	7.6
» 3 and 4	7.1	3.5	4.3	7.5	18.5	13.4	3.9	5.5	5.1	9.1	11.8	10.2
All	5.4	5.1	4.6	6.3	19.7	16.5	6.8	5.2	5.6	8.7	8.3	7.8

Hourly distribrution of the maximum (in °/₀).

	Hour	0	2	4	6	8	10	noon 12	14	16	18	20	22
S-storms.	Intensity 1	11.5	6.7	5.5	1.8	4.7	12.8	12.6	5.3	6.1	6.1	10.9	16.2
	» 2	16.9	9.1	5.9	1.2	1.4	7.3	7.6	3.9	7.6	10.8	13.5	15.2
	» 3 and 4	11.2	4.0	2.4	1.6	0.8	4.0	7.2	6.8	12.0	13.6	17.2	19.2
	All	14.1	7.4	4.9	1.5	2.4	8.6	9.2	4.8	7.8	9.7	13.3	16.3
G- storms.	Intensity 1	12.3	16.7	10.9	5.8	4.3	13.8	5.8	2.9	2.9	5.1	10.1	9.4
	» 2	11.3	7.7	3.6	5.6	3.3	8.5	11.3	8.5	6.1	5.2	14.1	14.9
	» 3 and 4	12.2	9.3	5.8	3.2	3.5	7.7	9.0	6.4	8.0	7.7	10.3	17.0
	All	11.9	10.2	6.0	4.6	3.6	9.2	9.2	6.5	6.3	6.3	11.6	14.8

These hourly numbers show for each intensity, and for both kinds of storms the same, strongly marked distribution over the hours of the day.

Thus the development of agitation during a storm is dependent on the position of the sun relatively to the station in a manner which is the same for S- and G-storms.

The period has a principal maximum at 10^h p. m. and a secondary one at noon; and being compared to the diurnal periodicity of the commencement of G-storms, it is evident, that: *On the hours when the chance for a maximum-agitation begins to increase, we may expect most storms to take a start.*

Hence we may come to the following supposition.

The susceptibility of the earth's magnetic field to magnetic agitation is liable to a diurnal and semidiurnal periodicity. Whatever may be the origin of the increase of agitation, sudden or gradual, this periodicity remains the same.

This was the same thing, that was revealed to me by the inspection of the hundreds of curves in preparing the list.

The agitation rises at about 8^h a. m. after some hours of great calm and reaches a maximum at about noon. A second period of calm, less quiet however than in the early morning, is reached in the afternoon, and a second rise follows till a maximum is attained shortly before midnight.

The day-waves however are smaller and shorter, the night-waves larger and longer and also more regular in shape. These regular night-waves are often restricted to one large wave, very suitable for the study of these waves.

Hourly distribution of the end of the storm.

Hour	Number of cases	Hour	Number of cases
0 a. m.	163	12	$\underline{\underline{66}}$
2	172	14	60
4	$\underline{\underline{\underline{204}}}$	16	$\underline{43}$
6	140	18	50
8	60	20	46
10	$\underline{36}$	22	49

Quite in agreement with the above mentioned conclusions, the curve representing the diurnal periodicity of the final-hour is nearly the reverse of that for the maximum.

Evidently the hour 0 (the end of the day) has been strongly favoured.

Resuming we may according to the Batavia disturbance-record draw the following conclusions:

1st. *the origin of* S-*storms is cosmical*;

2nd. *the origin of* G-*storms may be also cosmical, but the commencement is dependent on the local hour;*

3rd. *the development of all storms, concerning the agitation, is in the same way dependent on the local hour.*

Storms and sunspots.

In the following table the year has been reckoned from April 1s till April 1st of the following year, with the exception of 1882, the diagrams for the months Dec. '82, Jan.—March '83 missing. For 1880—'83 the yearly numbers have been increased in proportion to the number of missing record days.

Numbers in °/₀.

Year	Sunspot number	Intensity							
		1		2		3 and 4		All	
		S	G	S	G	S	G	S	G
1880/81	37.5	2.7	4.2	1.5	6.6	1.2	2.3	1.6	5.1
81/82	56.9	1.4	6.7	0.0	5.9	1.2	2.3	0.8	5.6
82	70.8	1.4	2.8	5.3	6.6	13.0	6.1	7.9	5.2
83/84	68.8	6.8	7.8	7.5	5.4	6.9	5.3	7.1	6.2
84/85	59.5	2.7	4.6	9.8	6.4	9.3	6.1	8.2	5.7
85/86	45.7	4.1	1.4	9.8	4.1	10.6	6.9	9.0	3.6
86/87	19.6	0.0	1.1	2.3	5.9	1.9	7.6	1.6	4.5
87/88	11.6	2.7	7.8	3.0	4.3	3.7	4.6	3.3	5.6
88/89	6.4	5.4	5.7	4.5	4.1	2.5	3.1	3.8	4.5
89/90	5.9	10.8	4.9	5.3	3.3	1.2	4.6	4.6	4.1
90/91	13.0	13.5	8.1	2.3	3.8	0.6	3.1	3.8	5.2
91/92	47.4	6.8	4.6	5.3	5.1	6.9	8.4	4.7	5.5
92/93	74.5	9.5	6.4	8.3	3.3	12.4	4.6	10.3	4.6
93/94	85.2	9.5	6.0	9.0	3.8	11.8	5.3	10.3	4.8
94/95	74.2	5.4	4.6	8.3	7.7	3.7	6.9	5.7	6.5
95/96	57.4	6.8	5.3	5.3	6.9	5.0	8.4	5.4	6.6
96/97	38.7	4.1	4.2	5.3	5.4	2.5	3.1	3.8	4.6
97/98	26.5	4.1	5.3	3.0	5.4	3.7	7.6	3.5	5.7
98/99	22.9	2.7	8.5	4.5	5.9	1.9	3.8	3.0	6.5

From these numbers it appears that those for the G-storms show no correspondence with the sunspot-numbers, also that those for the S-storms show a correspondence which is emphasised according as the intensity increases, and finally that the S-storms show a maximum when the G-storms have a minimum and the reverse.

This latter fact is apparently caused by the circumstance of the storms hiding each other, the G-storms being eclipsed by the S-storms in a higher degree during greater activity of the sun, than the S-storms by the G-storms. Indeed a simple inspection of the diagrams shows that the agitation of G-storms is greater during a sunspot maximum, than in minimum-years. Also in maximum-years the S-storms of intensity 1, are hidden by their stronger brothers to such an extent, that the eleven-yearly periodicity is nearly the reverse for them.

Annual distribution of S- and G-storms.
(Only the uninterrupted period April 1, 1883—April 1, 1899 has been considered).

Month	Numbers	
	S.	G.
January	$\underline{\underline{31}}$	54
February	$\underline{\underline{31}}$	53
March	29	60
April	$\underline{24}$	57
May	$\underline{24}$	61
June	27	51
July	31	61
August	29	47
September	$\underline{\underline{32}}$	55
October	31	64
November	22	58
December	$\underline{18}$	58

A strong difference in behaviour between G- and S-storms can be noticed. The G-storms have no annual periodicity as to their frequency, whereas the S-storms show a strong one.

This points, just like the daily periodicity of commencement, either to a different origin, or to a changing tendency of the development of the S-impulse during the day and year.

Comparison with Greenwich-storms.

Maunder derives from the reproduction of storms published in the volumes of the Greenwich Observations a maximum at 6^h p. m. and from the original recording-sheets on the contrary at 1^h p. m. The cause of this discrepancy he finds in the manner he looked for the commencement. He writes: "the times when the phases of diurnal disturbance are most strongly marked are naturally most often taken as the times of commencement."

At Greenwich these phases of agitation are most prominent at 1^h p. m. and 6^h p. m.

As I assumed for the hour of beginning the first increase of agitation it is clear my times of beginning are on an average much earlier.

Thus the difference shown by the hourly distribution of commencement between the Greenwich- and the Batavia-list, may be ascribed chiefly to difference of interpretation.

As appears from the figures given above, compared with those for Greenwich the annual periodicity is quite the same for both the northerly and the equatorial stations, which differ no less than 60 degrees in latitude. But the Greenwich dates, quoted from a complete magnetic calendar, prepared by Mr. Ellis and extending from 1848 to 1902 give no separation of G- and S-storms. Thus it is not possible to decide whether at Greenwich the G-storms lack an annual periodicity in their frequency.

The impulse at the start.

The material at present at my disposal for investigating the features of this phenomenon in other places on earth, is very small.

Notwithstanding this I may conclude: *that this phenomenon is of great constancy in features all over the earth, and consequently a phenomenon of great interest, which might teach us much about the manner the S-storms reach the earth.*

Description of its features for some places.

Greenwich. According to the reduced reproductions of disturbance-curves published in the volumes of the Greenwich-Observations, the impulse consists of a sudden movement in H, D and Z, instantly followed by the reversed movement, the latter being considerably greater. The direction of the movement is always the same.

I have measured 34 cases and have found on an average:

$H \Delta D$	ΔH	ΔZ	
25γ W	$+77\gamma$	$+39\gamma$	$(1\gamma = 0.00001$ C.G.S.).

Batavia. The preceding impulse is missing for H and Z, only for D it is often present.

Here also the direction of the movement is constant.

35 cases for the years 1891 and '92 gave on an average for the

magnitude of digression	$H\Delta D = 9\gamma W$;	$\Delta H = +45\gamma$;	$\Delta Z = -16\gamma$.
duration ,, ,,	3.5 min.;	5 min.;	12 min.

Though the movement of H and D are not sudden in absolute sense, that for Z is too gradual to justify the application of the word sudden to it.

The reproductions of disturbance-curves for Potsdam and Zi Ka Wei also show some cases of the preceding impulse. At both stations the direction of the movement is remarkably constant. In the publications of the Cape Hoorn observations (1882/83) I found three cases exposing also a constant direction.

Summarizing them, we have:

Station	H	D	Z
Potsdam	+	W	—
Greenwich	+	W	+
Zi Ka Wei	+	E	—
Batavia	+	W	—
Cape Hoorn	+	W	—

Consequently with one exception for D and one for Z we find that: *the commencing impulse of the S-storms is the reverse of the vector of postturbation, being deflected however to the West of it.*

Suppositions concerning the origin of disturbance.

The hypothesis on the existence of defined conical streams of electric energy, which strike the earth, though not quite new, has obtained increased plausibility by MAUNDER's results. From the statistics based on the record of disturbances at Batavia it might be concluded that it is chiefly the S-storms that find their origin in the sudden encounter of the earth with such a stream.

And as the earth is first struck at its sunset-arc, it is not impossible that the G-storms, which begin by preference shortly after sunrise and have no annual periodicity in their frequency as the S-storms have, are only partly caused by these encounters.

When in the case of the streams we admit that energy progresses from the sun in the form of negative electrons, we might think the G-storms find their origin by electrified particles being propagated by the light-pressure according to the theory set forth by Sv. ARRHENIUS.

Further we may suppose, that when the earth has received a charge the following development of the storm is the same as it is dependent on the local hour only. ARRHENIUS has already given an explanation of the nocturnal maximum.

In recent times it has often been attempted to explain magnetic fluctuations by the movement of electric charge through the higher layers of the atmosphere. (SCHUSTER, VAN BEZOLD, SCHMIDT, BIGELOW).

The remarkable analogies which are met with in many cases between the streamfield of atmospherical circulations and the fields of magnetic fluctuations, lead to such speculations.

I believe it is allowed to hazard analogous speculations concerning the cause of the beginning of impulse and postturbation.

We may suppose the streams to contain negative electrons. When they strike the earth the outer layers will be charged with negative electricity. These outer layers do not rotate in 24 hours, but in a longer time increasing with their height.

So a countercurrent of E—W direction charged with negative electrons will originate, causing an increase of H and a decrease of Z. The electrons, however, on entering the magnetic field of the earth, will follow the lines of force towards the magnetic south pole (the positive pole). The movement of negative electrons along the lines of force has been fairly well proved, as is well known, by the aurorarays.

By this movement, the current of electricity will become NE—SW and a westerly deflecting S-impulse will be the consequence.

The sudden charge of the extreme layers of the atmosphere with negative electricity, will attract the positive ions, with which the high layers may be supposed to be charged, to still higher layers.

These positive ions will thus enter into a faster moving counter current, and a positive charged counter current will be the consequence.

These ions will move along the lines of force towards the north, but much slower than the negative electrons, and therefore the resulting deflection of the magnetic force caused by such a + current viz. a force contrary to the ordinary one, will be of no appreciable magnitude. It is conceivable that the effect, which accordingly is in the same sense as the postturbation, will develop in a more gradual manner than the commencing impulse of the S-storms; moreover we may understand that it disappears still more gradually in proportion as the negative electrons again leave the earth or are neutralised by positive ions.

Only we should expect the current to follow the latitude-parallels and accordingly the vectors of postturbation to point to the true south and not to the southerly end of the earth's mean magnetic axis.

Perhaps we may find an explanation for this fact in the influence no doubt exerted by the earth's mean magnetic field and the distribution of positive ions in the atmosphere.

These speculations are indeed very rough, but they have one great advantage, viz. to avoid the difficulty, raised by Lord KELVIN, of allowing an expenditure of the sun's energy causing magnetic disturbances, much too great to be admitted.

CHREE (Terr. Magnet. X, p. 9) points to the fact, that also MAUNDER's defined streams require far too great an expenditure of energy.

According to my opinion we have only to deal with the charge received at the moment of the impulse, and by accepting an intermittent emission of the sun's energy, it is not necessary to integrate it over the entire time between one or more returns of the stream.

Part of the energy is also supplied by the rotation-energy of the earth; and it is curious to remark, that by such an influence the rotation of the earth would be lengthened for a minute fraction during a magnetic storm.

Chemistry. — "*Nitration of meta-substituted phenols*". By Dr. J. J. BLANKSMA. (Communicated by Prof. HOLLEMAN).

(Communicated in the meeting of September 30, 1906).

Some years ago[1]) I pointed out that by nitration of meta-nitrophenol and of 3-5-dinitrophenol tetra- and pentanitrophenol are formed. This showed that the NO_2-groups in the m-position do not prevent the further substitution of the H-atoms in the o- and p-position by other groups. I have now endeavoured to increase these two cases by a few more and have therefore examined the behaviour of some m-substituted phenols which contain, besides a NO_2-group in the m-position, a second group in the m-position, namely of

$$C_6H_3 . OH . NO_2 . (CH_3, OH, OCH_3, OC_2H_5, Cl, Br)\ 1 . 3 . 5.$$

Of these phenols the 5-nitro-m-cresol[2]) and the monomethylether of 5-nitroresorcinol[3]) were known. The still unknown phenols were made as follows:

The 5-nitroresorcinol (m.p. 158°) from its above cited monomethylether by heating for five hours at 160° with (30°/₀) HCl, or by reduction of 3-5-dinitrophenol with ammonium sulphide to 5-nitro-

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[1]) These Proc. Febr. 22, 1902. Rec. **21**. 241.

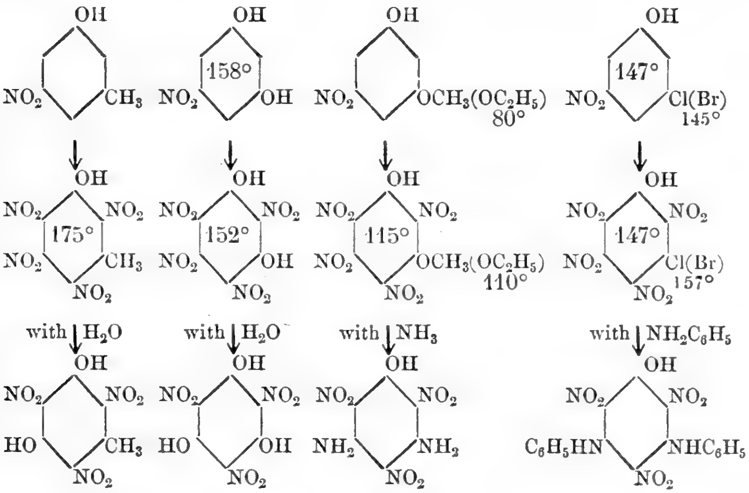
[2]) NEVILE en WINTHER Ber. **15**. 2986.

[3]) H. VERMEULEN Rec. **25**. 26.

3-aminophenol (m.p. 165°) and substitution of the NH_2-group in this substance by OH.

The monoethylether of 5-nitroresorcinol (m.p. 80°) was prepared (quite analogous to the methylether) from 5-nitro-3-aminophenetol; the 3-Cl (Br) 5-nitrophenol was obtained by substituting the NH_2-group in the 5-nitro-3-aminoanisol by Cl (Br) according to SANDMEYER and then heating the 3-Cl (Br)-5-nitroanisol so obtained m.p. (101°[1]) and 88°); with HCl as directed. We then obtain, in addition to CH_3Cl, the desired product 3-Cl (Br) 5-nitrophenol (m.p. 147° and 145°).

The 3-5-substituted phenols so obtained readily assimilate three atoms of bromine on treatment with bromine water and three nitro-groups are introduced on nitration with HNO_3 (Sp. gr. 1.52) and H_2SO_4. These last compounds, which all contain four NO_2-groups resemble picric acid, tetra- and pentanitrophenol. From a mixture of nitric and sulphuric acids they crystallise as colourless crystals which are turned yellow by a small quantity of water; the compounds have a bitter taste, an acid reaction and communicate a strong yellow colour to organic tissues (the skin), others strongly attach the skin and all are possessed of explosive properties owing to the presence of four NO_2-groups[2]).



In this scheme are given only the melting points of the as yet unknown compounds.

Tetranitro-m. cresol yields on boiling with water trinitroorcinol;

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[1]) 91° according to DE KOCK Rec. 20, 113.

[2]) A comparative research as to these properties in the different compounds has not yet been instituted.

in the same manner, tetranitroresorcinol [1]) yields trinitrophloroglucinol; tetranitrochloro- and bromophenol also yield trinitrophloroglucinol on boiling with water or, more readily, with Na_2CO_3 solution. By the action of NH_3 or $NH_2C_6H_5$ etc. in alcoholic solution various other products are obtained, such as those substances included in the scheme which have been obtained previously from pentanitrophenol [2]). We also see that water or alcohol cannot serve as a solvent for the purpose of recrystallising these compounds but that chloroform or carbon tetrachloride may be used.

If, in the above cited 3-5-substituted phenols the OH-group is substituted by OCH_3 it is not possible to introduce three nitro-groups. For instance the dimethylether of 5-nitroresorcinol yields two isomeric trinitroresorcinoldimethylethers (principally those with the melting point 195°, just as in the nitration of 5-nitro-m-xylene) [3]); similarly, the methylether of 5-nitro-m-cresol (m.p. 70°) yields the methylethers of three isomeric trinitro-m-cresols, principally the compound with m.p. 139°. The constitution of these substances is not yet determined.

Amsterdam, September 1906.

Chemistry. — Prof. Holleman presents a communication from himself and Dr. H. A. Sirks: "*The six isomeric dinitrobenzoic acids.*"

(Communicated in the meeting of September 29, 1906).

Complete sets of isomeric benzene derivatives $C_6H_4A_2B$ have been studied but little up to the present; yet, for a closer understanding of those derivatives, it must be deemed of great importance to subject the six possible isomers of which such sets consist, to a comparative investigation. A contribution hereto is the investigation of the six isomeric dinitrobenzoic acids which Dr. Sirks has executed under my directions.

The considerations which guided me in the choice of this series

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[1]) According to Henriques (Ann. Chem. **215**, 335), tetranitroresorcinol (m.p. 166°) is formed by the nitration of 2-5-dinitrophenol. In Beilstein's manual (vol. II, 926) a reasonable doubt is thrown on the correctness of this observation. The substance obtained has probably been an impure trinitroresorcinol formed by the action of water on the primary formed tetranitrophenol. (Rec. **21**, 258).

[2]) Rec. **21**, 264.

[3]) Rec. **25**, 165.

of isomers were the following. Firstly, all six isomers were known, although the mode of preparation of some of them left much to be desired. Secondly, this series gave an opportunity to test V. MEYER'S "ester rule" with a much more extensive material than hitherto and to study what influence is exercised by the presence of two groups present in the different positions in the core, on the esterification velocity, and to compare this with that velocity in the monosubstituted benzoic acids. Thirdly, the dissociation constants of these acids could be subjected to a comparative research and their values connected with those of the esterification constants. Finally, the melting points and sp. gr. of the acids and their esters could be investigated in their relation to these same constants in other such series.

The six dinitrobenzoic acids were prepared as follows. The symmetric acid 1, 3, 5, (1 always indicates the position of the carboxyl group) was obtained by nitration of benzoic acid or of *m*-nitrobenzoic acid. All the others were prepared by oxidation of the corresponding dinitrotoluenes. This oxidation was carried out partly by permanganate in sulphuric acid solution, partly by prolonged boiling with nitric acid (sp. gr. 1.4) in a reflux apparatus.

We had to prepare ourselves three of the dinitrotoluenes, namely, (1,3,4), (1,3,6) and (1,3,2), (CH_3 on 1); (1.2,4) and (1,2,6) are commercial articles whilst (1,3,5) was not wanted because the orresponding acid, as already stated, was readily accessible by direct nitration of benzoic acid. As will be seen the three dinitrotoluenes which had to be prepared are all derivatives of *m*-nitrotoluene and it was, therefore, tried which of those might be obtained by a further nitration of the same.

m-Nitrotoluene, which may now be obtained from DE HAEN in a pure condition and at a reasonable price was, therefore, treated with a mixture of nitric and sulphuric acids at 50°. On cooling the nitration-product a considerable amount of 1,3,4 dinitrotoluene crystallised out, which could be still further increased by fractionated distillation in vacuo of the liquid portion ; the highest fractions always became solid and again yielded this dinitrotoluene, so that finally about 65 grms. of dinitrotoluene (1,3,4) were obtained from 100 grms. of *m*-nitrotoluene,

As the fractions with a lower boiling point, although almost free from dinitrotoluene (1,3,4), did not solidify on cooling, it was thought probable that they might contain, besides a little of the above dinitrotoluene, more than one of the other isomers, whose formation in the nitration of *m*-nitrotoluene is theoretically possible. If we consider that, in the many cases which I have investigated, the presence of 1 % of an isomer causes about 0.5° depression in the melting point, the fact that the oil did not solidify till considerably below 0° and again melted at a slight elevation of temperature whilst the pure isomers did not liquefy till 60° or above, cannot be explained by the presence of relatively small quantities of 1,3,4-dinitrotoluene in presence of *one* other constituent, but it must be supposed to consist of a ternary system. This was verified when the fractionation was continued still further; soon, the fractions with the lowest boiling points began to solidify on cooling, or slowly even at the ordinary temperature, and the solidified substance proved to be 1,2,3 — dinitrotoluene. The fractionation combined with the freezing of the different fractions then caused the isolation of a third isomer namely 1,3,6 — dinitrotoluene, so that the three isomeric dinitrotoluenes desired had thus all been obtained by the nitration of *m*-nitrotoluene. The fourth possible isomer (1,3,5) could not be observed even after continued fractionation and freezing.

As regards the relative quantities in which the three isomers, detected in the nitration product, are formed, it may be mentioned that this product consists of more than one half of 1, 3, 4-dinitrotoluene, whilst (1, 2, 3) seems to occur in larger quantities than (1, 3, 6), as the isolation of the latter in sufficient quantity gave the most trouble.

The *corrected solidifying points* of the dinitrotoluenes (the sixth, symmetric one was prepared by BEILSTEIN's method A. **158**, 341 in order to complete the series) were determined as follows. Those of the dinitrobenzoic acids and of their ethyl esters are also included in the subjoined table.

	3.4	3.5	2.3	2.5	2.6	2.4
Dinitrotoluenes	58.3	92.6	59.3	50.2	65.2	70.1
Dinitrobenzoic acids	163.3	206.8	204.1	179.0	206.4	180.9
Ethyl esters	71.0	92.9	88.4	68.8	74.7	40.2

The *specific gravities* of the dinitrotoluenes and the ethyl esters were determined by means of EYKMAN's picnometer at 111°.0 with the following result:

CO_2H or CH_3 on 1	toluenes	esters
3.4	1.2594	1.2791
3.5	1.2772	1.2935
2.3	1.2625	1.2825
2.5	1.2820	1.2859
2.4	1.2860	1.2858
2.6	1.2833	1.2923

Water at 4° as unity. Corrected for upward atmospheric pressure and for expansion of glass.

Conductivity power. This was determined in the usual manner with a Wheatstone-bridge and telephone at 25° and at 40°. As the acids are soluble in water with difficulty $v = 100$ or 200 was taken as initial concentration; the end concentration was $v = 800$ or 1600. In the subjoined table the dissociation constants are shown.

Dinitrobenzoic acids		3.4	3.5	2.3	2.5	2.4	2.6
K = 100 k	at 25°	0.163	0.163	1.44	2.64	3.85	8.15
	at 40°	0.171	0.177	1.38	2.16	3.20	7.57

On comparing these figures it is at once evident that the acids with ortho-placed nitro-group possess a much greater dissociation constant than the other two, so that in this respect, they may be divided into two groups. In the acids without an ortho-placed nitro-group, the value of the dissociation constant is fairly well the same. In the other four, the position of the second group seems to cause fairly large differences. That second group increases the said constant most when it is also placed ortho: in $N/_{100}$ solution 2-6-dinitrobenzoic acid is ionised already to the extent of 90 $^0/_0$. Again, a NO_2-group in the para-position increases the dissociation constant more than one in the meta-position; and for the two acids 2,3 and 2,5 which both have the second group in the meta-position, K is considerably larger for 2,5, therefore for the non-vicinal acid than for the vicinal one, so that here an influence is exercised, not only by the position of the groups in itself, but also by their position in regard to each other. It also follows that OSTWALD's method for the calculation of the dissociation constants of disubstituted acids from those of the monosubstituted acids cannot be correct as is apparent from the subjoined table:

Dinitrobenzoic acid CO_2H on 1	K calculated	K found
3.4	0.23	0.16
3.5	0.20	0.16
2.4	4.1	3.8
2.5	3.6	2.6
2.3	3.6	1.4
2.6	64	8.1

In the two vicinal acids 2,3 and 2,6 the deviations from the calculated value are particularly large, as I have previously shown for other vicinal substituted acids (Rec. **20**, 363).

In view of the comparison of the figures for the dissociation constants of these acids and for their esterification constants, it seemed desirable to have also an opinion as to the molecular conductivity of these acids in alcoholic solution. They were, therefore dissolved in 95 vol. $^0/_0$ alcohol to a $N./_{200}$ solution and the conductivity power of those liquids was determined at 25°. The subjoined table shows the values found and also those of the aqueous solutions of the same concentration and temperature:

dinitrobenzoic acids	3.4	3.5	2.3	2.5	2.6	2.4
μ_{200} in alcoh. sol.	1.1	1.15	1.75	2.25	2.7	2.9
μ_{200} in aqueous sol.	161.5	162.5	293	321	355.5	335.5

from which it appears that also in alcoholic solution the acids with an ortho-placed nitro-group are more ionised than the others.

Esterification velocity. The method followed was that of GOLDSCHMIDT, who dissolved the acid in a large excess of alcohol and used hydrochloric acid as catalyzer. The alcoholic hydrochloric acid used here was 0,455 normal. Kept at the ordinary temperature it did not change its titre perceptibly for many months. As **Goldschmidt** showed that the constants are proportionate to the concentration of the catalyzer, they were all recalculated to a concentration of normal hydrochloric acid. Owing to the large excess of alcohol the equation for unimolecular reaction could be applied. The velocity measurements were executed at 25°, 40° and 50°. At these last two temperatures, the titre of the alcoholic acid very slowly receded (formation of ethylchloride) and a correction had, therefore, to be applied. The strength of the alcohol used was 98.2 °/₀ by volume.

In order to be able to compare not only the esterification-constants E of the dinitrobenzoic acids with each other but also with those of benzoic acid and its mononitroderivatives, the constants for those acids were determined at 25° under exactly the same circumstances as in the case of the dinitroacids. The results obtained are shown in the subjoined table:

Acids		E at 25°	E at 40°	E at 50°
	benzoic acid	0.0132	—	—
m. NO_2	»	0.0071	—	—
o. »	»	0.0010	—	—
3.4 dinitro	»	0.0086	0.033	0.077
3.5 »	»	0.0053	0.028	0.060
2.3 »	»	0.0005	0.0025	0.0071
2.5 »	»	0.0003	0.0027	0.0076
2.4 »	»	0.0002	0.0017	0.0056
2.6 »	»	unmeasurably small		

As will be seen, E is by far the largest for benzoic acid and each subsequent substitution decreases its value.

On perusing this table it is at once evident that in the dinitrobenzoic acids two groups can be distinguished. Those with an ortho-placed nitro-group have a much *smaller* constant than the other two. *Whilst therefore the dissociation constant for acids with an ortho-placed nitro-group is the largest their esterification constant is the smallest.* As shown from the subjoined table, this phenomenon proceeds quite parallel; the acids whose dissociation constant is greatest have the smallest esterification constant and vice versa.

Dinitrobenzoic acids	diss. const. at 40°	esterif. const at 40°
3.4	0.171	0.033
3.5	0.177	0.028
2.3	1.38	0.0025
2.5	2.16	0.0027
2.4	3.20	0.0017
2.6	7.6	< 0.0001

On perusing the literature we have found that this regularity does not exist in this series of dinitrobenzoic acids only, but is observed in a comparatively large number of cases. The strongest acids are the most slowly esterified. This might lead us to the conclusion that in the esterification by alcoholic hydrochloric acid it is not the ionised but the unsplit molecules of the acids which take part in the reaction.

A more detailed account of this investigation will appear in the Recueil.

Amsterdam } Sept. 1906, Laboratory of the University.
Groningen }

Chemistry. — Prof. Holleman presents a communication from himself and Dr. J. Huisinga. *"On the nitration of phthalic acid and isophthalic acid"*.

(Communicated in the meeting of September 29, 1906).

Of phthalic acid, two isomeric monoderivatives are possible, both of which are known particularly by a research of Miller (A. **208**, 233). Isophthalic acid can yield three isomeric mononitro-acids. Of these, the symmetric acid, which is yielded in the largest quantity during the nitration, is well known. As to the mononitrated by-products formed, the literature contains a difference of opinion; in any case, there is only made mention of one second mononitro-acid whose structure has remained doubtful.

The investigation of the nitration of phthalic and isophthalic acid was taken up by us in order to determine the relative amount of the isomers simultaneously formed, as in the case of the mononitrophthalic acids only a rough approximation (by MILLER) was known, whilst in the case of the mononitroisophthalic acids it had yet to be ascertained which isomers are formed there from.

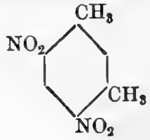
We commenced by preparing the five mononitro-acids derived from phtalic acid and isophthalic acid in a perfectly pure condition. In the case of the α- and β-nitrophthalic acids no difficulties were encountered, as the directions of MILLER, save a few unimportant modifications, could be entirely followed. The acids were therefore obtained by nitration of phthalic acid and separation of the isomers.

The *symmetric nitro-isophthalic acid* was prepared by nitration of isophthalic acid. It crystallises with 1 mol. of H_2O and melts at 255—256° whilst it is stated in the literature that it crystallises with $1^1/_2$ mol. of H_2O and melts at 248°. At first we hoped that the other two nitroisophthalic acids might be obtained from the motherliquors of this acid. It was, therefore, necessary to obtain the isophthalic acid in a perfectly pure condition, as otherwise it would be doubtful whether the byproducts formed were really derived from isophthalic acid. By oxidation of pure *m*-xylene (from KAHLBAUM) an isophthalic acid was obtained which still contained terephthalic acid which could be removed by preparing the barium salts.

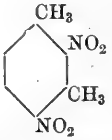
The motherliquors of the symmetric nitro-isophthalic acid appeared, however, to contain such a small quantity of the byproducts that the preparation of the nitro-acids (1, 3, 2) and (1, 3, 4) was out of the question. These were therefore, prepared as follows:

Preparation of asymmetric nitro-isophthalic acid (1, 3, 4). On cautious nitration of *m*-xylene at 0° with nitric acid of sp. gr. 1.48 a mixture is formed of mono- and dinitroxylene which still contains unchanged *m*-xylene. This, on distillation with water vapour, passes over first and when drops of the distillate begin to sink to the bottom of the receiver the latter is changed and the distillation is continued until crystals of dinitroxylene become visible in the condenser. 100 gr. of xylene gave about 85 gr. of mononitroxylol (1, 3, 4).

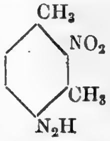
After rectification of this mononitroxylene (b. p. 238°) it was oxidised in alkaline solution with a slight excess of permanganate: 20 gr. yielded 12 à 13 gr. of acid which, however, consisted of a mixture of nitrotoluylic acid and nitro-isophthalic which could be separated by crystallisation from water. In this way, the as. nitro-isophthalic acid was obtained with a melting point of 245°. In water it is much more soluble than the symmetric acid, namely to the extent of about 1 $^0/_0$. at 25°. Unlike the symmetric acid, it crystallises without water of crystallisation in small, fairly thick, plate-like crystals. It is very readily soluble in hot water, alcohol and ether, *Preparation of the vicinal nitro-isophthalic acid* (1, 3, 2). GREVINGK has observed that in the nitration of m-xylene with nitric and sulphuric acid there is formed, besides the symmetric dinitro-m-xylene



as main product, also the vicinal isomer



. On reduction with hydrogen sulphide both dinitroxylenes pass into nitro-xylidenes which are comparatively easy to separate. The nitro-xylidene



yields by elimination of the NH$_2$-group vicinal nitro-m-xylene. Whilst however, GREVINGK states that he obtained a yield of 25$^0/_0$ of vicinal nitroxylidene we have never obtained more than a few per cent of the same so that the preparation of vicinal nitro-m-xylene in this manner is a very tedious one, at least when large quantities are required. When it appeared that the "fabrique de produits chimiques de Thann et Mulhouse" exported this nitroxylene, the oxidation, although to some extent with material of our own manufacture, has been mainly carried out with the commercial product. This oxidation was also done with permanganate in alkaline solution. The vicinal nitro-isophthalic acid is a compound soluble with great difficulty in cold, but fairly soluble in hot water, crystallising in small beautiful, shining needles, which melt at 300°. It crystallises without any water of crystallisation and is readily soluble in alcohol and ether, from which it is again deposited in small needles.

The three possible mononitroisophthalic acids having now been obtained, we could take in hand the problem to ascertain the nature of the byproduct formed in the nitration of isopthalic acid. After the bulk of the nitroisophtalic acid formed had been removed by crystallisation, a residue was left which was far more soluble in water than this acid, which pointed to the presence of the asymmetric nitro-acid and which, indeed, could be separated by fractional crystallisation. We will see presently how it was ascertained that the nitration product was really only a mixture of the symmetric and the asymmetric acid.

As in the determination of the relative quantities in which the nitration products are formed, use was made of solubility determina tions, we first give the solubilities in water at 25° of the five nitrophthalic acids, in parts per 100.

α-nitrophtalic acid
2.048

β-nitrophthalic acid
very soluble

symmetric nitroisophthalic acid
with water of crystallisation.
0.157

Asymmetric nitroisophthalic acid
0.967

Vicinal nitroisophthalic acid
0.216

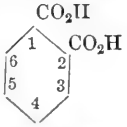
Quantitative nitration of phthalic acid. This was done with absolute nitric acid. It appeared that it proceeded very slowly even at 30°, and therefore the phthalic acid was left in contact with six times the quantity of nitric acid for three weeks. After dilution with water the acid was expelled by heating on a waterbath or else evaporated over burnt lime. The solid residue was then reduced to a fine powder and freed from the last traces of nitric acid by prolonged heating at 110°. As under the said circumstances the mononitrophthalic acids are not nitrated any further, it could be ascertained by titration whether all the phthalic acid had been converted into the mononitro-acid; the product had but a very slight yellow colour so that a contamination could be quite neglected. Of the product, now ready for analysis, different quantities were weighed and each time introduced into 100 c.c. of water, and after adding an excess of α-nitrophthalic acid they were placed in the shaking apparatus. The amount of acid dissolved was determined by titration and from these figures the content in β-acid was calculated by making use of a table which had been constructed previously and in which was indicated which β-nitroacid contents correspond with a definite titre of a solution so obtained. As the mean of four very concordant observations it was found that in the nitration of phthalic acid with absolute nitric acid at 30° is formed:

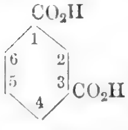
49.5 $^{0}/_{0}$ α- and 50.5 $^{0}/_{0}$ β-nitrophthalic acid.

The quantitative nitration of isophthalic acid was done in the same manner as that of phthalic acid; here also, a few weeks were required for the complete nitration at 30°. The contamination with yellow impurities could again be quite neglected as a but very faintly coloured nitration product was obtained. This nitration product so obtained contains the anhydrous symmetrical nitroisophthalic acid, so that in the solubility determinations by which its composition was determined the hydrated acid had to be employed as the anhydrous acid takes up water but very slowly and has a greater solubility. The determination of the total amount of byproduct showed that this had formed to the extent of 3.1 $^0/_0$ only. The qualitative investigation had shown already that this contains the asymmetric acid, and that it consists of this solely was proved in the following manner. If the 3.1 $^0/_0$ found were indeed simply asymmetric acid, a solution, obtained by shaking 100 grams of water with excess of symmetric and vicinal acid + 1 gram of nitration product (containing 0.031 gram of asymmetric acid), ought to have the same titre as a solution obtained by shaking 100 grams of water with excess of both acids + 0.031 gram of asymmetric acid. If on the other hand the nitration product also contained vicinal acid, therefore less than 0.031 gram of asymmetric acid, the titre ought to have been found less. This however, was not the case, which shows that the asymmetric acid is the sole byproduct. The result, therefore, is that in the nitration of isophthalic acid with absolute nitric acid at 30° there is formed:

96.9 $^0/_0$ of symmetric and 3.1 $^0/_0$ of asymmetric nitroisophtalic acid.

If we compare the above results with that of the nitration of benzoic acid where (at 30°) is formed 22.3 $^0/_0$ ortho-, 76,5 $^0/_0$ meta- and 1.2$^0/_0$ paranitrobenzoic acid the following is noticed.

As in phthalic acid 

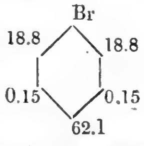
the positions 3 and 6 are meta in regard to the one carboxyl and ortho in regard to the other and the positions 4 and 5 are also meta in regard to the one carboxyl but para in regard to the other it might be expected from my theories that the *α*-acid (the vicinal) is the main product and the *β*-acid the byproduct, because in the latter the nitro-group must be directed by one of the carboxyles towards para and because *p*-nitrobenzoic acid is formed only in very small quantity in the nitration of benzoic acid. As regards the isophthalic acid 

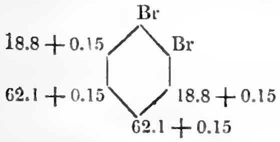
it might be expected that the chief product will be symmetric acid but that there will also be byproducts (1, 3, 2) and (1, 3, 4) the first in the largest quantity, although it should be remembered that a nitro-group seems to meet with great resistance if it must take a position between two other groups.

As regards the nitration of isophthalic acid the result of the above investigation is fairly satisfactory, although the total absence of the vicinal nitroisophthalic acid is somewhat remarkable. In the case of phthalic acid this is true in a less degree as about equal quantities are formed of the two possible isomers.

In his dissertation, Dr. Huisinga has now endeavoured to calculate, more accurately than before, from the relative proportion in which the isomers C_6H_4AC and C_6H_4BC are formed by the introduction of C in C_6H_5A or C_6H_5B, in what proportion the isomers C_6H_3ABC are formed by the introduction of C in C_6H_4AB. He observes first of all that in a substance C_6H_5A there are two ortho and two meta positions against one para position so that if the relation of the isomers is as C_6H_5AC p : q : r (ortho, meta, para) this relation for each of the ortho and meta positions and for the para position will be $^1/_2$ p : $^1/_2$ q : r

He further gives the preference to an addition of these figures of proportion instead of a multiplication, which had been used by me up to the present in the prediction of these isomers. He prefers the addition because he considers the figures of proportion to be proportional to the directing forces which are exercised by the groups A and B on the other positions of the core and that the cooperation of such directing forces on one H-atom should be represented by a sum. But only the proportion of those directing forces are known and not their absolute value; the force which, in the nitration of nitrobenzene, pushes the NO_2-group towards the *m*-position may be of quite a different order than the force which in the nitration of benzoic acid directs the same group towards the m-position. Therefore the figures which represent the directing forces (or are proportionate to the same) of two different groups cannot always be simply added together; this then will be permissible only when the two substituents present are equal.

As an example of his method of calculation the following may be mentioned. As in the nitration of bromobenzene 37.6°/₀ ortho, 62.1°/₀ para and 0.3°/₀ of meta nitrobromobenzene is formed, the substitution in the different positions of the benzene core takes place in the proportion 

; for the proportion in which the isomers are formed in the nitration of o-dibromobenzene the calculation gives 

or 62.25 : 18.95; or 76.7 °/₀ asymmetric nitro-o-dibromobenzene and 23.3 °/₀ vicinal whilst the experiment gave 81.3 °/₀ asymmetric and 18.3 °/₀ vicinal.

It cannot be denied that in a number of cases this method of calculation gives figures which approach to the experimental ones a good deal more than those obtained formerly when the undivided figures were simply multiplied. But on the other hand there are other cases, particularly those in which a metasubstituted substance is nitrated, where this calculation does not agree with the experiment by a long way. If we take into account the figures of proportion for the single positions we obtain as a rule a much better approach to the figures observed by means of the products than with the sums, even in the case where the two substituents present are unequal, when HUISINGA's method of calculation cannot be applied. The proof thereof is laid down in the subjoined table which gives the figures of proportion in which the isomeric nitroderiva tives are formed from the substances at the top of the columns, with the figures obtained from both the sums and the products.

	Cl:Cl ortho	Cl:Cl meta	Br:Br ortho	Br:Br meta	Co$_2$ H:CO$_2$ H ortho	CO$_2$ H:CO$_2$ H meta
found	7:93	4:96	18.3:81.7	4.6:95.4	49.5:50.5	3.1:96.9
product	18:82	9:91	23.3:76.7	13:87	82 :18	*10.6:89 4
sum.	18:82	15:85	23.3:76.7	19:81	55.6:44.4	*38 :62

*totalquantity byproduct.

	CO$_2$ H : Cl ortho	CO$_2$ H : Cl meta	CO$_2$ H : Br ortho	CO$_2$ H : Br meta
found	16.0:84.0	8.7:91.3	19.7:80.3	11.4:88.6
product	17.7:82.3	17.7:82.3	23.3:76.7	23.3:76.7

A fuller account of this investigation will appear in the Recueil.

Amsterdam, org. lab. Univ. 1906.

Astronomy. — *"The relation between the spectra and the colours of the stars."* By Dr. A. PANNEKOEK. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of September 29, 1906).

The close relation between a star's colour and its spectrum has long been known. The stars of the 1st, 2d and 3d types are usually called the white, the yellow and the red stars, although accurately spoken the colour of the so-called yellow stars is a very whitish unsaturated yellow colour and that of the so-called red stars is deep yellow mixed with very little red. In a paper read at Dusseldorf [1]) in

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[1]) Die Farben der Gestirne. Mittheilungen der V. A. P. Jahrg. 10. S. 117.

1900 we showed that in the different glowing conditions the colours must succeed each other in this order. If for a given high temperature we accept the colour to be white, we find that with decrease of temperature the colours in the triangular diagram of colours make a curve which from white first goes directly to yellow of λ 587 but which, as the colour becomes deeper, bends towards the red and corresponds to light of greater wavelength. With increase of temperature, on the contrary, the line of colour runs from white to the opposite side, to the blue of λ 466.

Because the colours which are produced by white light after having been subjected to different degrees of atmospheric absorption, also follow about this same line, we may expect that the colours of the self-luminous celestial bodies will in general lie on this line or near it; they are determined on this line by one coordinate, one number. This renders it comprehensible why on the one hand the designation by means of letters and words, or the measurement with ZÖLLNER's colorimeter, which produces quite different colours, has given so few satisfactory results, and on the other hand why the scale of SCHMIDT, who designates the colours by one series of figures, where 0 is white, 4 yellow, and 10 red has proved to be the best to work with. After this method has been drawn up the best and most complete list of stellar colours, published in 1900 by H. OSTHOFF at Cologne, in the A. N. Bd. 153 (Nr. 3657—58). This list in which the colours of all stars to the 5th magnitude are given, down to a tenth class of colour, and which was the fruit of systematic estimates during 14 years, enables us to accurately determine the relation between spectrum and colour.

In a former paper [1]) we remarked that we did not know where in the continuous series of spectra of the Oriontype and the first type we have to look for the highest temperature or at any rate the greatest luminosity. We may assume that it will be there where the colour is whitest; the spectral-photometric measurements, to which we have alluded in that paper, are still wanting, but for this purpose we can also avail ourselves advantageously of estimates of colour; this has been the reason for the investigation of which the results follow here.

In this case where we required a specification of the spectra, as detailed as possible, to serve as an argument for the colour, we have naturally used again MAURY's classes. In order, however, to determine a mean colour for each class we must correct the colours

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[1]) The luminosity of stars of different types of spectrum. Proceedings of June 30 1906 p. 134.

observed for two modifying influences, viz. the influence of the brightness and that of the altitude above the horizon. Quantitatively nothing is known about the values of these influences; experiments of Osthoff himself to determine the influence of the brightness have as yet yielded few results. Therefore we must derive them here from the material of stellar colours themselves, which serve for our investigation; this may be done in the very probable assumption that the real colour within each spectral class is an almost constant value and is independent of brightness.

§ 2. The stars of Osthoff's list which occur in the spectral catalogue of Maury, were arranged according to their classes and then (excluding those which are marked *c*, *ac*, *C*, *P* or *L*, as was always done in this investigation) always taking together some classes, we classified them according to their brightness and combined their magnitudes and classes to mean values. These mean values must show the influence of the brightness on the colour; they are given in the following tables:

Classe III— VI

Mg.	Col.
1.78	1.46 (5)
2.80	2.27 (6)
3.35	1.96 (5)
3.70	2.86 (7)
4.00	2.47 (8)
4.15	2.91 (7)
4.50	2.60 (9)
4.95	2.42 (11)

Classe VII—VIII

Mg.	Col.
0.1	1.2 (3)
2.4	1.83 (6)
3.17	2.59 (7)
3.55	2.57 (6)
3.82	2.95 (6)
4.00	2.86 (5)
4.10	2.60 (7)
4.20	2.50 (5)
4.36	2.96 (5)
4.62	2.72 (4)
4.96	2.66 (5)

Classe IX—XII

Mg.	Col.
1.0	2.7 (2)
2.69	2.97 (9)
3.18	3.06 (8)
3.65	3.73 (10)
3.85	3.40 (8)
4.10	3.69 (9)
4.29	4.17 (7)
4.65	3.79 (8)
5.10	3.34 (9)

Classe XIII—XIV

Mg.	Col.
0.2	3.4 (1)
3.07	4.71 (7)
3.54	4.61 (7)
3.98	4.72 (9)
4.24	4.88 (8)
4.84	4.88 (8)

Classe XV

Mg.	Col.
0.7	4.5 (2)
2.12	5.50 (6)
2.92	5.66 (9)
3.37	5.74 (9)
3.55	5.46 (9)
3.75	5.71 (8)
3.90	5.55 (10)
4.00	5.70 (7)
4.14	5.85 (11)
4.45	6.08 (6)
4.87	6.43 (7)

Classe XVI—XVIII

Mg.	Col.
0.95	6.45 (2)
2.50	6.40 (6)
3.22	6.65 (6)
3.72	6.65 (4)
4.15	6.75 (6)
4.63	7.07 (7)
4.88	7.22 (9)
5.28	7.22 (8)

In all these series we clearly see an increasing deepening of colour with decreasing brightness. We have tried to represent the colour as a linear function of the magnitude; and by a graphical method we found:

Cl. III—VI $c = 2.15 + 0.35\ (m - 3)$
„ VII—VIII $2.27 + 0.36$ „
„ IX—XII $3.17 + 0.39$ „
„ XIII—XIV $4.45 + 0.42$ „
„ XV $5.47 + 0.39$ „
„ XVI—XVIII $6.60 + 0.20$ „

Thus we find about the same coefficient in all groups except in the last. The value of the coefficients is chiefly determined by the difference between the observed colours of the very bright stars of the 1st magnitude and of the greater number of those of the 3d and 4th magnitudes. In order to make the coefficient of the last group agree with the others, it is necessary to assume for the apparent colour of α Tauri and α Orionis 5.6 instead of the real estimates 6,4 and 6,5. It does not do, however, to assume such a large error for these bright and often observed stars; therefore we must for the present accept the discordant coefficient of the red stars as real, although it is difficult at the present to account for it.

If now we combine the results of the five first groups by arranging the deviation of each observed value of c from the constant for the group (the value of c for $m = 3$), according to brightness and deriving thence mean values we find:

m	$c - c_3$	C_1	C_2	$O - C_1$	$O - C_2$
0.3	—1.03	—1.10	—0.91	+.07	—.12
1.6	—0.63	—0.54	—0.47	— 09	— 16
2.91	+0.02	+0.04	0.02	— 02	+ 04
3.73	+0.32	+0.31	+0.27	+ 01	+ 05
4.12	+0.48	+0.40	+0.39	+ 08	+ 09
4.73	+0.50	+0.52	+0.60	— 02	— 10

A linear relation $c = c_3 + 0{,}34\ (m - 3)$ yields the computed values given under C_2 and the differences obs.-comp. $O - C_2$. These are distributed systematically and show the existence of a non-linear relation. A curve, which represents as well as possible the mean values, gives the computed values C_1 and the differences, obs.-comp. $O - C_1$. For a greater brightness the curve gives a greater variation of the colour with the luminosity and for fainter stars a smaller one. In all the six groups, except the fifth and the sixth, we remark that the last values, which hold for the faintest magnitudes, show a decrease in the colour figures with regard to the preceding ones.

This phenomenon may be accounted for by the existence of the colourless perception of faint sources of light. In faint stars we do not see any colour at all; there the perception of colour disappears almost entirely and there remains only a colourless (i. e. whitish) impression of light. With stars which approach this limit, the impression of colour will be mixed up to a high degree with the colourless impression, and therefore they appear paler and will be indicated by a lower figure. As for the redder stars this colourless impression is relatively much weaker, the paleness of colour for these stars occurs only with a much less degree of brightness; in this manner we explain why the 5th and 6th groups do not show this decrease. Whether in these cases the phenomenon occurs with fainter stars cannot be decided because MAURY's spectral catalogue does not contain fainter stars.

For the practical purpose of reducing the observed colours to one brightness it is about the same which of the two relations is adopted, as long as we keep within certain limits of brightness, for instance between the magnitudes 1 and 5. To facilitate the reduction we have made use of the linear formula given above for the 5 first groups (down to class XV included) while for the redder classes 0,20 has been adopted as the coefficient of brightness.

To explain the long known phenomenon that the colour deepens with decreasing brightness as is shown in the tables on p. HELMHOLTZ in his *Physiologische Optik* has given a theory called "Theorie der kürzesten Linien im Farbensystem". In the diagram of colours in space, where each impression of light is represented by a point of which the 3 coordinates represent the quantities of the elemental colours, red, green, blue, the lines of equal colours are not straight radii through the origin, but curved lines which with increasing distance from the origin bend more and more towards the axes and so diverge more and more from one radius which is straight and represents the "Principalfarbe". Hence in the triangle of colours the points of equal colour diverge the more from the principal colour and run in curved lines towards the sides and the vertices as the triangle of colours is removed farther from the origin, and thus represents a greater brightness. HELMHOLTZ gives as principal colour a certain "yellow-white" to which with extremely great intensity all colours seem to approach. Therefore colours which lie on the blue side of this principal colour must become bluer by fading.

This does not agree with what we have found here, in the supposition that Helmholtz's "yellow-white" is also yellow-white in our scale, i. e. is also represented by a positive number in Schmidt's scale. We also find here with the whitest stars that when they become fainter the colour becomes more yellow to just the same degree as with the yellower stars. Now the expression "yellow-white" is vague, but if we consider that what is called white in the scale of Schmidt is whiter, that is to say bluer than the light of Sirius, and that the solar light, the standard for white for ordinary optical considerations, if weakened to the brightness of a star, in the scale of Schmidt would be called 3 à 4 (Capella 3, 4), then the principal colour, if Helmholtz's theory is true, instead of being yellow-white would still lie on the blue side of the Sirius light.

§ 3. After the colours had thus been reduced to the brightness 3,0, they had still to be freed from the influence of the atmosphere, which makes them redder. This cannot be done with the desired accuracy, because neither time nor altitude are given along with the observations. The influence at high and mean altitudes is probably very small, and the observer is sure to have taken care that most of the stars were observed at a proper altitude (for instance between 30° and 60°). Therefore this correction is only practically important for the few southern stars which always remain near the horizon; in these cases it will be possible to represent the variation of colour by a correction depending on the declination. Instead of the declination of the star we have taken the declination of the B. D.-zone which Osthoff has added to his catalogue.

For each spectral class we have determined mean colour-values for all stars north of the equator, and for the stars south of the equator we have formed the deviations from these class-means which then were arranged according to their declination and combined to mean values for groups of stars. We have excluded, however, those classes in which too few northern stars occurred, namely I, II and III.

The means found are:

Zone	Deviation	n.	Curve
0°0	+0.56	5	+0.05
—1 7	+0.35	4	+ 06
—3.3	—0.17	6	+ 09
—5.0	+0.50	5	+ 12
— 6.6	+0.22	4	+ 17
—8.0	—0.05	5	+ 22
—9°0	+0.14	5	+0.26
—10.2	+0.35	4	+ 32
—13.2	+0.33	6	+ 57
—15.0	+1.17	6	+ 79
—18.2	+0.93	6	+1.32

Through these values we have drawn a curve which from the equator towards the southern declinations ascends steeper and steeper and which gives the values of the last column. According to this curve we have applied the following corrections, for

zone	1°	2°–5°	6°–8°	9°–10°	11°	12°	13°	14°	15°	16°	17°	18° South
neg. corr.	0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,1	1,3

We may assume that by these corrections the variation of colour due to atmospheric absorption has at least for the greater part been eliminated.

§ 4. After the two corrections (§ 2 and § 3) had been applied we could determine for all spectral classes the mean values of the colour; they are given in the following table. Class XV was again subdivided into 3 classes according as the spectrum agreed with α Bootis (*A*) or with α Cassiopeiae (*C*) or was not accompanied by any such remark; the result shows indeed that here class *C* is considerably redder than class *A* while the *B*'s lie between the two.

Class	Colour	Number	Class	Colour	Number
I	2.47	6	XII	3.68	17
II	2.36	10	XIII	4.12	13
III	2.30	9	XIV	4.45	12
IV	1.94	14	*XIV*	5.09	9
IV	1.62	10	XVA	5.18	18
V	2.11	9	XVB	5.35	26
VI	2.16	10	XVC	5 55	31
VII	2.27	23	*XV*	6.34	5
VIII	2.37	34	XVI	6.47	17
IX	2.64	20	XVII	6.80	15
X	3.11	14	XVIII	6.74	15
XI	3.40	9	XIX	6.67	6
XI	3.41	4			

The deviations of the separate values from these mean values give, as a measure for the accuracy of the results, for the mean error of a colour-number, $\sqrt{0,20} = 0,45$; the real accuracy will be greater, however, and the mean error smaller because in these values are also included the errors of the adopted corrections for brightness and declination, the errors which may have been made by MAURY while classifying each star in a definite class, and also the real deviations of the single stars from their class-means.

With 9 stars (out of 355) the deviation exceeds a unit of colour; the reduced colours are here:

β Can. maj.	III	1,2	ε Hydrae	XIII	5,2	η Persei	XV*B*	6,8
o_1 Cygni	IX	1,4	μ Persei	XIV	5,5	11 Urs. min.	XV*B*	6,6
δ Delphini	IX	3,8	o_2 Cygni	*XIV*	6,5	5 Orionis	XVII	7,9

In this investigation we have, as it was said before, excluded the *c*- and *ac*-stars, the *L* (bright lines), the *P* (peculiar spectra) and the *C* (composed spectra). It is important to examine the *c* and the *ac*-stars among them more closely in order to see whether they show a distinct difference in colour from the *a*-stars of the same class-number. In the mean 11 *ac*-stars give a deviation of + 0,1 (from + 0,5 to — 0,3), and 12 *c*-stars + 0,7; so these last ones are a little redder than the *a*-stars. Here, however, the great individual deviations are very striking; the extreme values are:

ϱ Cassiop XIII + 2,5; χ_2 Orionis III + 1,8; 4*H* Camelop *VI* + 2,0;
3*H* Camelop *VI* + 1,5; η Leonis VII — 0,3; β Orionis VI — 1,2,

The differences are very great, but no regularity can be detected.

§ 5. The results found solve a problem which in my former paper remained unsolved, namely where in the continuous series of spectral classes shall we have to look for the maximum of radiating power. The colour-numbers show very distinctly a fall in the first classes, a *minimum* between the 4th and the 5th class and then a continual rise. The stars which in order of evolution directly follow on γ Orionis (μ Aurigae, μ Hydrae, *u* Herculis) have the whitest colours; both the earlier and the later stages of evolution are yellower; classes I and II agree in colour best with class VIII. Therefore, in so far as we are entitled to derive the entire radiation from the colour, the maximum of radiating power lies between the 4th and the 5th class.

The mean colour-numbers for each of the groups formed before are:

Cl. I—III	2.35
IV—V	1.87
VI—VIII	2.30
IX—XII	3.20
XIII—XIV	4.58
XV	5.43
XVI—XIX	6.66

Is it possible to derive from these numbers, even though only approximately, values for the radiating power per unit of surface? The two influences mentioned above which determine the colours of the self-luminous celestial bodies may be subjected to a calculation, if we disregard the specific properties of the composing substances and treat them as abstract theoretical cases. In other words we can investigate the radiation of a perfectly black body and in the absorption neglect the selective absorption in lines and bands in order only to examine the general absorption. As a first approximation this may be deemed sufficient.

In this calculation we have made use of the measurements of A. König on the relative quantities of the elemental colours red, green and blue as functions of the wavelength in white sunlight. If for an other source of light we know the relation of the brightness with regard to the former source as a function of the wavelength, we can calculate the quantities of the red, green and blue in this second source of light. If we call the numbers of König $R(\lambda)$, $G(\lambda)$, $B(\lambda)$, which are chosen so that

$$\int R(\lambda)\,d\lambda = 1000 \qquad \int G(\lambda)\,d\lambda = 1000 \qquad \int B(\lambda)\,d\lambda = 1000$$

and if $f(\lambda)$ represents the brightness of another source of light, then

$$\int f(\lambda)\,R(\lambda)\,d\lambda \qquad \int f(\lambda)\,G(\lambda)\,d\lambda \qquad \text{and} \qquad \int f(\lambda)\,B(\lambda)\,d\lambda$$

represent the quantities of R, G, and B occurring in this light. As the impression of brightness of a source of light is almost proportional to the quantity of red, this calculation gives at the same time a measure for the optical brightness.

The radiation of a black body may be represented by:

$$\lambda^{-\alpha}\,e^{-\frac{c}{T\lambda}}\,d\lambda$$

where T is the absolute temperature and α and c constants. For two sources of light of different temperatures the relation of the intensities is:

$$f(\lambda) = e^{-\frac{c}{\lambda}\left(\frac{1}{T}-\frac{1}{T_0}\right)} = e^{\frac{b}{\lambda}} = 10^{\frac{b'}{\lambda}},$$

if $b = c\left(\frac{1}{T_0} - \frac{1}{T}\right)$ and $b' = 0.43\,b$. As unit for λ we adopt 0,001 mm; T_0 is supposed to be given, then b' is a function of the variable temperature T only and may be called the degree of glowing with regard to the glowing of a body at a temperature T_0. If we adopt for b' different values ($c = 15000$ about) 1), we can calculate for each of them the brightness and colour of the light, as well as the temperature T. We then find for the degrees of glowing $+1$, 0 and -1

$$\begin{array}{rrrr} b' = +1 & 69200\,R\;+ & 68100\,G\;+ & 175800\,B \\ 0 & 1000\,R\;+ & 1000\,G\;+ & 1000\,B \\ -1 & 17{,}7\,R\;+ & 15{,}7\,G\;+ & 6{,}3\,B \end{array}$$

If we represent the colour contained in a total quantity of light of 1000 by the quantities R, G, B and the brightness by magnitudes, we shall find for

$$\begin{array}{lll} b' = +1 & Col. = 221\,R + 218\,G + 562\,B & Br. = +4{,}6\ Mg. \\ b' = -1 & Col. = 445\,R + 396\,G + 160\,B & Br. = -4{,}4\ Mg. \end{array}$$

Thus the first colour may be described as a mixture of 654 white and 347 of a blue consisting of 3 R and 344 B, hence corresponding in tint to λ 466; the second colour is a mixture of 480 white and 521 of a yellow consisting of 285 R and 236 G, hence corresponding to the wavelength λ 587. A degree of glowing $b' = -2$, corresponding in colour almost with the light of petroleum, involves a decrease in brightness of 8,6 magnitudes.

For the calculation of the atmospheric absorption we have assumed that the general absorption in a gas is inversely proportional to the fourth power of the wavelength. For a layer of gas adopted arbitrarily, which after a comparison with MÜLLER's spectral-photometric measurements appeared to correspond to 1,05 atmosphere, we have calculated $f(\lambda)$ and thence found for the remaining quantity of light, the initial quantity being $1000\,R + 1000\,G + 1000\,B$:

$$783\,R + 771\,G + 571\,B,$$

or reduced to 1000 as the sum,

$$368\,R + 363\,G + 269\,B;$$

the brightness is then 0,783 of the original brightness or is diminished by 0,27 magn.

The colouring due to the absorption by 1.05 atmospheres is almost equal to that brought about by a diminishing of the degree of glowing of $^1/_3$. For the latter yields

$$257\,R + 248\,G + 184\,B$$

hence when reduced to a sum of 1000

$$372\,R + 361\,G + 267\,B$$

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1) In the paper read at Dusseldorf (see note p. 292) wrong temperatures are given because the difference between b and b' was overlooked. The temperatures 16000°, 7500°, 5000°, 3750°, 3000° C do not differ inter se 1, but only 0.43 in degree of glowing.

which is nearly identical with the value above. Here, however, the brightness is diminished to 0.257 of the original, hence by 1.48 magnitude.

Therefore it appears here that these two different causes produce similar colours, but that they correspond to an entirely different decrease of brightness. When comparing the two we may say that atmospheric absorption is more apt to redden, a decrease of temperature more apt to fade the light. Therefore it is impossible to derive the radiating power from the colour only, as we do not know to what degree each of the two influences, temperature and absorption, is at work in the different spectral classes. Perhaps that one day accurate spectral-photometric measurements will enable us to separate the two influences, for they give a different distribution of intensity over the spectrum. For the log. of the brightness of different λ with regard to λ 500 we find

	$\lambda = 650$	600	550	500	450	400
with abs. 1.05 atm.	+ 0.114	+ 0.083	+ 0.051	0.000	−0.084	−0.231
with glowing — $^1/_3$	+ 0.154	+ 0.111	+ 0.061	0.000	−0.074	−.0166

For the latter the decrease in intensity from the red to the violet is more regular, for the former the decrease is slower for the greater and more rapid for the smaller wave-lengths.

These calculations show that it is not strictly true that, as has been said in the preceding paper, a redder colour must necessarily involve a smaller radiating power. Where we have two influences which in different ways bear on the colour and the brightness, the possibility exists that a redder colour may be accompanied by a greater radiating power, namely when one source of light has a much higher temperature and at the same time a greater atmospheric absorption than the other. An increase of the degree of glowing of + $^1/_3$ combined with an absorption of 2 atmospheres gives such a case according to the figures given above.

Herein we have therefore a new possibility to account for the peculiarities found in the *K* stars, namely by assuming that, as compared with the *G* stars, they have a much higher temperature, which causes a stronger radiation, and which by very strong atmospheric absorption, is only little faded but greatly reddened. We must add, however, that this explanation seems little probable to us as the band-absorption, which begins at the *K*-stars and which is characteristic for the *M* stars (the 3rd type) indicates a lower temperature.

Chemistry. — *"Action of Potassium hypochlorite on Cinnamide".*

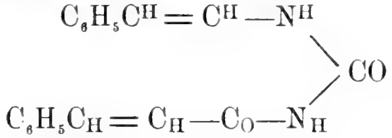
By Dr. R. A. WEERMAN (Communicated by Prof. HOOGEWERFF).

(Communicated in the meeting of September 29, 1906).

From the experiments of BAUCKE 1) on propiolamide and those of FREUNDLER 2), VAN LINGE 3) and JEFFREYS 4) on cinnamide it appears that in the case of these unsaturated acids, the HOFMANN reaction to prepare an amine from an amide by means of a halogen and an alkali does not succeed.

As to the non success we may form two hypotheses: first of all that the double bond 5) prevents the intramolecular rearrangement of atoms which must be assumed in the HOFMANN reaction, and secondly that the amine supposed to be formed, in this case $C_6H_5CH = CH\ NH_2$, suffers decomposition under the said circumstances. 6).

The first, however, is *not* the case as from cinnamide may be prepared the urea derivative:



where consequently one-half of the amide has undergone the transformation.

This being a case of an unsaturated amide, it is necessary to make use of the modification proposed by HOOGEWERFF and VAN DORP and not to work with free halogen. Further the hypochlorite solution must not contain any free alkali; on account of the insolubility of cinnamide and the consequent inertness, an alcoholic solution is employed.

Although at first sight it appears strange that in alcoholic solution the urea derivative is formed and not the urethane, this may be explained by the experiments of STIEGLITZ and EARLE 7), which show that isocyanates react very readily with halogen-amides 8).

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1) Rec. 15, 123.

2) BULL [3] 17, 420.

3) Dissertation VAN LINGE, Bazel 1896.

4) Am. Chem. Journ. 22, 43.

5) On account of the great analogy existing between the LOSSEN transformation of hydroxamic acids and the HOFMANN reaction, this first supposition was not very probable, as THIELE had prepared from the acylated cinnamohydroxamic acid the urethane $C_6H_5CH = CH—NH—CO_0C_2H_5$. A second indication, though less conclusive, in the more distant analogy between the BECKMANN rearrangement and the HOFMANN reaction was the formation of isochinolin from the oxime of cinnamaldehyde. (Ber. 27, 1954).

6) THIELE, Ann. 309. 197.

7) Am. Chem. Journ. 30, 412. C 1904, I, 239.

8) This is the reason why, in the preparation of urethanes according to JEFFREYS, the sodium ethoxide should be added all at once.

In order to prepare the urea derivative, the cinnamide is dissolved in eight times its weight of 96 pCt. alcohol, and when cooled to the temperature of the room the hypochlorite solution, prepared according to GRAEBE [1]), is slowly dropped in, the free alkali being neutralised with 2N hydrochloric acid immediately before use. For every 2 mols. of amide, 1 mol. of potassium hypochlorite should be added. The liquid gets warm, and very soon a crystalline mass composed of very slender needles is deposited. After a few hours the mass is collected at the pump; this does not go very readily on account of the fine state of division. The yellowish mass is treated with hot alcohol and then washed with water. A fairly pure urea derivative is thus obtained (m. p. about 218). By recrystallisation once or twice from glacial acetic acid it is obtained pure in needles (m. p. 225—226).

0,1733 grm. yielded 0,0894 grm. H_2O and 0,4682 grm. CO_2
0,1654 ,, ,, 0,1863 ,, ,, ,, 0,4467 ,, ,,
0,1654 ,, ,, 13,9 CC.N at 19½° and 765 m.M.

Found	73,68 73,66 pCt. C	5,78 5,85 pCt. H	9,70 pCt. N
Theory $C_{18}H_{16}N_2O_2$:	73,95 pCt. C	5,51 pCt. H	9,59 pCt. N

The compound is insoluble at a low temperature in water, ligroin, alcohol, methyl alcohol, ether, carbon disulphide and benzene; at the boiling temperature slightly soluble in alcohol and benzene and freely so in glacial acetic acid, chloroform and acetone. It is insoluble in alkalis or acids.

Chemical Laboratory, Technical High School, Delft.

Astronomy. "*Mutual occultations and eclipses of the satellites of Jupiter in* 1908. By Prof. J. A. C. OUDEMANS.

(Communicated in the meeting of September 29, 1906).

N.B. In the present communication the four satellites of Jupiter, known since 1608, have been denoted by I, II, III and IV in accordance with their mean distances from the planet. The further letters *n* and *f* indicate whether the satellite is *near* or *far*, i.e. whether it is in that half of the orbit which is nearest to or furthest from the Earth. The jovicentric longitudes as well as the geocentric amplitudes are counted in "signs" and "degrees", the latter beginning from the superior

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[1]) Ber. 35, 2753.

geocentric conjunction. Eastern elongation, denoted by $\dot{e}.e$, has an amplitude of 3^s, western elongation, $w.e$, one of 9^s .

Not to interrupt the text unnecessarily, all particulars have found a place at the end of the paper.

FIRST PART. OCCULTATIONS.

In the numbers 3846 and 3857 of the *Astronomische Nachrichten* we find two communications relative to observations of the occultation of one satellite of Jupiter by another. The first (1) is by Mr. Ph. Fauth at Landstuhl, dated 8 December 1902, with postscripts of 29 December 1902 and 14 January 1903. The other (2) by Mr. A. A. Nijland at Utrecht, dated 27 February 1903.

Fauth notes in addition that Houzeau, in his *Vademecum*, p. 666 mentions a couple of similar observations (3), and further that Stanley Williams, on the 27th March 1885 at $12^h\,20^m$, saw the third satellite pass the first in such a way that the two satellites combined had a pear-shaped appearance. (4)

The satellites of Jupiter move in orbits but little inclined to the plane of Jupiter's equator. Laplace assumed a fixed plane for each satellite; the plane of the satellite's orbit has a constant inclination on this fixed plane, whereas the line of intersection, the line of the nodes, has a slow retrograde motion. The inclinations of the fixed planes on the plane of Jupiter's equator amount only to a few minutes; their intersection with the plane of Jupiter's orbit is identical with the line of the nodes of the equator. The value generally adopted for the inclination of the latter plane on the orbit of Jupiter is $3°4'$, whereas the longitude of the ascending node, which therefore is also that of the fixed planes, is at present about $315\frac{1}{2}°$.

In order to be able to assign the time at which, as seen from the Earth, an occultation of one satellite by another is possible, it is necessary to know the longitude of the ascending node and the inclination of the mean fixed plane on the orbit of the Earth. At the time that the mean fixed plane, prolonged, passes through the Earth, occultations of one satellite by another may be observed. As Jupiter completes a revolution around the sun in nearly 12 years, these times will succeed each other after periods of six years. Jupiter will pass alternately through the ascending and the descending node of the plane which passes through the centre of the sun parallel to the mean fixed plane.

It follows that, as occultations of one satellite by another have been observed in 1902, we must expect that these phenomena will be again visible in 1908 (5).

To facilitate these observations I thought it desirable to calculate in advance the conjunctions of any two satellites for the most favourable part of 1908.

We have to consider that while formerly the orbits of the satellites were determined by repeatedly measuring the distances and their angles of position relatively to the planet, this method is now replaced by the measurement of the distances and the angles of position of the satellites relative to each other (especially with the heliometer) (6). For observations during a moderate interval the periodic times of the satellites may be assumed to be accurately known. Admitting this, if, leaving out of consideration KEPPLERS third law, we introduce the major axis of each satellite as an unknown quantity, the total number of such unknowns will be six for each orbit at a determined time. If, as was done by BESSEL at Köningsberg in 1834—39, and by SCHUR at Göttingen in 1874—1880, the distance and the angle of position between the planet and the satellite are measured, we get two equations with six unknown quantities. If however we measure the distance and the angle of position of two satellites relative to each other, the number of unknown quantities in these equations is doubled and thus becomes 12. If finally all the combinations two by two, are observed, as was done by GILL and FINLAY at the Observatory of the Cape, we get a great number of equations with a total of 24 unknown quantities. These equations must then be solved by the method of least squares. This number becomes 29 if we add the masses of the satellites, (only to be found by the perturbations caused by one satellite in the motion of the others,) and the compression of Jupiter (7), given by the retrogradation of the lines of the Nodes on the fixed planes.

Now the observation of an occultation, even of a conjunction without an occultation, can be made by everybody possessing a telescope of sufficient power. Such an observation also furnishes two equations between the unknown quantities, at least if, for a non central occultation or a simple conjunction, the difference in latitude is measured at the filar micrometer. This consideration engaged me to compute in advance the time of these conjunctions for the most favourable part of 1908. If by experience we find that this preliminary work leads to valuable results, it might be worth while to continue it for some future period, for instance for 1914.

For the moment at which the mean fixed plane passes through the centre of the Earth, I find, 1908 July 8, 19^h,6 Mean Time at Greenwich, (5).

This date, it is to be regretted, is very unfavourable. For on that day Jupiter culminates at Greenwich at 2^h10^m M. T., its declination being 16°48′·5 North, whereas the Sun's declination is 22°30′ North. From these data I find for the 8th of July, for Utrecht, duly making allowance for refraction :

Setting of the upper limb of the sun at 8^h20^m mean time,
,, ,, Jupiter ,, 9 44 ·5 ,, ,, .

So there is but a poor chance for an observation of the computed occultation at Utrecht. For southern observatories it is somewhat better. At the Cape for instance, we have;

Sunset at 5^h 5^m mean time,
Setting of Jupiter ,, 7 25 ,, ,, .

We thus find that on July 8, 1908, at Utrecht, the setting of the sun precedes that of Jupiter by $1^h24^m{\cdot}5$; at the Cape by 2^h20^m.

We have computed all the conjunctions of the satellites of Jupiter which will occur between 31 May and 20 July 1908. In what follows a short account is given of the way which led to our results.

In the *Nautical Almanac* are given the *Geocentric Superior Conjunctions*; in the Almanac of 1908 they will be found on pp. 504, 505.

To begin with, a separate drawing was made of the four orbits, which were supposed to be circular, for each interval of two periods of I (about 85^h). On these orbits we plotted the positions of the satellites for each second hour, making use of divided pasteboard arcs. The number of hours elapsed since the moment chosen as a starting-point were noted for each position. The equation of the centre etc. was neglected.

The scale of this drawing gave 4″ to 1 mm. The radii, of the orbits therefore were: for I 27·9 mm.; for II 44·45 mm.; for III 70·9 mm. and for IV 124·7 mm.

The direction from the Zero of I to the common centre of all the circles showed the direction towards the Earth. Knowing this, we could easily find for each of the six possible combinations of two of the satellites, those equal hour numbers, the connecting line of which is parallel to this direction.

These connecting lines show the approximate times at which, as seen from the Earth, one of the satellites is in conjunction with another. The want of parallelism of the real lines joining the Earth with the satellites, in different parts of their orbits, may safely be disregarded. The plate annexed to this paper represents, reduced to half the scale, the drawing for the period of 85 hours, following 12 July 1908, $11^h2^m{\cdot}3$ M. T. Greenwich.

The dotted lines indicate the lines connecting the equal numbers.

Each of them represents a conjunction of two satellites. The corresponding hours read off from the figure are :

$6^{u}{\cdot}2$: IV_f occulted by III_n,
21 ·8 : IV_f ,, ,, I_n,
25 ·0 : IV_f ,, ,, II_n,
35 ·0 : I_f ,, ,, II_n,
66 ·25: II_f ,, ,, I_n,
71 ·0 : III_f ,, ,, I_n,

They were added to the instant which must be regarded as the startingpoint for this figure. The instants of the conjunctions were next converted into civil time of Paris by the addition of $12^h9^m21^s$. The elongation and the latitude of both the satellites, expressed in radii of Jupiter, were then computed by the aid of the *Tables écliptiques* of DAMOISEAU, 2nd part. (8). In the case that the elongations did not perfectly agree, a slight computation led to a more accurate result for the time of conjunction (9).

In the case that the two satellites moved apparently in opposite directions, (which happens if the one is in the further part of its orbit, the other in the nearer part), the correction to the adopted time was mostly insignificant.

If, on the contrary, they moved the same way (which happens if both are "far" or if both are "near", so that the one has to overtake the other) the correction amounted sometimes to an hour or more. In every case, in which the correction exceeded 20 minutes, the computation was repeated with the corrected time. Further below will be found the list of the results. From May 31 to July 19, i.e. during a period of fifty days, there occur 72 conjunctions. It is to be regretted that at a determined place of observation but very few of them will be visible. For only those conjunctions are visible which occur between sunset and the setting of Jupiter. For Utrecht we have, in mean time :

	Setting of the upper limb of the Sun	Setting of Jupiter	Difference
1908 June 1	8^h10^m	11^h54^m	3^h44^m
,, 11	8 20 ·5	11 19	2 58 ·5
,, 21	8 24	10 44	2 20
July 1	8 24	10 9	1 45
,, 11	8 18	9 34	1 16
,, 21	8 7 ·5	8 59	0 51 ·5

For the Cape of Good Hope:

1908 June 1	$4^{h}59^{m}$	$9^{h}18^{m}$	$4^{h}19^{m}$
„ 11	4 57 ·5	8 46 ·5	3 49
„ 21	4 58	8 16	3 18
July 1	5 2	7 46	2 44
„ 11	5 6 ·5	7 16	2 9 ·5
„ 21	5 13	6 47	1 34

The circumstances are thus seen to be considerably more favourable for a southern than for a northern observatory.

Several of the occultations will not be visible because the common elongation falls short of unity i. e. of the radius of Jupiter. This is the case of Nos. 8, 9, 12, 13, 15, 16, 20, 23, 39 and 64. In the first eight of these cases and in the last one the planet stands between the two satellites. In case No. 39 both the satellites I and IV are covered by the planet [1]).

For other conjunctions it may happen that one of the satellites is invisible because of its being in the shadow of the planet. Such cases are:

(N°. 21), June 13 $9^{h}28^{m}$ M. T. Grw., II eclipsed,
(N°. 31), „ 20 12 51 „ „ II „ ,
(N°. 51), July 4 18 15 ·7 „ „ II „ ,
(N°. 65), „ 13 12 3 „ „ IV „ .

If the satellite which at the conjunction is nearest to the Earth is eclipsed by the planet's shadow, it might, as seen from our standpoint, project itself wholly or partially as a black spot on the other satellite. The case however has not presented itself in our computations.

Possibly the last of the conjunctions just mentioned may really be visible; for according to the *N. Almanac*, the reappearance of IV from the shadow of the planet takes place at $12^{h}7^{m}15^{s}$ M. T. Greenwich and the predicted eclipses of this satellite are occasionally a few minutes in error. A few minutes later, according to the *N. Almanac* at $12^{h}16^{m}$, II enters the disc of Jupiter.

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[1]) According to the Nautical Almanac we have for this night (M. T. of Greenwich):

IV. Occultation Disappearance $10^{h}19^{m}$,
I. Occultation Disappearance 11 20,
I. Eclipse Reappearance 14 26 27^{s},
IV. Occultation Reappearance 15 13,
IV. Eclipse Disappearance 18 5 6 ,
IV. Eclipse Reappearance 22 52 2 .

NOTES.

(1) The article of FAUTH, abridged, runs thus:

— — — Ausser den in HOUZEAU, Vademecum p. 666 aufgeführten Beobachtungen, (vid. below Note 3), kenne ich aus neuerer Zeit nur einen Fall: STANLEY WILLIAMS sah am 27 März 1885 an einem 7 cm. Rohre mit 102-facher Vergrösserung um 12^h 20^m den III Trabanten vor dem I, wobei beide ein birnformiges Objekt bildeten.

— — — In fünf Wochen konnte ich drei Bedeckungen verfolgen, wobei auzunehmen ist, dass mir durch schlechte Witterung etwa 10 andere Gelegenheiten entgangen sein mögen, unter denen sicher einige Bedeckungen vorkommen. Nach meiner Erfahrung können Konjunctionen der Jupitermonde unter sich weit genauer beobachtet werden als Bedeckungen durch Jupiter oder Vorübergänge vor ihm. Somit möchten die hier angegebenen Beispiele Anlass bieten, in den späteren Oppositionen Jupiters den durchaus nicht seltenen Bedeckungen oder wenigstens Berührungen und sehr nahen Konjunktionen der Trabanten unter sich mehr Aufmerksamkeit zu schenken, zumal schon kleine Instrumente zur Wahrnehmung der Phasen einer event. Bedeckung genügen. Die Beobachtungen der letzten Zeit sind:

1. Oct. 7; II bedeckt I; die S. Ränder berühren sich und I ragt im N. etwas hervor. Konj. um 9^h 16^m M. E. Z. [1])

2. Oct. 23; II bedeckt III so, dass die Mitte von II nördlich am N. Rand von III vorbeigeht; Konjunktion um 8^h 7^m 3^s,5.

3. Nov. 10; III bedeckt I so, dass der S. Rand von III die Mitte von I streift (gute Luft); Konjunktion um 7^h 33^m 20^s.

Instrument: 178 mm., Vergrösserung 178 fach.

Landstuhl, 1902 Dez. 8.

P.S. vom 29 Dezember. Am Abend des 24 Dezember gelang nochmals die Beobachtung einer Bedeckung, bei welcher I über IV hinwegzog. Aus je fünf vor- und nachher notierten Zeitmomenten folgen als Mittelwerte 6^h 24^m,25, 24^m,625, 24^m,50, 24^m,625 und 24^m,50. Die Konjunktion fand also statt 6^h 24^m 30^s.

Der Uhrstand war um 3^h mit dem Zeitsignal verglichen worden. IV Stand ein wenig südlicher als I, vielleicht um ein Viertel seines Durchmessers. Die weitaus interessantere Konjunction zwischen II und IV am 25 Dezember blieb gegenstandslos, weil IV um etwa zwei Durchmesser vorüberging,

P.S. vom 14 Januar (1903). Heute Abend, am 14 Januar, bewegte

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[1]) i. e. Mittlere Europäische Zeit, 1^h later than Greenwich-time.

sich der Trabant III über II hinweg. Die sehr schlechte Luft liess nur den ersten Kontakt auf etwa $6^h\ 2^m$ feststellen. Um $6^h\ 18^m$ mochten sich beide Komponenten so weit getrennt haben, dass dies in einem weniger schlechten Augenblick bemerkt wurde; um $6^h\ 32^m$, dem nächsten blickweisen Auftauchen der beiden Lichtpunkte, waren diese um etwa einen Durchmesser von einander entfernt. Die Bedeckung war fast genau central. Ph. F.

(2) Mr. Nijland writes in N°. 3857 of the *Astronomische Nachrichten*:

— — — Am 15 Juli 1902 fand eine Konjunktion der Trabanten II und III statt, welche ich bei guter Luft am Refraktor (Brennweite 319 cm., Oeffnung 26 cm.) mit Vergr. 248 beobachten konnte. Es wurde III nahezu central von II bedeckt. Einige Minuten lang blieb eine feine schwarze Linie zwischen den beiden Scheibchen sichtbar, welche um $14^h10^m11^s$ M.Z. Utrecht verschwand and um $14^h20^m31_s$ wieder erschien; die Konjunktion musz also um $14^h15^m21^s$ stattgefunden haben. Dass diese Trennungslinie vor und nach der Konjunktion immer dieselbe Richtung hatte, und zwar scheinbar senkrecht auf der Bahnebene der Trabanten stand, mag als Beweis dafür gelten, dass der Vorübergang wirklich nahezu central gewesen ist. Dann lässt sich aber aus dieser centralen Passage die Summe der Durchmesser der Monde II und III mit erheblicher Genauigkeit bestimmen.

Nehme ich für die mittlere Entfernung ♃ — ⊙ die Halbmesser der Bahnen gleich $177'',8$ und $283'',6$, so finde ich für die relative Bewegung von II und III zur Beobachtungszeit $13'',86$ pro Stunde. Aus der beobachteten Zeitdauer von $10^m20^s = 0^h172$ folgt dann für die Summe der beiden Durchmesser, $2'',38$. Wird (siehe die Angaben von Douglass, Astr. Nachr. 3500) für das Verhältniss der Durchmesser von II und III $^4/_{11}$ angenommen, so finde ich, in vorzüglicher Uebereinstimmung mit den a. a. O. genannten Werten, für den Durchmesser von II $0'',87$ und von III $1'',51$ (in mittl. Entf.).

Utrecht, 1903 Febr., 27. A. A. Nijland.

Remark. As from the observed instants I derived a result slightly different from that of Mr. Nijland, this gentleman allowed me to consult his reduction of the observation. It appeared that, in order to find the amplitudes, he had combined the preceding geocentric superior conjunction with the following transit, from the ingress and egress of which the inferior conjunction could be derived. A slight error had however been committed in the computation. After correction the relative motion of the two satellites was found to be $13''\cdot786$ and the sum of the diameters $2''\cdot374$. Moreover their proportion was, evidently erroneously and against the real intention, put at 4 to 11 instead of at 4 to 7. We thus get for the diameters 0″·863 and 1″·511, which is still in good agreement with the result of Mr. NIJLAND. As values have been assumed for the radii of the orbits which hold for the mean distance of Jupiter from the sun, these values need no further reduction.

(3) We find in HOUZEAU, *Vademecum* (Bruxelles, 1882), p. 666: On rapporte une occultation du satellite II par le satellite III, observée à Sommerfeld, près de Leipzig, par C. ARNOLDT, le 1^er^ novembre 1693, (WHISTON, *The longitude discovered by the eclipses*, 8°, London, 1738), et une autre du satellite IV, également par le III^me^, vue par LUTHMER à Hanovre, le 30 octobre 1822 (*Nature*, 4°, London; vol. XVII, 1877, p. 148).

1st Remark. The little book of WHISTON here quoted is in the library of the University at Utrecht, Division P, 8vo, number 602. We have turned over the leaves several times, but have not found any mention of the observation of C. ARNOLDT. It is true that the author, in § XVIII, recommends the observation of the mutual occultations of the satellites. He remarks that, if at such an occultation they have opposite motions, the relative velocity is "doubled". He mentions the complaint of DERHAM[1], that the strong light of Jupiter renders the observation of these occultations rather difficult. He remarks that, the interval being equal, their number must be one and a half time as large as that of the eclipses. Again he mentions that LYNN is the first who, in the *Philosophical Transactions* N^0. 393, has proposed to apply these conjunctions to the determination of the longitude, seeing that they can often be observed with an accuracy of less then half a minute[2]. But I do not find the observation of a single occultation nor its prediction.

It needs hardly be said that the conjunctions, visible from places, the difference in longitude of which is to be determined, are too rare to be of much importance for the purpose. In accuracy of observation they are at all events surpassed by occultations of stars. But they may well be compared with the eclipses of the satellites of Jupiter and are indeed superior to them in this respect that they yield a result in a few minutes which is independent of the optical power of the telescope. For the eclipses this is only true in the case of the combination of a disappearance with a reappearance.

2nd Remark. The original account of the observation of LUTHMER was communicated by him to BODE who inserted it in the (Berliner) *Astronomisches Jahrbuch* für 1826, p. 224:

"Am 30 Oct. Ab. 6^u 55′ Bedeckung des vierten ♃ Trabanten vom dritten."

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[1] POGGENDORFF's *Biographisches Wörterbuch*, (article W. DERHAM) gives no reference to the passage where this complaint is to be found, nor even to any paper on the observation of the satellites of Jupiter.

[2] At least if there were no undulation of the images. See at the end of note 4

> If we assume 9°42′ = 38m48s East of Greenwich for the longitude of Hannover, this is = 6h 16m 12s M. T. of Greenwich, at least supposing that at that time it was already usual to give the observations expressed in mean time.
>
> In *Nature*, XVII (Nov. 1877—April 1878) p. 149 (not 148) we find in "*Our Astronomical Column*":
>
> "JUPITER'S SATELLITES. — Amongst the recorded phenomena connected with the motions of the satellites of Jupiter are several notices of observed occultations of one satellite by another, and of small stars by one or other of the satellites.[1] The following cases may be mentioned: — On the night of November 1, 1693, CHRISTOPH ARNOLDT, of Sommerfeld, near Leipzig, observed an occultation of the second satellite by the third at 10h 47m apparent time. On October 30, 1822, LUTHMER, of Hannover, witnessed an occultation of the fourth satellite by the third at 6h 55m mean time.
>
> It thus appears that the editor of *Nature* also took it for granted that the statement must be understood to have been made in mean time.

(4) I did not succeed in finding the account of this observation of STANLEY WILLIAMS in any of the journals accessible to me, and therefore applied to the author, who lives at Hove near Brighton, for particulars about the place of its publication.

He kindly replied on the 7th instant, that the details of his observation of 27 March 1885 were published both in the 41th volume of the "*English Mechanic*" and in the volume for 1885 of the German Journal "*Sirius*".

He had moreover the courtesy of communicating to me the original account of the observation in question. From this account the following passages may be quoted:

Occultation of satellite I by satellite III.

1885 March 27, ... $2^3/_4$ inch refractor. Power 102.

11^h55^m (Greenwich mean time). They are now only *just* free from contact. $_{\mathrm{III}}$  I, like an elongated star with little more than a black line between the components.

12^h00^m to 12^h04^m. After steady gazing I cannot see any certain separation between the satellites, and therefore with this instrument and power first contact must have occurred about 12^h02^m. Definition is very bad, however, and in a larger telescope there probably might still be a small separation between the limbs.

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[1] It is to be regretted that these "several notices of observed occultations of one satellite by another" are not more fully quoted.

$12^{h}10^{m}$. They now appear as one elongated satellite. At times a trace of the notches is apparent.

$12^{h}20^{m}$. The elongation is now very nearly at right angles to the direction of the motion of the satellites, and is so slight as to be scarcely noticeable in this bad and unsteady definition. I think from the smallness of the elongation that nearly half satellite I must be concealed behind III. In this bad definition it is not possible to say which satellite is in front of the other from the appearance alone.

In his letter Mr. STANLEY WILLIAMS mentions the remarkable fact that he too observed on 15 July 1902 the same conjunction which has been described by NIJLAND. His instrument was a reflector of $6^{1}/_{2}$ inch, with a power of 225. The following are the particulars as communicated :

1902 July 15, $13^{h}45^{m}\cdot2$. Satellites II and III are in contact. The one will occult the other. See diagram 

.

$13^{h}52^{m}$. The satellites form one disc, which has the slightest possible elongation in a north and south direction. Owing to confused seeing this disc always appeared more or less fuzzy, and it is impossible from the appearance alone to say, which satellite is occulting the other.

$13^{h}56^{m}$. The combined disc is considerably elongated now.

$14^{h}02^{m}\cdot2$. Satellites II and III in contact as in diagram adjoining 

.

$14^{h}04^{m}$. Satellites clearly separated. The occultation must have been nearly central. II is a little more south now relative to III, than it was before occultation. Possibly the slight elongation noted at $13^{h}52^{m}$ was not real.

The above times are Greenwich mean times. Satellite III was on the farther side of its orbit moving east, II on the near side moving west. As the disc of III is larger than that of II, the phenomenon should be described as a transit of II over or across III, rather than an occultation of one satellite by the other.

The arithmetical mean of $13^{h}45^{m}\cdot2$ and $14^{h}2^{m}\cdot2$ is $13^{h}53^{m}\cdot7$, which is $1^{m}\cdot1$ earlier than NIJLAND's observation.

(5) For the numbers which follow we refer to KAISER's "*Sterrenhemel*", 4th Edition, p. 707 and following.

In the 4th Vol. of his *Mécanique Celeste*, p. 62, TISSERAND, following SOUILLART, adopts inclinations for the orbits of III and IV, which respectively exceed those given in the "*Sterrenhemel*" by + 4″ and — 8″.

According to **Leverrier** we have, for the orbit of Jupiter in 1908,0:

Ascending Node = 99°31′56″,
Inclination = 1 18 29 .

The fixed plane of the first satellite coincides with the plane of Jupiter's equator: the longitude of the ascending node on the plane of Jupiter's orbit, for the beginning of 1908 is therefore 315°33′35″, the inclination 3° 4′ 9″.

Furthermore we have for the four fixed planes relative to the plane of Jupiter's orbit:

	Long. asc. node	Inclination	
I	315°33′35″	3° 4′ 3″	Epoch 1908.0.
II	315 33 35	3 3 4	
III	315 33 35	2 59 11	
IV	315 33 35	2 39 57	

For the mean fixed plane of the three first satellites we thus find: longitude of ascending node on the plane of Jupiter's orbit at the beginning of 1908: 315°33′35″, inclination 3° 2′ 6″.

Moreover we have for the respective fixed planes in 1908, according to **Tisserand**:

	long. asc, node	Change in 1000 days	Inclination
II	122°·293	— 33°·031	0°28′ 9″
III	26 ·173	— 6 ·955	0 10 44
IV	238 ·982	— 1 ·856	0 13 51

The effect of these inclinations, however, is but trifling. At the distance of 90° from the node they produce only deviations

for II of 1″·46,
,, III ,, 0″·89,
,, IV ,, 2 ·01.

The determination of the position of the fixed planes, as also that of the planes of the orbits of the satellites relative to these, will be much improved by the measurements which **De Sitter** at Groningen is making on photographic plates. Eventual observations of conjunctions of the satellites, rather even of occultations, will contribute their part in this determination and will furnish a test for the adopted values.

In the meeting of our section of last March a provisional account of these measures by DE SITTER was communicated by Messrs J. C. KAPTEYN and E. F. VAN DE SANDE BAKHUYZEN [1]).

Our computations were then already too far advanced to keep them back altogether; but we hope that by the side of these measures they still may have their use, for this reason that conjunctions and mutual occultations of the satellites may well be observed at several observatories which are not equipped for taking photographs.

From the preceding numbers we find for the position of the fixed plane relative to the ecliptic (for 1908,0).

$$\text{Ascending Node } 336°48'23'' = \Omega,$$
$$\text{Inclination } \quad 2 \;\; 7\,17 \;\; = \mathrm{I},$$

Now, if $R_{♃}$, $L_{♃}$ and β represent the radius vector, the longitude and the latitude of Jupiter; $R_{♁}$, $L_{♁}$ the radius vector and the longitude of the Earth, (those given in the N. Almanac after correction for aberration), the condition that the fixed plane must pass through the Earth is expressed by:

$$R_{♃} \cos\beta \sin(L_{♃} - \Omega) - R_{♃} \sin\beta \cot I = R_{♁} \sin(L_{♁} - \Omega)\,,$$

which is satisfied July 8, 1908 at $19^{h}38^{m}\!\cdot\!3$. For at that moment

$$\begin{array}{llll} \log R_{♃} = 0{\cdot}728527 & & \log R_{♁} = 0{\cdot}007179 \\ L_{♃} = \quad 141°23'\;9''{\cdot}0 & & L_{♁} = 286°40'\;3''{\cdot}5 \\ \beta \;\; = + \quad 0\;52\;26\;{\cdot}73 & & \Omega \;\; = 336\;48\;52\;{\cdot}0 \end{array}$$

so that our equation becomes

$$1{\cdot}423706 - 2{\cdot}204190 = -0{\cdot}780484$$

Similarly we find for the instant at which the same plane passes through the centre of the sun:

25 April 1908 at $18^{h}\!\cdot\!5$ M. T. Grw.

On both sides of this latter epoch there exists the possibility of an eclipse of one satellite by another, at the time of the heliocentric conjunctions. We hope to treat this subject in the second part of this communication.

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[1]) This provisional account may be considered as a sequel to the thesis of Mr. DE SITTER. This thesis, maintained by him at Groningen on 17 May 1901, bears the title: *Discussion of Heliometer-observations of Jupiter's satellites made by sir* DAVID GILL *K.C.B. and* W. H. FINLAY *M.A.* Further particulars will be given in the *Annals of the Royal Observatory at the Cape of Good Hope.*

(6) In 1833—39 **Bessel**, at the Heliometer, measured not only distances of all the satellites from both limbs of the planet, but also angles of position of the centre of the planet to III and IV.

His heliometer was the first big instrument of the sort made in the establishment of **Fraunhofer**; the objective had an aperture of 70·2 Par. lines and a focal distance of 1131·4 Par. lines = 7 feet 10 inches 3·4 lines, Paris measure, (15·84 and 255·22 c.M.). The mean error of a single observation of distance (which properly was the mean of eight pointings) appeared to be

for I	± 0″26,	for the mean distance resulting from all the measures,	± 0″055
„ II	± 0·24,	„ „ „ „ „ „ „ „ „	± 0·067
„ III	± 0·31,	„ „ „ „ „ „ „ „ „	± 0·042
„ IV	± 0·43,	„ „ „ „ „ „ „ „ „	± 0·045
Mean.	± 0·31,	„ „ „ „ „ „ „ „ „	± 0·052

Schur, at Göttingen, used the heliometers which were made by **Merz** at München for the observation of the transits of Venus in 1874 and 1882. The aperture of the objectives of these instruments was 34 Par. lines, something less than half that of the heliometer of Köningsberg; the focal distance was 3½ feet (113·7 cM.).

At these heliometers the reading, instead of being made on the drums of two micrometers, was made by a microscope at right angles to two scales fitted to the two halves of the objective. As however in this way more time was required than for reading the druns of a micrometer of **Bessel**'s instrument, **Schur**, instead of taking the mean of eight pointings, was content with the mean of four pointings, which also make a complete measurement.

The mean errors of each observation obtained by **Schur** for a complete set of four measures was:

for I	± 0″·34,
„ II	± 0 ·44,
„ III	± 0 ·37,
„ IV	± 0 ·42,
Mean:	± 0″·39,

a result, which, taking into account the shorter focal distance, may be considered fairly good. **Bessel** as well as **Schur** aimed not so much at the determination of the position of the orbits of the satellites as at that of the mass of Jupiter.

Schur improved in different respects the reduction of the observations of the measures made by Bessel. In consequence, the mean errors of the single determinations of Bessel were considerably lessened. The numbers quoted just now, became:

for I ± 0″·21,
,, II ± 0 ·10,
,, III ± 0 ·26,
,, IV ± 0 ·30,
Mean: ± 0″·24.

As has been mentioned already, Gill and Finlay, acting on a suggestion formerly made by Otto Struve[1]), did not measure the distances and the angles of position of the satellites relative to the centre of the planet, but relative to each other. (The instrument at their disposal, a heliometer of Repsold, aperture 7½ inch = 19·05 cm., focal distance somewhat over 2 Meter, far surpassed in perfection all the instruments used up to that time). These observations can be made with much more precision. The drawback is that the formation of the equations of condition and their solution become more complex and absorb much more time. Both the gentlemen named and Mr. de Sitter have not been deterred by this consideration. They found ± 0″·087, a number considerably less than that of Bessel, for the probable error of the measurement of a single distance. Mr. de Sitter even finds that the probable error of the mean distances (the real unknown quantities) does not exceed ± 0″·020 or ± 0″·021.

(7) It may be remarked that Mr. de Sitter found it expedient to alter the choice of the unknown quantities. He retained for each satellite: the longitude in the orbit, the inclination and the ascending node relative to an adopted position of the fixed plane, but not the eccentricity nor the position of the perijovium and the mass. There thus remained as unknown quantities only three elements of each satellite. On the other hand he introduced corrections of the coefficients of the perturbations or rather of the periodic terms, which afterwards must lead to the knowledge of the mass of the satellites, to that of the eccentricities and of the position of the

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[1]) *Vide* the first report of Hermann Struve, in the first supplementary vol. of the Pulkowa observations, 1st page at the bottom.

apsides. He further introduced two unknown quantities, *viz.* the constant errors which might vitiate the observations of the two observers GILL and FINLAY. He thus also obtained a total of 29 unknown quantities. It need not be said that the solution of about 400 equations with so many unknown quantities, is an enormous labour. Still, owing to the help of some other computers, this labour has been brought to a happy issue.

We must not enter here into further particulars about this important work, though we did not feel justified in omitting to mention it altogether. I will only remark that it is not sufficient to determine the position of the planes of the orbits of the satellites for one epoch; for as was already remarked the position of these planes changes continually. It seems that these changes may be sufficiently represented by assuming a regular retrogradation of the line of intersection with a fixed plane, the inclination remaining the same.

The main cause of this retrogradation is the polar compression of Jupiter. It is desirable however to establish the amount of this retrogradation by the observations, and to derive afterwards the compression by means of this amount. Consequently the position of the planes of the orbits has to be determined for different epochs. In this respect too Mr. DE SITTER has done good work, *vide* the communication already mentioned, presented in the meeting of last March by Messrs KAPTEYN and E. F. VAN DE SANDE BAKHUYZEN.

(8) The same volume, which contains the ecliptic tables of DAMOISEAU, contains also in a second part (not mentioned on the title) tables "*pour trouver les configurations des satellites de Jupiter.*"

We have contemplated whether it would not be desirable not to use these tables, unmodified, for our computations. We have therefore taken note of the investigations of SOUILLART, ADAMS, MARTH, GILL, FINLAY, and de SITTER, but it appeared that such a course would aggravate our labour very considerably. We would have had to determine new elements for all the satellites and to compute new tables. This would have caused considerable retardation, unnecessary for our purpose, which was no other than to prepare astronomers for the observation of the conjunctions visible in 1908.

We therefore have based our computations on the tables of DAMOISEAU, but we have first examined in how far they represent the observed conjunctions. The following summary shows not only the difference between the observation and the tables in the elongations x and x', of the two satellites, expressed in radii of Jupiter, but also their difference in time.

Observer	Date	Occultation of	by	Error	Relative hourly motion	Corr. of Table	$y'-y$
				r	r	m	r
Fauth	1902 Oct 7	II_f	I_n	0,025	1,278	+ 1,2	+ 0,04
»	» » 23	III_f	II_n	0,02	1,130	+ 1,1	+ 0,08
»	» Nov. 10	I_f	III_n	0,00	0,883	0,0	+ 0,13
»	» Dec. 24	IV_f	I_n	0,10	1,089	— 5,5	+ 0,00⁵
»	1903 Jan. 14	II_n	III_n	0,11	0,374	—19,2	— 0,05
Nijland	1902 July 15	III_f	II_n	0,08	0,751	+ 6,4	— 0,01
Stanley Williams	» » »	»	»	0,07	0,751	+ 5,3	— 0,01
» »	1885 March 27	I_n	III_n	0,00	0,292	0,0	+ 0,01

The observation of LUTHMER in Hannover, of Octob. 30, 1822 is not contained in this table. Its calculation yields the result:

	Jovic. Long.	Amplitude	x	y en y'
III	$10^s26^\circ{\cdot}77$	$8^s,22^\circ{\cdot}25$	$-15^r{\cdot}21$	$+0^r{\cdot}18$
IV	9 6·74	7 2·22	$-14{\cdot}40$	$-0{\cdot}74$
		Difference	$+0^r{\cdot}81$	$+0^r{\cdot}92$

So there is a difference in the amplitudes, of $0^r{\cdot}81$, $= 0{\cdot}81 \times 18''{\cdot}37 = 14''{\cdot}9$, in the latitudes, of $0^r{\cdot}92 = 16''{\cdot}9$. Probably the observation has been made with an unsatisfactory instrument, for it is impossible to suppose an error of this amount in the tables of DAMOISEAU for 1822. The difference in sign of the latitudes y and y' is explained by the fact that the longitude of the ascending node of the fixed plane was $10^s14^\circ{\cdot}37$, which is intermediate between the two jovicentric longitudes.

As the two satellites moved in the same direction, the hourly change of distance was small, *viz.* $0^r{\cdot}280$. It would thus require nearly three hours to annul the difference of $0^r{\cdot}81$.

The remaining conjunctions, however, show a satisfactory accuracy and we may thus expect that the table, as given below, will serve its purpose.

As a second test I have computed, by the aid of the second part of DAMOISEAU, the two superior conjunctions and the intermediate inferior conjunctions of II, and I have compared these to those given in the *Nautical Almanac* of 1902. The epochs were found a little earlier, to wit:

superior conjunction of	10 July,	$10^{h}46^{m}\cdot9$	M.T. Grw.	$0^{m}\cdot7$	earlier
inferior conjunction (mean of ingress and egress)	16 July	$5^{h}40^{m}\cdot0$	,, ,,	$0^{m}\cdot3$	,,
superior conjunction	17 July	$23^{h}54^{m}\cdot4$	,, ,,	$0^{m}\cdot7$	,,

all three less than a minute.

Now, as the conjunctions in the *Nautical Almanac* have been calculated by the aid of DAMOISEAU's *tables écliptiques* (making allowance for some slight corrections indicated by ADAMS) the differences must be solely due to the fact that in DAMOISEAU's second part the *main* terms only of the equations and perturbations have been taken into account.

The same tables represent as accurately the superior conjunction of I on January 1, 1908, $14^{h}4^{m}\cdot2$ M.T. Grw. = January 2, $2^{h}13^{m}\cdot55$ civil time of Paris; the error amounts to $0^{\circ}\cdot07$ or $0^{r}\cdot01$ linear measure only, an arc traversed by the satellite in $0^{m}\cdot5$.

(On the terms taken into account in the second part of the tables of DAMOISEAU *vide* 3rd appendix below).

In his letter Mr. STANLEY WILLIAMS mentions another rare observation, made as well by himself as by the Spanish observer J. COMAS of Valls, (near Taragona), on 14 August 1891, to wit of the coincidence and of the subsequent separation of the shadows of two satellites on the planet. He concludes that an eclipse must have taken place. These phenomena will be treated in the second part of this communication.

(9) Below follows the table which has served for this computation. The unit, the radius of Jupiter, is $18''\cdot37$. SOUILLART states that he found mentioned in the papers of DAMOISEAU that this number was borrowed from ARAGO. According to HOUZEAU, ARAGO must have made the determination by means of the double image micrometer (an invention made nearly simultaneously by himself and PEARSON; of the latter the observatory at Utrecht possesses a specimen). Particulars about these measures are not known. The number is smaller than that found by other astronomers, *vide* for instance HOUZEAU, p. 647—650; SEE, *Astron. Nachr.* N°. 3670 (15 Aug. 1900).

Hourly change of the elongation x as a function of the amplitude.

+				I		II		III		IV		—			
				r		r		r		r					
0^s	0^c	$0^s(12)$	0^c	0 895	4	0,708	3	0,560	2	0,420	2	**6^s**	0^c	**6^s**	0^m
	5	11	25	0,891	10	0,705	8	0,558	7	0,418	4		5	5	25
	10	11	20	0,881	17	0,697	14	0,551	10	0,414	8		10	5	20
	15	11	15	0,864	23	0,683	18	0,541	15	0,406	11		15	5	15
	20	11	10	0,841	30	0,665	23	0,526	18	0,395	14		20	5	10
	25	11	5	0,811	36	0,642	29	0,508	23	0,381	17		25	5	5
1	0	**11**	0	0,775	42	0,613	33	0,485	26	0,364	20	**7**	0	**5**	0
	5	10	25	0,733	48	0,580	37	0,459	30	0,344	22		5	4	25
	10	10	20	0,685	53	0,543	42	0,429	33	0,322	25		10	4	20
	15	10	15	0,632	57	0,501	46	0,396	36	0,297	27		15	4	15
	20	10	10	0,575	62	0,455	49	0,360	39	0,270	29		20	4	10
	25	10	5	0,513	66	0,406	52	0,321	41	0,241	31		25	4	5
2	0	**10**	0	0,447	69	0,354	55	0,280	43	0,210	32	**8**	0	**4**	0
	5	9	25	0,378	72	0,299	57	0,237	45	0,178	34		5	3	25
	10	9	20	0,306	75	0,242	59	0,192	47	0,144	35		10	3	20
	15	9	15	0,231	76	0,183	60	0,145	48	0,109	36		15	3	15
	20	9	10	0,155	77	0,123	61	0,097	48	0,073	36		20	3	10
	25	9	5	0.078	78	0,062	62	0,049	49	0,037	37		25	3	5
3	0	**9**	0	0,000		0,000		0,000		0,000		**9**	0	**3**	0

Finally we will give below, *vide* pp. 334 and 335, two instances of computation; one of a case in which the apparent motion of the two satellites was opposed, the other in which it was in the same direction.

1st Appendix. *What is the maximum duration of the several occultations of one satellite by another?*

We have seen above that it took $19^m{\cdot}2$ to annul the small difference of the elongations of $0^r{\cdot}11$ ($2''{\cdot}0$). This was caused by the minuteness of the relative motion of the satellites. But in the case that the hourly motions, which we will denote by u and u', are *absolutely* equal, the denominator of the fraction $\dfrac{x' - x}{u' - u}$ is *zero*.

The case then corresponds to that of the "Station of Venus" and it is a very ancient problem to compute its epochs.

Let be r and r' the radii vectores of two satellites; θ and θ' the corresponding amplitudes, then for the occultation:

$$r \sin \theta = r' \sin \theta'.$$

The condition of an equal change of longitude leads to:

$$r \cos \theta \frac{d\theta}{dt} = r' \cos \theta' \frac{d\theta'}{dt}.$$

Now, if T and T' represent the sidereal periods, we have, neglecting the apparent movement of Jupiter:

$$\frac{d\theta}{dt} : \frac{d\theta'}{dt} = \frac{1}{T} : \frac{1}{T'} = \frac{1}{r^{3/2}} : \frac{1}{r'^{3/2}},$$

consequently:

$$r^{-1/2} \cos \theta = r'^{-1/2} \cos \theta',$$

from which:

$$\cos^2 \theta = \frac{r}{r'} \cos^2 \theta' = \frac{r}{r'} - \frac{r}{r'} \sin^2 \theta'.$$

Adding

$$\sin^2 \theta = \frac{r'^2}{r^2} \sin^2 \theta',$$

we get

$$1 = \frac{r}{r'} + \left\{ \left(\frac{r'}{r}\right)^2 - \frac{r}{r'} \right\} \sin^2 \theta',$$

Therefore, putting $\frac{r'}{r} = \mu$,

$$\sin^2 \theta' = \frac{1 - \frac{1}{\mu}}{\mu^2 - \frac{1}{\mu}} = \frac{\mu - 1}{\mu^3 - 1} = \frac{1}{\mu^2 + \mu + 1}$$

and

$$\sin^2 \theta = \frac{\mu^2}{\mu^2 + \mu + 1}.$$

The equality of the hourly changes of the two elongations of course only lasts for an instant; very soon inequality sets in and the two satellites begin to separate. Meanwhile it may be long ere such becomes perceptible at the telescope, only, in a case like the present, the satellites do not pass each other, but after the conjunction they have the same position the one to the other as before.

As an example take a conjunction of I and II under the circumstances in question. Let the amplitudes be between 0 and 3 signs, so that both the satellites, as seen from the Earth, (the head being turned to the North Pole), are to the left of and both receding from the planet. Before the conjunction I is to the right of II, but the motion of I is quicker than that of II. I will overtake II as soon as its amplitude is 44°39′, that of II being then 26°14′. At the same time, however, the apparent velocities are equal. Now as I approaches its greatest elongation it retards its motion much more considerably than II, the amplitude of which is so much smaller. The consequence is that, after the conjunction, I is left behind, and gets again to the right of II as before conjunction.

This case represents a transition between two other cases. 1. If, under the same circumstances I is somewhat more in advance (has a greater amplitude), it will pass II, but after a while will be overtaken by II, which then, as seen from the Earth, passes behind it. 2. If, however, I is somewhat less ahead, it will continue to be seen to the right of II, the distance I — II going through a minimum but not reaching zero.

Now, in order to answer the question, how long will be the duration of the occultation counted from the first external contact, the apparent radii of the satellites must be known. Owing to the irradiation they are greater at night than in daytime[1]) as several observers have actually found. The observations of the satellites of Jupiter being made nearly exclusively at night time, we will adopt the apparent radii holding for the night. I took the mean of the values found by SEE at the giant telescope at Washington on the one hand and that found by several observers on the other. (I have taken the values as summarised by SEE himself). For the reduction to the unit used throughout for these computations, *viz* the radius of the equator of Jupiter, this radius is taken $= 18''\cdot37$ in accordance with DAMOISEAU.

	Diameter		Radius
I	$1''\cdot07 =$	$0^{r}\cdot058$	$0^{r}\cdot029$
II	0 ·95	0 ·052	0 ·026
III	1 ·56	0 ·085	0 ·0425
IV	1 ·41	0 ·076	0 ·038

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[1]) Vide e.g. T. J. J. SEE, Observations of the Diameters of the Satellites of Jupiter, and of Titan, the principal Satellite of Saturn, made with the 26 inch Refractor of the U. S. Naval Observatory, Washington; 19 Oct. 1901. *Astr. Nachrichten* N⁰. 3764, (21 Jan. 1902).

Therefore;

	Sum of the diameters	Sum of the radii
I + II . . .	$0^{r}\cdot110$	$0^{r}\cdot055$
I + III . .	$0\cdot143$	$0\cdot0715$
I + IV . .	$0\cdot134$	$0\cdot067$
II + III . .	$0\cdot137$	$0\cdot0685$
II + IV . .	$0\cdot128$	$0\cdot064$
III + IV . .	$0\cdot161$	$0\cdot0805$

For the mean radii vectores we will take two figures more than did Damoiseau in his tables, and we will adopt for the purpose the values found by Souillart in Damoiseau's papers, (Souillart, second paper, Mémoires présentés par divers savants a l'Académie des Sciences, Tome XXX, 2^{me} Série, 1889; p. 10) 1).

I	6·0491,
II	9·6245,
III	15·3524,
IV	27·0027.

The result of our computation is, that the time between the first contact and the central occultation is:

for I and II I and III I and IV II and III II and IV III and IV
$1^{h}\cdot324$, $1^{h}\cdot245$, $1^{h}\cdot103$, $2^{h}\cdot263$, $1^{h}\cdot774$, $3^{h}\cdot725$;
between the central occultation and the second contact:
$1^{h}\cdot204$, $1^{h}\cdot161$, $1^{h}\cdot059$, $2^{h}\cdot190$, $1^{h}\cdot767$, $3^{h}\cdot725$,
therefore in all
$2^{h}\cdot528$, $2^{h}\cdot406$, $2^{h}\cdot162$, $4^{h}\cdot453$, $3^{h}\cdot541$, $7^{h}\cdot450$,
or
$2^{h}32^{m}$ 2) $2^{h}24^{m}$, $2^{h}10^{m}$, $4^{h}27^{m}$, $3^{h}32^{m}$, $7^{h}27^{m}$.

Still even these numbers do not represent the maximum of the time during which the two satellites may be seen as a single body. For we can imagine the case that the shortest distance becomes equal to $-(r+r')$, i. e. that between two central conjunctions there

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1) According to Souillart, Damoiseau derived these numbers in the following way: He adopted the mean distance of IV, in accordance with Pound's determination $= 496''0$, and took $18''\cdot37$ for Jupiter's semidiameter, so that, by division $r_{IV} = 27\cdot00102834$. The mean distances of the other satellites were then derived from the sidereal periods by the application of Keppler's third law. But to these mean distances he added the constant terms produced in the radii vectores by the perturbing force.

I beg leave to remark that $496''0 : 18''\cdot37$ is not $27\cdot00102834$ but $27\cdot000544366$. Happily the 4th, 5th, 6th, 7th and 8th figure have no appreciable influence on our computations, nor probably on those of Souillart. For the rest the 2nd appendix, further below, may be consulted on such numbers of many decimals.

2) On June 4, 1908, such a conjunction must take place according to our computation. *Vide* the table further below.

occurs a contact on the other side. In this case the duration will, very nearly indeed, have to be multiplied by $\sqrt{2}$. It thus becomes

for	I and II,	I and III,	I and IV,	II and III,	II and IV,	III and IV
	$3^{h}{\cdot}574$,	$3^{h}{\cdot}402$,	$3^{h}{\cdot}057$,	$6^{h}{\cdot}296$,	$5^{h}{\cdot}006$,	$10^{h}{\cdot}43$,
or:	$3^{h}34^{m}$,	$3^{h}24^{m}$,	$3^{h}\,3^{m}$,	$6^{h}18^{m}$,	$5^{h}\,0^{m}$,	$10^{h}26^{m}$.

These numbers hold only for those very rare occasions in which 1st. the occultation is central and 2nd. the rate of change of the elongation is equal or nearly so for the two satellites. As soon as there is some difference of latitude the time during which the two satellites are seen as a single body is of course smaller.

2nd. Appendix. *Investigation of the uncertainty, existing in the determination of the synodic periods of the satellites.*

In his introduction to the *Tables Ecliptiques*, p. XIX, Delambre says: "Nous n'avons aucune observation d'éclipse antérieure à 1660". Now let us assume that the difference in time between the first eclipse observed in 1660 and the last observed in 1816, two years before the publication of these tables, (taking into account also the next ones in 1660 and the preceding ones in 1816) leaves an uncertainty, in the case of the four satellites, of 20, 30, 40 and 60 seconds, which will be too favourable rather than too unfavourable. If we divide this uncertainty by the number of synodic periods in 156 years, to wit 32193, 16032, 7951 and 3401, we get for the uncertainty of a single period

for I	for II	for III	for IV
$0^{s}{\cdot}00062$,	$0^{s}{\cdot}00188$,	$0^{s}{\cdot}0050$,	$0^{s}{\cdot}0176$.

Therefore, if we find that Delambre gives these periods to 9 places of decimals of the second, we cannot attach much importance to the fact.

When Damoiseau, 20 years after Delambre, published new eclipse-tables[1]) for the satellites of Jupiter, he adopted the period of I un-

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[1]) The tables of Delambre and Damoiseau were destined mainly to serve for the prediction, in the astronomical ephemerides, of the eclipses of the satellites caused by the shadow of Jupiter. It is for this reason that both he and Delamrre, united all those terms of the perturbations in longitude which have the same argument at the time of the opposition of the satellites, even though these arguments might be different for all other points in the orbit. Therefore it becomes necessary once more to separate these terms as soon as tables have to be computed from which may be derived the longitude and the radii vectores of the four satellites for any point of their orbits, tables such as have been given by Bessel in his *Astronomische Untersuchungen* and by Marth in the *Monthly Notices of the Royal Astronomical Society*, Vol. LI, (1891).

changed, but applied the following corrections to the remaining ones:

$$\text{II} + 0^{s}\cdot 005\,127\,374,$$
$$\text{III} + 0\cdot 029\,084\,25,$$
$$\text{IV} - 0\cdot 092\,654\,834,$$

the amount of which is even respectively nearly 3, nearly 6 and somewhat over 5 times that of the uncertainties derived just now. But even if we increase the number of intervening years from 156 to 176, our estimated uncertainties are only diminished by about $\frac{1}{9}$ of their amount. We thus conclude that these periods can only be considered to be determined with certainty:

that of I to 3 decimals of the second
„ „ II, III and IV to 2 decimals „ „ „ .

The Nautical Almanac, which, where it gives the superior conjunctions of the satellites, gives also the synodic periods, wisely confines itself to three decimals. The use of 9 decimals may therefore provisionally be taken for astronomical humbug. Some other instances of the same kind might be quoted *e. g.* the formerly well known constants, 20″·4451 for the aberration and 8″·57116 for the parallax of the sun!

3rd Appendix. *Meaning of the equations taken into account in the 2nd part of the tables of* Damoiseau.

On p. 321 we have referred to the 3rd appendix for information as to the equations which have been taken into account for each satellite in the second part of the tables of Damoiseau. We will now supply this information; we will denote by U, u_o, u_{I}, u_{II}, u_{III} and u_{IV} the mean longitudes of the sun, of Jupiter and of the four satellites; by π_o the longitude of the perihelium of Jupiter, by π' that of the Earth, by π_{III} and π_{IV} the perijovia of III and IV; by Π the longitude of the ascending node of Jupiter's equator on its orbit; finally by $\varLambda_{\text{II}}$, $\varLambda_{\text{III}}$ and $\varLambda_{\text{IV}}$ the longitudes of the ascending nodes of II, III and IV each on its own fixed plane.

In order to be able to supply the data following below we have taken the daily motion of the argument of each equation from the tables in the second part of Damoiseau. This amount was then multiplied by the synodic period expressed in days; the product thus obtained was then compared with the factor by which, in the first part, p.p. (III), (V), (VII) and (VIII) the letter i (the number of synodic periods) is multiplied.

These daily motions are so nearly equal for several of the equations of II, III and IV that, in order to make them out, we must take from the tables the motions for a long interval, *e.g.* for 10 years, (duly taking into account the number of periods). These must then be divided by the number of days (10 years = 3652 or 3653 days). Multiplying this quotient by the synodic period in days, we get 360° + a fraction. The 360° are of no account; the fraction is the factor of i; we thus recognise which is the equation we have to deal with. In the preface of the second part of DAMOISEAU we look in vain for any information on the subject.

I. For this satellite five terms have been taken into account.

N°. 1 with an amplitude of 1°·16, is the equation of the velocity of light; its argument is $U - u_0$.

N°. 2, (amplitude 0°·29), is the equation caused by the ellipticity of Jupiter's orbit; the argument is the mean anomaly of Jupiter $u_0 - \pi_0$.

N°. 3 is 180° + the mean anomaly of the Earth, $U - \pi'$; by its aid and that of N°. 1 *i. e.* the difference in longitude between the Sun and Jupiter, we find, in the table of double entry IX, one term of the geocentric latitude of the satellite.

N°. 4 with an amplitude of 0°·45, shows the perturbation caused by II in the motion of I. The argument is $u_{\rm I} - u_{\rm II}$.

N°. 5, (amplitude 3°·07) gives the jovicentric latitude of I, necessary to find the second term of the geocentric latitude. The argument is $u_{\rm I} - \Delta_{\rm I}$.

II. Seven terms. N°. 1, 2 and 3 have the same arguments as the analogous terms for I; the amplitudes of N°. 1 and 2 are half those of I. The term of the latitude to be taken from IX, by the aid of 1 and 3, is of course the same for all the satellites.

N°. 4, (amplitude 1°·06), shows the perturbation caused by III in the motion of II. The argument is $u_{\rm II} - u_{\rm III}$.

N°. 5, 6 and 7 serve for the latitude.

N°. 5, (amplitude 3°·05), has the argument $u_{\rm II} - \pi_{\rm IV}$;
N°. 6, (,, 0 ·47), ,, ,, ,, $u_{\rm II} - \Delta_{\rm II}$;
N°. 7. (,, 0 ·03), ,, ,, ,, $u_{\rm II} - \Delta_{\rm III}$.

III, Nine terms. Nos. 1, 2 and 3 are the same as for I and II; the amplitudes of N°. 1 and N°. 2 are 0°·29 and 0°·07.

N°. 4, (amplitude 0°·07), has the same argument as N°. 4 for II, but it now shows the perturbation caused by II.

N°. 5, (amplitude 0°·15), is the equation of the centre; argument $u_{III}—\pi_{III}$.

N°. 6, (amplitude 0°·04), has the argument $u_{III}—\pi_{IV}$, it thus must account for a perturbation in III depending on the longitude of the perijovium of IV.

Nos. 7, 8 and 9, with the amplitudes 2°·98, 0°·18 and 0°·03, serve for the latitude. The arguments are respectively $u_{III}—\pi$, $u_{III}—\Lambda_{III}$ and $u_{III}—\Lambda_{IV}$.

IV. Seven terms.

Nos 1, 2 and 3 are similar to those of the preceding satellites.

N° 4, (amplitude 0°·83), is the equation of the centre, argument $u_{IV} — \pi_{IV}$.

Nos 5, 6 and 7 serve for the latitude. N° 5, (amplitude 2°·64) depends on the mean anomaly of Jupiter; its argument therefore is $u_0 — \pi_0$.

N° 6, (amplitude 0°·24), depends on the argument of the latitude of the satellite itself; argument $u_{IV}— \Lambda_{IV}$.

N° 7, (amplitude 0°·04), is a minute perturbation, caused by III; its argument is $u_{IV}—\Lambda_{III}$.

Now in regard to the following table of the computed conjunctions. The first column contains the ordinal numbers.

The second shows the epoch of the conjunction, accurate to the nearest minute, expressed in civil time of Paris. This time is reckoned from midnight and has been used by DAMOISEAU in his tables; it thus represents the direct result of our computations. In the cases that the computed time was just a certain number of minutes and a half, the half minute has been set down. By subtracting $12^u\ 9^m$ or, where necessary, $12^u\ 9^m{\cdot}35$, the mean time of Greenwich was found, which is contained in the third columm.

The 4th and the 5th columm contain the numbers of the occulted and the occulting satellite. The appended letters *f* and *n* show whether the satellite is *far* or *near* (vide supra p. 304). The satellite is *far* if its amplitude is between 9^s and 3^s, *near* if it is between 3^s and 9^s. Furthermore *ee* denotes an eastern elongation, for which the amplitude is about 3^s and *w e* a western elongation, for which the amplitude differs little from 9^s.

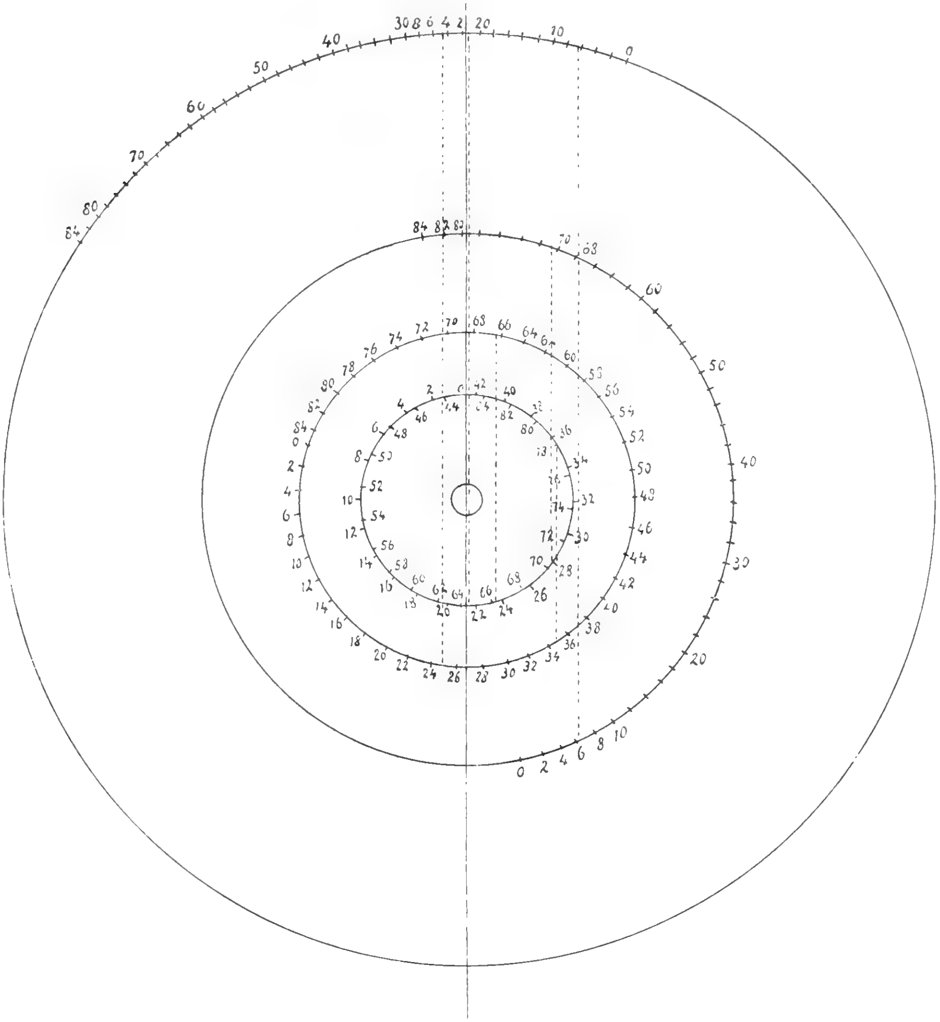
At the conjunction the elongations, counted along the orbit of Jupiter, are equal; they are to be found in the next column. If the elongation is +, the satellite, as seen by a northern observer, using a terrestrial telescope, will be to the left of the planet. Therefore if he uses an inverting telescope, as is the rule for the observation of the heavenly bodies, he will see it to the right.

The three following columns contain the ordinates of the two satellites and their difference; northerly latitudes are positive. The tenth column shows the duration, which the eclipse would have, if the conjunction were central. In a few cases (Nos. 20, 23, 30, 48, 53 and 64), we find $y' = y$, consequently $y' - y = 0$. If the tables were correct these conjunctions would be central. But in testing the tables by the conjunctions observed by Messrs FAUTH, NIJLAND and STANLEY WILLIAMS the difference of the y's did not completely agree with the observations and even a small difference may considerably change the duration of any eventual occultation. Therefore, not to fill a column with figures, which, likely enough, may be contradicted by the observations, I omitted the value found by calculation for the true duration.

We remarked before (p. 308) that, if at all, any conjunction will be visible at a determined place of observation only for a short time, *viz.* between sunset and the setting of Jupiter. As a consequence the list will be of little use, unless observatories distributed over the whole of the earth cooperate in the work. The last column was added as a help to such cooperation. It contains on every line an observatory, at which the conjunction of that line will be visible. It is certainly desirable that other astronomers also, at observatories in the vicinity, examine whether the phenomenon will be visible, and, if so, prepare for its observation.

A. C. OUDEMANS. „Mutual Occultations and Eclipses of the Satellites of Jupiter in 1908.”

Starting point: the geocentric superior conjunction of I on July 12, 1908, at 11h 2m.3 M. T. Greenwich = 11h 11m.65 M. T. Paris = 23h 11m.65 civil time Paris.



Scale $\frac{1}{30\,168\,000\,000}$; 1mm. = 8″ heliocentric.

Unit: the radius of the earth's equator.

RESULTS.

Geocentric conjunctions of two satellites in June and July 1908.

No.	Civil time at Paris	Mean time at Greenwich	n = near f = far		$x = x'$	Occulted satellite y	Occulting satellite y'	$y' - y$	Duration of central occultation	visible at
			Occulted satellite	Occulting satellite						
1	1 June 5^h55^m	31 May 17^h46^m	I_n	II_n	$+2^r18$	-0^r16	-0^r12^5	$+0,03^5$	45^m	Mt. Hamilton
2	1 » 18 25	1 June 6 16	I_{we}	II_n	−6, 03	+0, 31	+0, 29	−0, 02	11	Cape
3	2 » 1 55	1 » 13 46	I_f	IV_n	−3, 15	+0, 18	−0, 12	−0, 30	7	Washington
4	2 » 13 16	2 » 1 7	III_f	II_f	−8, 51	+0, 51	+0, 38	−0, 13	60	Madras, H. Kong
5	2 » 14 0	2 » 1 51	III_f	IV_n	−8, 16	+0, 51	+0, 13	−0, 38	11	Madras, H. Kong
6	2 » 14 4,5	2 » 1 55	II_f	IV_n	−8, 20	+0, 37	+0, 13	−0, 24	10	Madras, H. Kong
7	2 » 21 10	2 » 9 1	III_f	II_f	−4, 54	+0, 31	+0, 20	−0, 11	41	Utrecht
8	3 » 3 15	2 » 15 6	II_f	I_n	$-0,33^5$	0, 00	−0, 03	−0, 03	4	At the same time ☌ ♃
9	3 » 3 50	2 » 15 41	III_f	I_n	−0, 87	+0, 15	0, 00	−0, 15	6	
10	4 » 14 46	4 » 2 37	I_n	II_n	$x=+5,01^5$ $x'=+5,07$	−0, 29	$-0,25^5$	$+0,03^5$		Two contacts at the same side. II just reaches central conjunction but then retraces its steps. Madras
»	4 » 16 0	4 » 3 51	»	»	4, 34					
»	4 » 17 15	4 » 5 6	»	»	$x=+3,54$ $x'=+3,48^5$	−0, 23	$-0,19^5$	$+0,03^5$		
	The satellites will be visible as one body during nearly 2½ hours.									
11	5 » 7 51	4 » 19 42	I_{we}	II_f	−6, 05	+0, 33	+0, 28	−0, 05	12	Sydney
12	6 » 16 24	6 » 4 15	II_f	I_n	−0, 48	0, 00	−0, 01	−0, 01	4	At the same time ☌ ♃
13	6 » 18 11,5	6 » 6 2	II_f	III_n	+0, 82	−0, 06	−0, 17	−0, 11	6	and II eclipsed?
14	9 » 5 6	8 » 16 57	IV_f	II_f	−9, 19	+0, 59	+0, 43	−0, 16	13	Mt. Hamilton
15	10 » 4 26	9 » 16 17	IV_f	I_n	+0, 29	+0, 14	$-0,05^5$	$-0,19^5$	6	At the same time ☌ ♃
16	10 » 5 23	9 » 17 14	II_f	I_n	−0, 58	+0, 02	−0, 01	−0, 03	5	
17	10 » 6 28	9 » 18 18,5	III_f	I_n	−1, 54	+0, 15	+0, 05	−0, 10	6	Mt. Hamilton
18	11 » 3 0	10 » 14 51	IV_f	III_f	+9, 01	−0, 32	−0, 52	−0, 20	183	Washington
19	12 » 10 34	11 » 22 25	I_{we}	II_n	−6, 03	+0, 32	+0, 28	−0, 04	11	Wellington
20	13 » 18 46,5	13 » 6 37	II_f	I_n	−0, 82	$+0,01^5$	$+0,01^5$	0, 00	4	☌ ♃
21	13 » 21 37	13 » 9 28	II_f	III_n	+1, 31	−0, 07	−0, 16	−0, 09	6, 5	II eclipsed (Utrecht)
22	15 » 23 55	15 » 11 46	I_{we}	II_n	−5, 99	+0, 32	+0, 29	−0, 03	10	(Atl. Ocean)
23	17 » 7 53	16 » 19 44	II_f	I_n	−0, 92	+0, 02	+0, 02	0, 00	4	☌ ♃

No.	Civil time at Paris	Mean time at Greenwich	n = near f = far		$x = x'$	Occulted satellite y	Occulting satellite y'	$y' - y$	Duration of central occultation	Visible at
			Occulted satellite	Occulting satellite						
24	17 June 9^h39^m	16 June 21^h30^m	III_f	I_n	-2^r44	$+0^r18$	$+0^r10$	-0^r08	6^m	Wellington
25	17 » 20 47	17 » 8 38	II_f	IV_n	+7, 33	—0, 37	—0, 52	—0, 15	9	Utrecht
26	18 » 0 33	17 » 12 24	III_f	IV_n	+5, 75	—0, 28	—0, 44	—0, 16	10	(Atl. Ocean)
27	18 » 7 30	17 » 19 21	I_f	IV_n	+2, 86	—0, 16	—0, 30	—0, 14	6, 5	Sydney
28	18 » 8 28	17 » 20 18	III_f	II_{ee}	+9, 52	—0, 51	—0, 45	+0, 06	15	Sydney
29	19 » 13 13	19 » 1 4	I_{we}	II_n	—5, 94	+0, 32	+0, 29	—0, 03	9, 5	Hong Kong
30	20 » 21 3	20 » 8 54	II_f	I_n	—1, 07	+0, 02	+0, 04	+0, 02	4	Utrecht
31	21 » 1 3	20 » 12 54	II_f	III_n	+1, 79	—0, 11	—0, 15	—0, 04	6, 5	II eclipsed
32	21 » 11 54	20 » 23 45	I_f	III_n	—4, 21	+0, 24	+0, 18	—0, 06	7	Hong Kong
33	23 » 2 32	22 » 14 23	I_{we}	II_n	—5, 90	+0, 32	+0, 29	—0, 03	9	Washington
34	24 » 10 13	23 » 22 4	II_f	I_n	$-1,22^5$	+0, 03	+0, 01	—0, 02	4	Sydney
35	24 » 12 37	24 » 0 27	III_f	I_n	—3, 21	+0, 20	+0, 16	—0, 04	6, 5	Hong Kong
36	26 » 11 17	25 » 23 8	IV_f	I_n	—5, 60	+0, 35	$+0,30^5$	$-0,04^5$	11	Hong Kong
37	26 » 13 43.5	26 » 1 34	IV_f	II_n	—4, 61	+0, 31	+0, 25	—0, 06	7	Madras, H. Kong
38	26 » 15 49	26 » 3 40	I_{we}	II_n	—5, 84	+0, 32	+0, 30	—0, 02	9	Madras
39	27 » 0 27	26 » 12 18	IV_f	I_f	—0, 18	—0, 01	+0,	+0, 04	20	☌ ♃
40	27 » 13 44	27 » 1 35	IV_f	I_n	+5, 66	—0, 17	—0, 3	—0, 14	11	Madras, H. Kong
41	27 » 18 56	27 » 6 47	IV_f	III_n	+7, 38	—0, 20	—0, 45	—0, 25	10	Cape
42	27 » 23 24	27 » 11 14	II_f	I_n	—1, 38	+0, 03	+0, 07	+0, 04	4	(Atl. Ocean)
43	28 » 14 57	28 » 2 48	I_f	III_n	—3, 49	+0, 20	+0, 17	—0, 03	7	Madras
44	30 » 5 5.5	29 » 16 56	I_{we}	II_n	—5, 75	+0, 31	+0, 31	0, 00	4	Mt. Hamilton
45	1 July 12 34	1 July 0 25	II_f	I_n	—1, 53	+0, 09	+0, 04	—0, 05	4	Hong Kong
46	1 » 15 40	1 » 3 31	III_f	I_n	—3, 93	+0, 23	+0, 21	—0, 02	5	Central Asia
47	2 » 16 21.5	2 » 4 12	III_f	II_n	+9, 14	—0, 48	—0, 42	+0, 06	12	» »
48	3 » 18 21	3 » 6 12	I_f	II_n	—5, 68	+0, 31	+0, 31	0, 00	7	Cape
49	3 » 20 8	3 » 7 58.5	III_{ee}	IV_n	+15, 30	—0, 85	—0, 79	+0, 06	32	Berlin etc.
50	5 » 1 44	4 » 13 35.0	II_f	I_n	—1, 67	+0, 03	+0, 10	+0, 07	4	Washington
51	5 » 6 25	4 » 18 16	II_f	IV_n	+1, 66	—0, 12	—0, 15	—0, 03	7	II eclipsed

Pathology. — *"On the Amboceptors of an Anti-streptococcus serum."*

By H. Eysbroek. (From the Pathological Institute of Utrecht).
(Communicated by Prof. C. H. H. Spronck.)

(Communicated in the meeting of September 29, 1906).

As is known, there exists in the serum of an animal which is treated with the bloodcorpuscles of an animal of another species, a substance, which is capable of bringing the bloodcorpuscles of the second animal to solution with the aid of another substance, which is already present in normal serum. The first substance, which only appears in immune-sera, is thermostatic and is named differently by different investigators, according to the idea which they make of its influence (Amboceptor of Ehrlich, Substance sensibilisatrice of Bordet, Fixateur of Metchnikoff). The other substance, which normally is present in all sorts of sera in greater or smaller quantities, is easily made inactive by heating to 55—56° C. or by being exposed to light. It has been proved, that the last mentioned substance is identical with a bactericidal substance, demonstrated by Fodor [1]) and Flügge [2]) in normal blood-serum, to which is given the name of alexin by Buchner. Next to this name at present the denominations complement (Ehrlich) and cytase (Metchnikoff) are used.

Had Metchnikoff in 1889 already pointed out the analogy between hemolytic and bacteriolytic processes, later investigations have completely comfirmed this supposition.

In 1901 Bordet and Gengou [3]) published a method to demonstrate the presence of a "substance sensibilisatrice" in the serum of an animal, which was immunized against a certain micro-organism, by means of a combination with the complement. At the same time they found, that this amboceptor is specific; for instance, the amboceptor, present in the bloodserum of animals which were immunized against cholera spirilla, is indeed active against the cholera spirilla, but not against other bacteria, such as the typhoid bacilli.

On the other hand one is capable of distinguishing with the aid of an amboceptor at hand, the micro-organism belonging to it from others, by means of a combination with the complement.

Using the above mentioned method of Bordet—Gengou, Besredka [4]) succeeded in pointing out an amboceptor also in an anti-streptococcus

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[1]) Deutsche Med. Wochenschrift, 1887, N⁰. 34, S. 745.

[2]) Zeitschrift für Hygiene, Bd. IV, S. 208.

[3]) Annales de l'Inst. Pasteur, T. 15, 1901, p. 289.

[4]) Annales de l'Inst. Pasteur, T. 18, 1904, p. 363.

serum prepared by himself. This serum was obtained from a horse, which for some time was injected intravenously with a mixture of 6—8 different streptococci, which but for one exception originated immediately, so, without passage through animals, from pathological processes of man. Besides, he has made use of the presence of an amboceptor in his serum to investigate, whether it might be possible to separate different races of streptococci from each other with the aid of this substance.

Among the principal difficulties, which are still experienced in the preparation of an anti-streptococcus serum, must be mentioned in the first place, that the streptococci proceeding directly from pathological processes of man and being very virulent for him (scarlatina, erysipelas, septicemia etc.) possess in general for our common test-animals a comparatively small degree of virulency. By this the preparation of a very powerful serum is somewhat impeded and on the other hand it is almost impossible to controll the obtained serum. In the second place the question prevails, whether all streptococci, cultivated from different processes of disease, must be regarded as representatives of one and the same species, and to be taken as varieties, or that the mutual affinity is much smaller. A solution of this question in such a sense, that it might be possible to come to a rational sub-division in the large group of the pathogenic streptococci, would be of great importance for the bloodserum-therapy.

Some years ago SCHOTTMÜLLER [1]) tried to give a new division, based on biological grounds instead of the older morphological division in streptococcus longus and streptococcus brevis (VON LINGELSHEIM [2]), BEHRING [3]). By cultivating different races of streptococci on blood-agar, he was enabled to discern two types: firstly dark grey colonies with lucid area, secondly greenish ones without area. The streptococci, belonging to the first group, are very virulent for man and are found in erysipelas, septicemia, scarlatina, phlegmon etc., while those, belonging to the second group, are generally less pathogenic for man and animals. Therefore SCHOTTMÜLLER divides the pathogenic streptococci as follows:

1. Streptococcus pyogenes s. erysipelatos.
2. Streptococcus mitior s. viridans.
3. Streptococcus mucosus.

Several other investigators (EUG. FRAENKEL [4]), SILBERSTROM [5]),

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[1]) Münch. Med. Wochenschrift, 1903, N⁰. 20, S. 849; N⁰. 21, S. 909.

[2]) Zeitschrift für Hygiene, Bd. X, S. 331.

[3]) Centralblatt. für Bakteriologie, Bd. 12, S. 192.

[4]) Münch. Med. Wochenschrift, 1905, N⁰. 12, S. 548; N⁰. 39, S. 1869.

[5]) Centralblatt für Bakt., 1e Abth., Orig., Bd. 41, S. 409.

Baumann [1]) have latterly come to the same result in an almost similar way.

Besredka [2]) on the contrary tried to separate the different streptococci from each other with the aid of the method of the combination with the complement. The conclusion to which he comes, is, that the "substances sensibilisatrices" present in his serum, are "rigoureusement" specific; that the serum of a horse, immunized with the streptococcus *A*, only contains the amboceptor *A''*, which corresponds with that special streptococcus. Thus he found this amboceptor *A''* not only active against the streptococcus *A*, but also against other races (*B*, *C*), from which Besredka decides on the identity or at least on the near relationship of the above mentioned streptococci *A*, *B* and *C*.

According to these results, some experiments have been taken by me, to trace, in how far a separation of the different pathogenic streptococci is really possible by means of the specific action of the amboceptors.

The anti-streptococcus serum, which I used, Prof. Spronck willingly provided me with, for which I offer him my best thanks as well as for his further assistance in my work.

The above mentioned serum originated from a horse, which was injected for a great length of time viz. from Jan. 1905 till July 1906, with a number of specimens of streptococci and staphylococci of different origin. These injections, which were subcutaneous, took place weekly. The quantities used were gradually increased during the first months; whilst after that on an average 40—60 c.C. of a mixture, composed of even parts of a culture in ascitic-bouillon of the different streptococci and of a bouillon-culture of the staphylococci, were administered. The mixture was twice heated for half an hour to 55° C. Strepto- as well as staphylococci originated directly from man, without passage through animals.

That the serum really possesses curative qualities is evident, not only from observations in the clinical surgery, but also from experiments upon animals. Rabbits, which were injected with a mixture of strepto- and staphylococci, could be kept alive by administering comparatively small quantities of the anti-streptococcus serum, whilst animals used for controll died shortly after.

The method, followed by me, is that of Bordet—Gengou [3]). For

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[1]) Münch. Med. Wochenschrift, 1906, N°. 24, S. 1193.

[2]) l. c.

[3]) l. c.

each experiment six tubes were used, which contained consecutively [1]:

N°. 1: $^2/_{10}$ c.C. complement, $^1/_2$ c.C. emulsion of streptococci, $^1/_2$ c.C. anti-streptococcus serum.

N°. 2: $^2/_{10}$ c.C. compl., $^1/_2$ c.C. emulsion of str., $^1/_2$ c.C. normal horse-serum.

N°. 3: $^2/_{10}$ c.C. compl., $^1/_2$ c.C. physiological NaCl, $^1/_2$ c.C. anti-streptococcus serum.

N°. 4: $^2/_{10}$ c.C. compl., $^1/_2$ c.C. physiol. NaCl, $^1/_2$ c.C. normal horse-serum.

N°. 5: $^2/_{10}$ c.C. physiol. NaCl, $^1/_2$ c.C. emulsion of str., $^1/_2$ c.C. anti-streptococcus serum.

N°. 6: $^2/_{10}$ c.C. physiol. NaCl, $^1/_2$ c.C. emulsion of str., $^1/_2$ c.C. normal horse-serum.

The tubes are stirred and then remain at the same temperature as the room. Afler 3—5 hours to each of the tubes is added $^2/_{10}$ c.C. of a mixture, composed of 2 c.C. of hemolytic serum and 1 c.C. corpuscles of a rabbit, which were suspended in physiol. NaCl to remove the adherent serum. Very soon, mostly within ten minutes the tubes 2, 3 and 4 distinctly show the phenomenon of hemolyse; which is naturally not brought about in tubes 5 and 6, the complement being absent. The absence or presence of an amboceptor in the examined serum is proved by the existence or non-existence of the hemolyse in the first tube.

It is necessary to repeat all these controll-experiments each time; firstly, because some streptococci produce a hemolysin at their growth; secondly, because bacteria are able to combine the complement without the aid of an amboceptor, although in a much smaller degree. This may be observed very distinctly in vitro; for instance: in six tubes successive dilutions of a culture of diphtheria bacilli were made; to each tube $^2/_{10}$ c.C. of the complement was added. After three hours $^2/_{10}$ c.C. of a mixture, composed of 2 c.C. of hemolytic serum (heated to 56° C.) and 1 c.C. corpuscles of a rabbit, suspended in physiol. NaCl, was added. The result after half an hour was as

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[1] As complement, the fresh blood-serum of a guinea-pig was used. The streptococci, which were to be examined, were cultivated on LOEFFLER's coagulated blood-serum and after 24 hours suspended in physiological NaCl to a homogeneous emulsion. The antistreptococcus serum was heated in advance for one hour to 56° C., as well as the fresh normal horse-serum, used for controll, and the hemolytic serum originating from guinea-pigs, which were treated 3 or 4 times with 5 c.C. of defibrinated blood of rabbits. The physiological NaCl used, was always a solution f 0,9%.

follows: no hemolyse in the first (least diluted) tube, a little hemolyse in the 2nd tube, more and more hemolyse in tubes 3, 4 and 5 whilst in the sixth (most diluted) tube it was perfect.

The same experiment was made with different other bacteria with a similar result.

It may be easily understood, that it sometimes occurs, that no hemolyse is formed in the first of the tubes, used in the method of BORDET—GENGOU, in consequence of a surplus of bacteria, as is seen by the absence of the hemolyse in the second tube at the same time. Without the controll-tubes, one might wrongly decide on the presence of an amboceptor in the examined serum.

In the first place an investigation was made, whether in the anti-streptococcus-serum, used by me, an amboceptor was present against some five streptococci used at the immunization. The result was positive. After this, different other streptococci were investigated. These streptococci originated directly from different diseases of man, such as: scarlatine, cholecystitis, septicemia, febris puerperalis, angina, and had not served at the immunization. Among these streptococci there were some of patients who during their lifetime had been injected with the same anti-streptococcus serum, but without success.

The latter streptococci were cultivated from the blood or from the spleen post mortem. Others were cultivated from patients with whom the injections of the serum had had a very distinct curative effect. It was therefore supposed that against the first streptococci no amboceptor would be found in the anti-streptococcus serum.

The investigation however did not confirm this supposition. *All streptococci, no matter what their origin, showed a strong combination with the complement under the influence of the anti-streptococcus serum.*

Keeping to the specific of the amboceptors, the conclusion of BESREDKA [1]) might be accepted, regarding all the latter streptococci as identic or at least closely related to those used at the immunization. Continued experiments with some pathogenic streptococci originating from animals, have led to a different interpretation. A streptococcus was used, which was cultivated from the lungs of a guinea-pig, which had died spontaneously from pneumonia; further the well-known streptococcus equi and a couple of other streptococci, which were cultivated with the Str. equi from pus, originating from horses suffering from strangles. Also against the latter streptococci, the presence of an amboceptor in the used serum was an undoubted fact.

Considering that the str. equi by its qualities, apparently from its

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[1]) l. c.

deviating growth on the usual culture-media, shows very distinct differences from the other pathogenic streptococci, whether from man or from animals, the conclusion is at hand, that at least in the anti-streptococcus serum, used by me, very little of the specific working of the amboceptor is left. It is however quite possible that all pathogenic streptococci, originating from man as well as from animals, are very closely related, by which supposition one might keep at least to the specific of the amboceptors.

However later experiments have shown that the anti-streptococcus serum is also active against micro-organisms, which do not belong to the streptococci viz, pneumococci and meningococci.

By the above is fully shown, that the specific action of the amboceptors in the serum of a horse to which large quantities of streptococci have been administered for a very long time, has strongly decreased and made room for a more general action. Probably this general working might be put to the account of one and the same amboceptor, although the presence of more amboceptors in the same cannot be denied.

The above mentioned serum exercises, though in a small degree, also a distinctly sensitive action on anthrax, typhoid and tubercle bacilli.

From the above it appears, that the method of the combination with the complement of Bordet—Gengou, is not to be used, if it is necessary to distinguish nearly related bacteria from each other, which in other ways are also difficult to separate.

Granted that it must be accepted, that such a diminution of the specific activity only takes place with sera of animals which have been treated for a great length of time, so that the specific activity of the amboceptor is more asserted in proportion to the shorter time in which the animals are immunized, it is evident here, that there is no question about a certain method being used, because one never knows, — and this is also the case with sera of animals which have only shortly been immunized — how far the specific action extends. Even if it may be accepted that the horse, from whom the anti-streptococcus serum originates, is a most favourable test-animal as regards the forming of anti-bodies, then the above mentioned facts would remain the same.

Dopter[1]) has recently found, that the amboceptor, present in the serum of a horse which has been treated with dysenteria bacilli (type Shiga) during 18 months, next to the action on these bacilli,

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[1]) Annales de l'Inst. Pasteur, T. 19. 1905, p. 753.

also presented the self-same effect against the so-called pseudo- or para-dysenteria bacilli (type FLEXNER, KRUSE). Asserting the specific activity of the amboceptor, he decides on "l'unité specifique" of the dysenteria bacilli. This conclusion appears to me, looking at the above, very venturesome.

At the same time it is evident, that we must not attach too much importance to the presence of an amboceptor in a serum for the effect of that serum. It is not to be accepted, that the anti-streptococcus serum will have a favourable effect on patients suffering from pneumonia, typhus, anthrax etc. although a certain effect is to be observed in vitro against the respective causes of these diseases. I purposely treated this for anthrax bacilli. Different guinea-pigs of nearly the same weight received partly a small quantity of anti-streptococcus serum (2—3 c.C.), which contained some anthrax bacilli (one eye of a deluted twelve hours, old culture on bouillon-agar), partly normal horse-serum (2—3 c.C.) with an equal dose of anthrax bacilli. A favourable effect of the anti-streptococcus serum compared to normal serum was never perceptible. The animals died generally about the same time, within 48 hours.

Yet PREDTETSCHENSKY [1]), who has made such investigations with rabbits, is of opinion that a favourable effect can be perceived from anti-diphtheria as well as from anti-streptococcus serum, but the colossal quantities of serum, which he used, justify the supposition, that here is only question of the favourable effect, which, as is known, is already produced in several cases by the injection of normal horse-serum.

It is therefore not permissible, to ascribe a favourable effect to a serum by force of the presence of an amboceptor, still less, to base on this a quantitative method for the determination of the force of such a serum, such as KOLLE and WASSERMANN [2]) do with regard to a meningococcus serum prepared by them. In the meningococcus serum of JOCHMANN (E. MERCK) the presence of an amboceptor could not only be clearly discerned against meningococci, but also, naturally in a smaller degree, against some streptococci.

The question, if such a diminishing of the specific activity in relation to a prolonged administering of antigens is known for other substances in immune-sera too, must be answered in the affirmative. This is especially the case with regard to the precipitins. It is well known that it is not possible to obtain them absolutely specific. Thus NUTTALL [3]) was able to get a precipitation with the blood-serum of all kinds

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[1]) Centralblatt für Bakt., 1e Abth., Ref., Bd. 38, S. 395.

[2]) Deutsche Med. Wochenschrift, 1906, n⁰ 16, S. 609.

[3]) Blood immunity and blood relationship, Cambridge, 1904, p. 74, 135, 409.

of mammals even with a very strong precipitin-serum, which was obtained with and against an arbitrary mammifer-albumen ("mammalian reaction"). HAUSER [1]) comes to a similar result; only quantitative differences remain.

Also with relation to the amboceptor such a diminution of the specific action seems to me sufficiently well pointed out.

Physics. — "*Arbitrary distribution of light in dispersion bands, and its bearing on spectroscopy and astrophysics.*" By Prof. W. H. JULIUS.

In experimental spectroscopy as well as in the application of its results to astrophysical problems, it is customary to draw conclusions from the appearance and behaviour of spectral lines, as to the temperature, density and motion cf gases in or near the source of light.

These conclusions must in many cases be entirely wrong, if the origin of the dark lines is exclusively sought in absorption and that of the bright ones exclusively in selective emission, without taking into account the fact that the distribution of light in the spectrum is also dependent on the anomalous dispersion of the rays in the absorbing medium.

It is not in exceptional cases only that this influence makes itself felt. Of the vapours of many metals it is already known that they bring about anomalous dispersion with those kinds of light that belong to the neighbourhood of several of their absorption lines [2]). In all these cases the appearance of the absorption lines must to a greater or less extent be modified by the above mentioned influence, since the mass of vapour, traversed by the light, is never quite homogeneous.

Hence it is necessary, separately to investigate the effect of dispersion on spectral lines; we must try to separate it entirely from the phenomena of pure emission and absorption.

A first attempt in this direction were the formerly described experiments with a long sodium flame [3]), in which a beam of white

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[1]) Münch. Med. Wochenschrift, 1904, n⁰ 7, S. 289.

[2]) After WOOD, LUMMER and PRINGSHEIM, EBERT, especially PUCCIANTI has investigated the anomalous dispersion of various metallic vapours. In Nuovo Cimento. Serie V, Vol. IX, p. 303 (1905) PUCCIANTI describes over a hundred lines, showing the phenomenon.

[3]) W. H. JULIUS, "Dispersion bands in absorption spectra." Proc. Roy. Acad. Amst. VII, p. 134—140 (1904).

light alternately travelled along different paths through that flame. With these relative displacements of beam and flame the rays of the anomalously dispersed light were much more bent, on account of the uneven distribution of the sodium vapour, than the other rays of the spectrum; absorption and emission changed relatively little. The result was, that the distribution of the light in the neighbourhood of D_1 and D_2 could be made very strongly asymmetrical, which could easily be explained in all details as the result of curvature of the rays. The existence of "dispersion bands" was thus proved beyond doubt.

But the pure effect of emission and absorption was not absolutely constant in these experiments and concerning the density of the sodium vapour in the different parts of the flame only conjectures could be made. Moreover, the whirling ascent of the hot gases caused all rays, also those which suffered no anomalous dispersion, sensibly to deviate from the straight line, so that the phenomena were too complicate and variable to show the effect of dispersion strictly separated from that of emission and absorption.

So our object was to obtain a mass of vapour as homogeneous as possible and, besides, an arrangement that would allow us to bring about arbitrarily, in this vapour, local differences of density in such a manner, that the average density was not materially altered. The absorbing power might then be regarded as constant. At the same time it would be desirable to investigate the vapour at a relatively low temperature, so that its emission spectrum had not to be reckoned with.

In a series of fine investigations on the refractive power and the fluorescence of sodium vapour R. W. WOOD[1]) caused the vapour to be developed in an electrically heated vacuum tube. It appeared possible, by adjusting the current, to keep the density of the vapour very constant. Availing myself of this experience I made the following arrangement for the investigation of dispersion bands.

Apparatus.

NN' (see fig. 1) is a nickel tube of 60 centimetres length, 5.5 cms. diameter and 0,07 cm. thickness. Its middle part, having a length of 30 cms., is placed inside an electrical furnace of HERAEUS (pattern E 3). Over its extremities covers are placed, the edges of which fit into circular rims, soldered to the tube, and which consequently

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[1]) R W. WOOD, Phil. Mag. [6], 3, p. 128; 6, p. 362.

shut air-tight when the rims are filled with cement. When the furnace is in action a steady current of water, passing through the two mantles *M* and *M'*, keeps the ends of the tube cool. Each of the two caps has a rectangular plate glass window and also, on both sides of this, openings *a* and *b* (*b'* and *a'*), placed diametrically

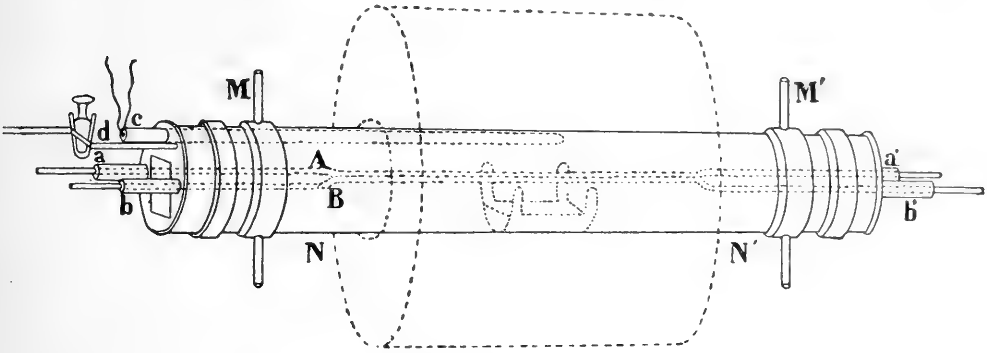

Fig. 1.

opposite to each other and provided with short brass tubes, the purpose of which will appear presently. Moreover in one of the two caps (see also fig, 2) two other short tubes *c* and *d* are fastened in openings: through *c* the porcelain tube of a Le Chatelier pyrometer is fitted air-tight, while on *d* a glass cock with mercury lock is cemented, leading to a manometer and a Geryk air-pump. As soon as the sodium (a carefully cleaned piece of about 7 grammes) had been pushed to the middle of the tube in a small nickel dish provided with elastic rings, the tube had been immediately closed and exhausted.

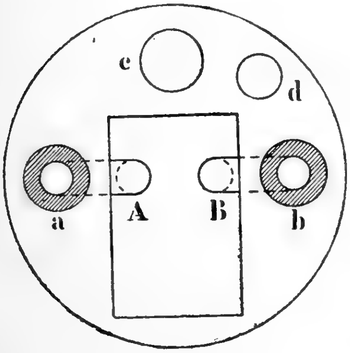

Fig. 2.

We shall now describe the arrangement by which inside the mass of vapour arbitrary inequalities in the density distribution were produced. It consists of two nickel tubes *A* and *B* of 0,5 cm. diameter, leading from *a* to *a'* and from *b* to *b'* and so bent that in the heated middle part of the wide tube they run parallel over a length of 30 centimetres at a distance of only 0.8 cms. In the four openings of the caps, *A* and *B* are fastened air-tight by means of rubber packing, This kind of connection leaves some play so that by temperature differences between the wide and the narrow tubes these latter need not alter their shape through tension. At the same time the rubber insulates *A* and *B* electrically from *NN'*. The four ends of the narrow tubes which stick out are kept cool by mantles with streaming water (these are not represented in the figure).

If now an electric current is passed through *A* or *B*, the temperature of this tube rises a little above that of its surroundings; if an air-current is passed through it, the temperature falls a little below that of its surroundings. The intensities of the currents and, consequently, the differences of temperature can in either case be easily regulated and kept constant for a long time.

Fig. 3.

Fig 3 gives a sketch of the whole arrangement. The light of the positive carbon *L* is concentrated by the lens *E* on a screen *Q*, having a slit-shaped aperture of adjustable breadth. The lens *F* forms in the plane of the slit *S* of the spectrograph a sharp image of the diaphragm *P*. The optical axis of the two lenses passes through the middle of the tube containing the sodium vapour, exactly between the two small tubes *A* and *B*.

If now the opening in the diaphragm *P* has the shape of a vertical narrow slit and if its image falls exactly on the slit of the spectograph, then in this latter the continuous spectrum of the arc-light appears with great brightness. If the tube *NN'* is not heated, D_1 and D_2 are seen as extremely fine dark lines, attributed to absorption by the sodium, which is always present in the neighbourhood of the carbons. In order that this phenomenon might always be present in the field of view of the spectograph as a comparison spectrum, also when the tube is heated, a small totally reflecting prism was placed before part of the slit *S*, to which part of the principal beam of light was led by a simple combination of lenses and mirrors without passing the electric furnace. So on each photograph that was taken the unmodified spectrum of the source is also seen.

The spectral arrangement used consists of a plane diffraction grating 10 cms. diameter (ruled surface 8 by 5 cms.) with 14436 lines to the inch, and two silvered mirrors of ZEISS; the collimator mirror has a focal distance of 150 cms., the other of 250 cms. Most of the work was done in the second spectrum.

When heating the sodium for the first time a pretty large quantity of gas escaped from it (according to WOOD hydrogen), which of course was pumped off. After the apparatus had functionated a couple of times, the tension within the tube remained for weeks less than 1 mm. of mercury, also during the heating, which, in the experiments described in this paper, never went beyond 450°. The inner wall of NN' and also the small tubes A and B are after a short time covered with a layer of condensed sodium, which favours the homogeneous development of the vapour in subsequent heatings. It is remarkable that scarcely any sodium condenses on the parts of the tube that stick out of the furnace, so that also the windows remain perfectly clear. The density of saturated sodium vapour at temperatures between 368° and 420° has been experimentally determined by JEWETT [1]). He gives the following table.

temperature	density
368°	0.00000009
373	0.00000020
376	0.00000035
380	0.00000043
385	0.00000103
387	0.00000135
390	0.00000160
395	0.00000270
400	0.00000350
406	0.00000480
408	0.00000543
412	0.00000590
418	0.00000714
420	0.00000750

These densities are of the same order of magnitude as those of mercury vapour between 70° and 120°. At 387° the density of

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[1]) F. B. JEWETT, A new Method of determining the Vapour-Density of Metallic Vapours, and an Experimental Application to the Cases of Sodium and Mercury. Phil. Mag. [6], 4, p. 546. (1902).

saturated sodium vapour is about $\frac{1}{1000}$ of that of the atmospheric air at 0° and 76 cms.

Observations.

If we now regulate the intensity of the current in the furnace in such a manner that the thermo-couple indicates a steady temperature (in many of our experiments 390°), then within the tube the density of the vapour is not everywhere the same, to be sure, for the temperature falls from the middle towards the ends, but since the surfaces of equal temperature are practically perpendicular to the beam of light, all rays pass nearly rectilinearly through the vapour. Accordingly the spectrum is only little changed; the two *D*-lines have become somewhat stronger, which we shall, for the present, ascribe to absorption by the sodium vapour in the tube.

We now blow a feeble current of air through the tube *A* which thus is slightly cooled, so that sodium condenses on it, the vapour density in its neighbourhood diminishing. We soon see the sodium lines broaden considerably. This cannot be the consequence of increased absorption, since the average vapour density has decreased a little. The reason is that rays of light with very great refractive indices are now bent towards q' (fig. 3), rays with very small indices towards q; hence in the image of the slit P which is formed on S, rays belonging to regions on both sides of the *D*-lines no longer occur, while yet this image remains perfectly sharp since the course of all other rays of the spectrum has not been perceptibly altered. If now at the same time the tube B is heated by a current of e.g. 20 Ampères, by which the density gradient in the space between the tubes is increased, the breadth of the lines becomes distinctly greater still. The heat generated in the tube by the current is about 1 calory per second; it is, however, for the greater part conducted away to the cooled ends of the tube, so that the rise of temperature can only be small.

By switching a current key and a cock, A and B can be made to suddenly exchange parts, so that A is heated, B cooled. The dark bands then shrink, pass into sharp *D*-lines and then expand again, until, after a few minutes, they have recovered their original breadth.

Fine and sharp, however, the lines in the transition stage are only if the temperature of the furnace is very constant. If it rises or sinks the minimal breadth appears to be not so small. In this case, however, there certainly exist currents in the mass of vapour which cause the distribution of density to be less regular. Also when A and B are at equal temperatures, we sometimes see the sodium lines slightly broadened; it stands to reason to attribute this also to refraction in such accidental irregularities.

That spectral lines possess some breadth is commonly ascribed either to motion of the light-emitting molecules in the line of sight or to changes in the vibrational period of the electrons by the collisions of the molecules. We now have a third cause: anomalous dispersion in the absorbing medium. The whole series of phenomena, observed in our sodium tube, corroborates the opinion that this latter cause must in general be regarded as by far the most important. It will appear that this conclusion holds not only for dark but also for bright spectral lines.

If the slit in the diaphragm P is made much broader towards p', this has no influence on the spectrum as long as A and B are at the surrounding temperature. The D-lines appear as in α, Pl. I. If now A is cooled below this temperature, B raised above it, the dark D-lines only broaden in the direction of the shorter wave-lengths, while at the side of the longer wave-lengths the intensity of the light is even increased, since now also anomalously bent rays from the radiation field p' can reach the point S through the slit Q. (see β, Pl. I). The spectrum β passes into γ when the temperature difference between A and B is made to change its sign or also when the original temperature difference is maintained and the slit in P is made much broader towards p instead of towards p'. A small shifting of the whole diaphragm P (starting from the condition in which it was when taking β) so that S falls exactly in the shadow, causes the spectrum δ to appear, which makes the impression of an emission spectrum of sodium with slightly shifted lines, although it is evidently only due to rays from the field p' which have undergone anomalous dispersion in the vapour.

Let us now return to the diaphragm P with a narrow slit placed on the optical axis. (A piece of glass coated with tinfoil in which a slit was cut out, was generally used). The spectrum then shows broad bands when there is a density gradient between A and B. If beside the slit an opening is cut in the tinfoil, a group of rays of definite refractivity (and consequently also of definite wave-lengths) is given an opportunity to reach S through Q, and a bright spot is formed in the dark band, the shape of which depends on the shape of the opening in the tinfoil, but is by no means identical with it.

If e. g. the opening in the diaphragm has the shape of fig. 4, then the spectrum ε is obtained. When the density gradient is diminished the figure shrinks, ζ; if now the density gradient is made to change its sign and to increase, the spectrum proceeds through the stages α (gradient exactly zero) and η to θ.

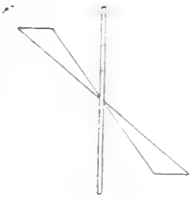

Fig. 4.

The relation between the shape of the opening in the diaphragm and that of the bright spots in the spectrum might easily have been foretold from the shape of the dispersion curve. Having, however, experimentally found the relation between the two figures for a simple case as the one above, it is not difficult to design for any desired distribution of light the shape of the required opening in the diaphragm. The flower ι and its inversion $\varkappa$ required the diaphragm, represented in fig. 5. By reversing the gradient the image ι passes into $\varkappa$.

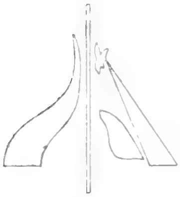

Fig. 5.

So in this way one may also arbitrarily produce duplications, reversals, bright or dark ramifications of spectral lines and it would e. g. be possible faithfully to reproduce all phenomena observed in this respect in the spectra of sun-spots, faculae or prominences. On Plate II a number of arbitrary distributions of light have been collected. They were all produced in sodium vapour of 390° on the average; α' is again the spectrum with equal temperatures of the tubes A and B. In ν on the dark dispersion band D_2 a bright double line is seen, reminding us of the spectrum of the calcium flocculi of Hale. In the same negative D_1 also shows a fine double line, which however is no longer visible in the reproduction. The spectra φ, χ, ψ imitate the origin of a sun spot and prominence spectrum; φ namely represents the spectrum of the quiet solar limb with radially placed slit; in χ a prominence appears and a spot with phenomena of reversal; ψ shows all this in a stronger degree. If now the density gradient is made to change sign, the image first shrinks again to φ after which it expands to ω, in a certain sense the inversion of ψ. The remarkable aspect of these gradual changes, admitting of perfect regulation, is only imperfectly rendered by the photographs.

The relation between the curvature of the rays and the density gradient.

The question arises whether it is *probable* that circumstances as were realised in our experiments are also met with in nature, or in common spectroscopical investigations undertaken with entirely different purposes.

We remark in the first place that curiously shaped diaphragm openings are not absolutely essential for the production of phenomena as those described above. If e.g. our source of light had a constant, say circular shape; if on the other hand the direction and magnitude of the density gradient in our tube had not been so regular, but very different in various places of the field reproduced by the lens F, then the D-lines would also have shown all sorts of excrescences, now determined by the configuration of the density distribution.

In the second place we will try to form some idea of the quantitative relations.

The radius of curvature ϱ of the path of the most deviated rays, occurring in our photographs, may be easily estimated from the distance d of the diaphragm to the middle of the furnace, the distance δ of the most distant diaphragm openings to the optical axis, and the length l of the space in which the incurvation of the rays is brought about. For:

$$\varrho : l = d : \delta.$$

Putting $\delta = 1$ cm., $d = 110$ cms., $l = 27$ cms. this gives: $\varrho = 3000$ cms. The average density Δ of the sodium vapour was in this case about $\frac{1}{1000}$ of that of the atmospheric air.

Let us see how ϱ changes with the density gradient.

We always have:

$$\varrho = \frac{n}{n'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

if n represents the local index of refraction of the medium for the ray under consideration and $n' = \frac{dn}{ds}$ the change of this index per cm. in the direction of the centre of curvature. Approximately we have, for a given kind of light:

$$\frac{n-1}{\Delta} = \text{constant} = R$$

$$n = R\Delta + 1$$

$$n' = \frac{dn}{ds} = R\frac{d\Delta}{ds}$$

From this follows:

$$\varrho = \frac{R\Delta + 1}{R\frac{d\Delta}{ds}};$$

but since for rarefied gases n differs little from unity, even for the anomalously dispersed rays which we consider, $R\Delta$ may be neglected with regard to 1 and we may write

$$\varrho = \frac{1}{R\frac{d\Delta}{ds}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For every kind of light ϱ is consequently inversely proportional to the density gradient of the vapour in the direction perpendicular to that of propagation.

An estimate of the magnitude of the density gradient existing, in our experiments, between A and B, may be obtained in two ways. It may namely be inferred from the produced difference of temperature, or from formula (2).

The temperature difference between A and B would have been pretty easy to determine thermo-electrically; up to the present, however, I had no opportunity to make the necessary arrangement. Besides, the relation between the density distribution in the space, passed by the rays, and the temperatures of A and B cannot be so very simple, since we have to deal not with two parallel planes but with tubes, from which moreover hang many drops of liquid sodium.

The second method at once gives an average value of $\frac{d\Delta}{ds}$ for the space passed by the rays. It requires a knowledge of $R = \frac{n-1}{\Delta}$ for a kind of ray for which in our experiments also ϱ has been determined.

Now Wood (Phil. Mag. [6], 8, p. 319) gives a table for the values of n for rays from the immediate vicinity of the D-lines. These data, however, refer to saturated sodium vapour of 644°; but we may deduce from them the values of n for vapour of 390° by means of the table which he gives in his paper on page 317.

For, when we heat from 389° to 508°, the refractive power of the vapour (measured by the number of passing interference fringes of helium light $\lambda = 5875$) becomes $\frac{98}{9} = 11$ times greater, and at further heating from 508° to 644° again $\frac{50}{4} = 12{,}5$ times greater (now found by interference measurement with light from the mercury line $\lambda = 5461$); hence from 390° to 644° the refractive power increases in ratio of 1 to $11 \times 12{,}5 = 137$.

Since now for rays, situated at 0,4 Ångström-unit from the D-

lines [1]) we have $n-1 = \pm 0.36$, (as the average of three values taken from **Wood**'s table on page 319), we ought to have with sodium vapour at 390° for the same kind of rays

$$n-1 = \frac{0.36}{137} = 0.0026.$$

The density Δ at 390° is, according **Jewett**, 0.0000016. hence

$$R = \frac{n-1}{\Delta} = \frac{0.0026}{0.0000016} = 1600.$$

Then from formula (2) follows

$$\frac{d\Delta}{ds} = \frac{1}{R\varrho} = \frac{1}{1600 \times 3000} = 0{,}0000002.$$

Dispersion bands in the spectra of terrestrial sources.

It is very probable that, when metals evaporate in the electric arc, values of the density gradient are found in the neighbourhood of the carbons that are more than a thousand times greater than the feeble density gradient in our tube with rarefied sodium vapour [2]).

The radius of curvature will, therefore, in these cases be over a thousand times smaller than 30 meters and so may be no more than a few centimetres or even less. A short path through the vapour mass is then already sufficient to alter the direction of certain rays very perceptibly.

If now an image of the carbon points is produced on the slit of a spectroscope, then this is a *pure* image only as far as it is formed by rays that have been little refracted in the arc, but the rays which undergo anomalous dispersion do not contribute to it. Light of this latter kind, coming from the crater, may be lacking in the image of the crater and on the other hand penetrate the slit between the images of the carbon points. Thus in ordinary spectroscopic observations, not only broadening of absorption lines, but also of emission lines, must often to a considerable extent be attributed to anomalous dispersion.

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[1]) The spectrum ε in our plate shows that the extremities of the peaks correspond pretty well to light of this wave-length; for they approach the D-lines to a distance which certainly is no more than $^1/_{15}$ of the distance of the D-lines which amounts to 6 Ångstr.-units. For these rays the opening of the diaphragm was 1 cm. distant from the optical axis.

[2]) If we e. g. put the vapour density of the metal in the crater, where it boils, at 0.001, the density of the vapour outside the arc at a distance of 1 cm. from the crater, at 0.0001, then we have already an average gradient 5000 times as large as that used in our experiments.

When we bear this in mind, many until now mysterious phenomena will find a ready explanation. So e.g. the fact that LIVEING and DEWAR[1]) saw the sodium lines strongly broadened each time when vapour was vividly developed after bringing in fresh material, but saw them become narrower again when the mass came to rest, although the density of the vapour did not diminish. If by pumping nitrogen into the evaporated space the pressure was gradually increased, the lines remained sharp; but if the pressure was suddenly released, they were broadened. All this becomes clear as soon as one has recognised in the lines dispersion bands, which must be broad when the density of the absorbing vapour is irregular, but narrow, even with dense vapour, if only the vapour is evenly spread through the space.

Another instance. According to the investigations of KAYSER and RUNGE the lines, belonging to the second secondary series in the spectra of magnesium, calcium, cadmium, zinc, mercury, are always hazy towards the red and are sharply bordered towards the violet, whereas lines, belonging to the first secondary series or to other series are often distinctly more widened towards the violet. With regard to the spectrum of magnesium they say:[2]) "Auffallend ist bei mehreren Linien, die wir nach Roth verbreitert gefunden haben, dass sie im ROWLAND'schen Atlas ganz scharf sind, und dann stets etwas kleinere Wellenlänge haben. So haben wir 4703,33, ROWLAND 4703,17; wir 5528,75, ROWLAND 5528,62. Unschärfe nach Roth verleitet ja leicht der Linie grössere Wellenlänge zuzuschreiben; so gross kann aber der Fehler nicht sein, denn die ROWLAND'sche Ablesung liegt ganz ausserhalb des Randes unserer Linie. Wir wissen daher nicht, woher diese Differenz rührt." KAYSER has later[1]) given an explanation of this fact, based on a combination of reversal with asymmetrical widening; but a more probable solution is, in my opinion, to regard the widened serial lines as dispersion bands.

If we namely assume that, when we proceed from the positive carbon point, which emits the brightest light, to the middle of the arc, the number of the particles associated with the second secondary series decreases, then rays coming from the crater and whose wavelength is slightly greater than that of the said serial lines will be curved so as to turn their concave side to the carbon point. Their origin is erroneously supposed to be in the prolongation of their final direction, so they *seem* to come from the arc, and one believes

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[1]) LIVEING and DEWAR, On the reversal of the lines of metallic vapours, Proc. Roy. Soc. 27, p. 132—136; 28, p. 367—372 (1878—1879).

[2]) KAYSER und RUNGE, Über die Spektren der Elemente, IV, S. 13.

[1]) KAYSER. Handbuch der Spektroskopie II, S. 366.

to see light emitted by the vapour, in which light different wave-lengths occur, all greater than the exact wave-length of the serial lines. The observed displaced lines of the second secondary series are consequently comparableto apparent emission lines of the spectrum σ of our plate I.

In this explanation things have been represented as if the light of these serial lines had to be *exclusively* attributed to anomalous dispersion. Probably however in the majority of cases emission proper will indeed perceptibly contribute to the formation of the line; the sharp edge must then appear in the exact place belonging to the particular wave-length.

How can we now explain that lines of other series are diffuse at the opposite side? Also this may be explained as the result of anomalous dispersion if we assume that of the emission centres of these other series the density *increases* when we move away from the positive carbon point. In this case namely the rays originating in the crater, which are concave towards the carbon point and consequently seem to come from the arc, possess shorter wave-lengths than the serial lines, i. e. the serial lines appear widened towards the violet. This supposition is not unlikely. For the positive and negative atomic ions which according to STARK's theory are formed in the arc by the collision of negative electronic ions, move in opposite directions under the influence of the electric field; hence the density gradients will have opposite signs for the two kinds. Series whose lines are diffuse towards the red and series whose lines flow out towards the violet would, according to this conception, belong to atomic ions of opposite signs — a conclusion which at all events deserves nearer investigation.

The examples given may suffice to show that it is necessary systematically to investigate to what extent the already known spectral phenomena may be the result of anomalous dispersion. A number of cases in which the until now neglected principle of ray-curving has undoubtedly been at the root of the matter are found in KAYSER's handbook II, p. 292—298, 304, 306, 348—351, 359—361, 366.

Dispersion bands in the spectra of celestial bodies.

Since almost any peculiarity in the appearance of spectral lines may be explained by anomalous dispersion if only we are at liberty to assume the required density distributions, we must ask when applying this principle to astrophysical phenomena: can the values of the density gradient for the different absorbing gases in celestial bodies really be such, that the rays are sufficiently curved to exert such a distinct influence on the distribution of light in the spectrum?

In former communications [1]) I showed that the sun e.g. may be conceived as a gaseous body, the constituents of which are intimately mixed, since all luminous phenomena giving the impression as if the substances occurring in the sun were separated, may be brought about in such a gaseous mixture by anomalous dispersion. We will now try to prove that not only this *may* be the case, but that it *must* be so on account of the most likely distribution of density.

Let us put the density of our atmosphere at the surface of the earth at 0.001293. At a height of 1050 cms. it is smaller by $\frac{1}{760}$ of this amount, so that the vertical density gradient is

$$\frac{0.001293}{1050 \times 760} = 16 \times 10^{-10}.$$

The horizontal gradients occurring in the vicinity of depressions are much smaller; even during storms they are only about $\frac{1}{1000}$ of the said value [2]). Over small distances the density gradient in the atmosphere may of course occasionally be larger, through local heating or other causes.

Similar considerations applied to the sun, mutatis mutandis, cannot lead however to a reliable estimate of the density gradients there occurring. A principal reason why this is for the present impossible is found in our inadequate knowledge of the magnitude of the influence, exerted by *radiation pressure* on the distribution of matter in the sun. If there were no radiation pressure, we might presuppose, as is always done, that at the level of the photosphere gravitation is 28 times as great as on the earth; but it is counteracted by radiation pressure to a degree, dependent on the size of the particles; for some particles it may even be entirely abolished. The radial density gradient must, therefore, in any case be much smaller than one might be inclined to calculate on the basis of gravitational action only.

Fortunately we possess another means for determining the radial density gradient in the photoshere, at any rate as far as the order of magnitude is concerned. According to SCHMIDT's theory the photosphere is nothing but a critical sphere the radius of which is equal

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[1]) Proc. Roy. Academy Amsterdam, II, p. 575; IV, p. 195; V, p. 162, 589 and 662; VI, p. 270; VIII, p. 134, 140 and 323.

[2]) ARRHENIUS. Lehrbuch der kosmischen Physik, S. 676.

to the radius of curvature of luminous rays whose path is horizontal at a point of its surface. This radius of curvature is consequently $\varrho = 7 \times 10^{10}$ cms., a value which we may introduce into the expression for the density gradient:

$$\frac{d\Delta}{ds} = \frac{1}{R\varrho}$$

The refractive equivalent R for rays that undergo no anomalous dispersion varies with different substances, to be sure; but in an approximate calculation we may put $R = 0{,}5$. Then at the height of the critical sphere we shall have:

$$\frac{d\Delta}{ds} = \frac{1}{0.5 \times 7 \times 10^{10}} = 0.29 \times 10^{-10},$$

(this is 50 times less than the density gradient in our atmosphere). All arguments supporting SCHMIDT's explanation of the sun's limb, are at the same time in favour of this estimate of the radial density gradient in the gaseous mixture.

Let us now consider rays that do undergo anomalous dispersion. In order that e.g. light, the wave-length of which differs but very little from that of one of the sodium lines, may seem to come from points situated some arc seconds outside the sun's limb, the radius of curvature of such anomalously bent rays need only be slightly smaller than 7×10^{10} cms. Let us e.g. put

$$\varrho' = 6 \times 10^{10} \text{ c.m.}$$

If we further assume that of the kind of light under consideration the wave-length is 0.4 Ångström-units greater than that of D_1, then for this kind of light $R' = 1600$, as may be derived from the observations of WOOD and of JEWETT [1]); we thus find for the density gradient of the sodium vapour

$$\frac{d\Delta'}{ds} = \frac{1}{R'\varrho'} = \frac{1}{1600 \times 6 \times 10^{10}} = 0.0001 \times 10^{-10},$$

a quantity, 2900 times smaller than the density gradient of the gaseous mixture.

Hence if only $\frac{1}{3000}$ part of the gaseous mixture consists of sodium vapour, then, on account of the radial density gradient, the critical sphere will already seem to be surrounded by a "chromosphere" of light, this light having a striking resemblance with sodium light. This kind of light has, so to say, its own critical sphere which is larger than the critical sphere of the not anomalously refracted light. If the

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[1]) See page 352.

percentage of sodium were larger, the "sodium chromosphere" would appear higher.

It is customary to draw conclusions from the size of the chromospheric and flash crescents, observed during a total eclipse with the prismatic camera, as to the *height* to which various vapours occur in the solar atmosphere. According to us this is an unjustified conclusion. On the other hand it will be possible to derive from these observations data concerning *the ratio in which these substances are present in the gaseous mixture,* provided that the dispersion curves of the metallic vapours, at known densities, will first have been investigated in the laboratory.

Until now we only dealt with the normal radial density gradient. By convection and vortex motion however irregularities in the density distribution arise, with gradients of various direction and magnitude. And since on the sun the resultant of gravitation and radiation pressure is relatively small, there the irregular density gradients may sooner than on the earth reach values that approach the radial gradient or are occasionally larger.

The incurvation of the rays in these irregularities must produce capriciously shaped sodium prominences, the size of which depends, among other causes, on the percentage of sodium vapour in the gaseous mixture.

So the large hydrogen and calcium prominences prove that relatively much hydrogen and calcium vapour is present in the outer parts of the sun; but perhaps even an amount of a few percents would already suffice to account for the phenomena [1]).

If we justly supposed that non-radially directed density gradients are of frequent occurrence in the sun, and there disturb the general radial gradient much more than on the earth, then not only rays from the marginal region but also rays from the other parts of the solar disc must sensibly deviate from the straight line. Chiefly concerned are of course the rays that undergo anomalous dispersion. *Every absorption line of the solar spectrum must consequently be enveloped in a dispersion band.*

To be sure, absorption lines of elements which in the gaseous mixture only occur in a highly rarefied condition, present themselves as almost sharp lines, since for these substances all density gradients are much smaller than for the chief constituents, and so the curvature of the rays from the vicinity of these lines becomes imperceptible.

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[1]) This result would be in accordance with a hypothesis of SCHMIDT (Phys. Zeitschr. 4, S. 232 and 341) according to which the chief constituent of the solar atmosphere would be a very light, until now unknown gas.

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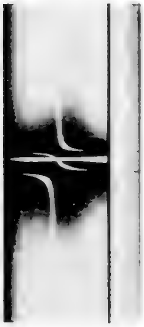

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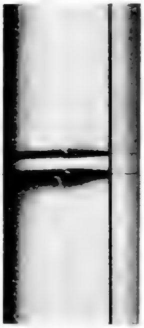

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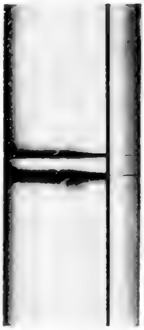

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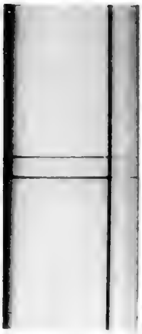

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Proceedings Royal Acad. Amsterdam. Vol IX.

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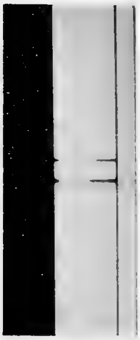

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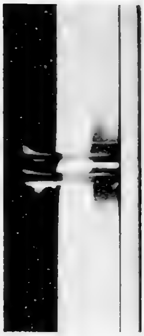

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Proceedings Royal Acad. Amsterdam. Vol. IX.

Heliotype, Van Leer, Amsterdam.

Also of strongly represented elements some lines may appear sharp, since not all lines of the same element, with given density, cause anomalous dispersion in the same degree. Perhaps even there are absorption lines which under no condition give rise to this phenomenon; though this were rather improbable from the point of view of the theory of light.

Be this as it may, the mentioned limitations do not invalidate our principal conclusion: that the general interpretation of the solar spectrum has to be modified. We are obliged to see in FRAUNHOFER's lines not only absorption lines, as KIRCHHOF does, but chiefly dispersion bands (or dispersion lines). And that also on the distribution of light in the stellar spectra refraction has a preponderant influence, cannot be doubted either.

We must become familiar with the idea that in the neighbourhood of the celestial bodies the rays of light are in general curved, and that consequently the whole interstellar space is filled with *non-homogeneous radiation fields* [1]) of different structure for the various kinds of light.

Chemistry. — "*On a substance which possesses numerous* [2]) *different liquid phases of which three at least are stable in regard to the isotropous liquid.*" By Dr. F. M. JAEGER. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

§ 1. The compound which exhibits the highly remarkable phenomena to be described, is *cholesteryl-cinnamylate*: $C_{27}H_{45}O_2C.CH:CH C_6H_5$.

I have prepared this substance by melting together equal quantities of pure cholesterol and cinnamyl-chloride in a small flask, which was heated for about two hours in an oilbath at 190°. It is of the greatest importance, not to exceed this temperature and the time of heating, as otherwise the liquid mass, which commences to darken, even under these conditions, yields instead of the desired derivative a brown resin which in solution exhibits a green fluorescence.

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[1]) Das ungleichmässige Strahlungsfeld und die Dispersionsbanden. Physik. Zeitschr. 6, S. 239—248, 1905.

[2]) In the Dutch publication, I have said: five. Since that time however, more extended microscopical observation has taught me, that probably there are an infinite number of anisotropous liquid phases, no sharply fixed transition being observed in this manner. The hypothesis, that the transition of the first anisotropous liquid phase into the isotropous should be continuous, would therefore be made more probable in this way. However there are observed some irreversibilities by passing from solid to liquid state and vice-versa, which yet I cannot explain at this moment.

The solidified mass is dissolved in boiling ether, and the brown liquid is boiled with animal charcoal for an hour in a reflux-apparatus. To the filtrate is then added absolute alcohol, heated to 40°, until the liquid gets turbid. On being set aside for a few hours the ester deposits in small, almost white glittering leaflets. These are collected at the pump, washed with a little ether-alcohol, and then recrystallised several times from boiling ethyl acetate, to which each time some alcohol may be added to precipitate the bulk of the ester. The pure, quite colourless, beautifully crystallised compound shows no heterogenous components under the microscope.

§ 2. The following experiments were carried out in the usual manner; the substance was contained in small, thin-walled testtubes, whilst surrounded of a cylindrical air-bath, and whilst the thermometer was placed in the liquid completely which covered the mercury reservoir. The temperature of the oilbath was gradually raised with constant stirring and now the following facts were noticed.

At about 151° the solid mass begins to soften [1]) while brilliant colours appear here and there at the sides, principally green and violet, with transmitted light the complimentary colours red and yellow. At about 157° the mass is a thick fluid and strongly doubly refracting; the ground tone of the phase is orange-red, whilst, on stirring with the thermometer, the liquid crystals everywhere form links of lustrous bright green and violet slides. Afterwards, by the construction of the cooling curve, I determined sharply the temperature *t* [155°.8 C.] at which the substance solidifies; the break in the curve is distinct as the heat effect is relatively large and the undercooling was prevented by inoculation with a solid particle of the ester.

The colour of the liquid phase is now but little changed on further heating; on the other hand its consistency becomes gradually more and more that of a thin liquid. At 199°.5 it is nearly colourless and one would expect it to become presently quite clear.

But at that temperature the mass becomes all of a sudden enamel-white, and rapidly thickens, while still remaining doubly-refracting. We now observe plainly a separation into two liquid layers which are here both anisotropous. The interference colours have now totally disappeared. Then, on heating slowly, the liquid phase becomes isotropous at 201.3° and quite clear. The isotropous liquid is colourless.

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[1]) Bondzynski and Humnicki (Zeitschr. f. physiol. Chem. **22**, 396, (1896), describe a cinnamylate which as regards solubility etc. agrees with mine, but which melts at 149°. This is evidently identical with my first temperature of transition.

On cooling, the following phenomena occur: At about 200° the isotropous liquid becomes turbid, at 198° the doubly-refracting mass attains its greatest viscosity; at 196° it has already become thinner, but now at about 198° it again becomes thicker and the whole appearance of the phase is strikingly altered, although still remaining doubly refracting. It then seems to pass gradually into the green and red coloured, doubly refracting liquid phase, which, if we prevent the undercooling by inoculation, solidifies at 155°.8.

If the solid substance is melted under LEHMANN's crystallisation-microscope, — where the conditions of experimenting are naturally quite others than before, — it seems, that but *one* liquid phase, the green and red coloured, is *continually* changed into the isotropous one: no sudden changing is observed. On cooling, the aspect of the anisotropous phase now obtained, is quite different from the first mentioned.

I also think I must come to the conclusion that the liquid phase ($t =$ about 190°) occurring on cooling is perhaps only the passage to the other three, so that here, *three stable* liquid phases might occur. It is very remarkable that the transitions of the two stable anisotropous phases into the intermediate one appear, when we work carefully, quite continuous; the viscosity appears to pass gradually into that of the more stable phases. Remarkable also is the impossibility to find the temperatures of transition exactly the same on the rising, or falling, temperature of the external bath. The values obtained for the initial and final temperature of each phase-traject vary within narrow limits. The same is the case when, on melting the solid substance, one wishes to determine the point where the first softening of the mass takes place; in the determination of the temperature, intervals such as from 147° to 156° are noticed. The progressive change of the cooling of isotropous-liquid to solid resembles here in a high degree a process where a continuous transition exists between the different stadia. It is as if the labile phase is composed of an entire series of conditions which occur successively to form the connection on one side between anisotropous and isotropous-liquid. The whole shows much resemblance to a gradual dissociation and association between more or less complicated molecule-complexes. It is quite possible that the transitions solid-liquid occur really *continuously* instead of *suddenly*, in which case an uninterrupted series of labile intermediate conditions — which cannot be realised in most substances — are passed, some of which intermediate conditions might be occasionally fixed in those substances which like these cholesteryl-esters usually display the phenomena of the doubly-refracting liquid-conditions. All this seems probable to the investigator, the more so as it has been proved by LEHMANN, that in my other cholesteryl-esters, even in the case of the caprinate, *both* or one of the two anisotropous liquid-phases were always labile and only realizable on undercooling; some of them, such as the *iso*butyrate, only exhibited their labile anisotropous liquid-phases, when containing some impurities and not when in a pure condition. With the idea of a gradual dissociation of compound molecule-complexes into more simple ones, agrees the fact that the anisotropous liquid phases have never been known yet to occur *after* the isotropous ones; this is always the end-phenomenon, which is accounted for by the fact that a dissociation of this kind is always found to increase with a rise of temperature.

That the cooling between solid and anisotropous-liquid does not proceed so suddenly as may be predicted from the great calorific effect is shown in the case of the cinnamylate from the fact that, after the solidification, particularly at the side of the test tubes, the interference-colours, which are characteristic before the transition of the phases into each other, remain visible for a very long time, often many hours, then slowly disappear. Even with great enlargement, no well defined crystals can be discovered in those coloured parts; the whole conveys the impression of a doubly-refracting, irregular network of solidified liquid droplets, just like the liquid crystals which present themselves to the eye with the aid af a powerful enlargement [1]).

In these obscure phenomena we are bound to notice the more or less labile and partially realized intermediate stadia in a continuous transition liquid $\leftrightarrows$ solid. The view expressed by LEHMANN, that there should be present a difference between the kinds of molecules in the different aggregate conditions, is adopted here with this difference, that such a difference of association of the molecules is thought quite compatible with the phenomenon of the *continuity* of the aggregate conditions, treated of here.

§ 3. I wish to observe, finally, that cholesteryl-cinnamylate when subjected frequently to these melting experiments, soon undergoes a small but gradually increasing decomposition, which shows itself in the yellow colour of the mass and the fall of the characteristic temperature-limits.

Zaandam, 26 Oct. '06.

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[1]) A still more distinct case of this phenomenon has now been found by me in *α-phytosteryl-propionate*, which I hope soon to discuss in another communication.

Chemistry. *"The behaviour of the halogens towards each other".* By Prof. H. W. Bakhuis Roozeboom.

If the phase-doctrine in its first period was concerned mainly with

By an omission the pagination of the Proceedings of the Meeting of Saturday October 27, 1906 begins with page 249 instead of page 237, so pages 238—248 do not exist.

Finally it now appears from an investigation by Miss Karsten that Chlorine and Bromine only give mixed crystals on cooling and that in a connected series, whilst, in agreement with this no indication for the existence of the compound in the liquid or vapour could be deduced from the form of the boiling point line.

We, therefore come to the conclusion that ICl_3 is a feeble and ICl a strong compound. IBr is also a feeble compound and no compound exists between Cl and Br. The combining power is, therefore,

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[1] Still closer than represented in Fig. 7, p. 540. These proceedings [VIII] 1904.

[2] These proceedings VI, p. 331.

steryl-esters usually display the phenomena of the doubly-refracting liquid-conditions. All this seems probable to the investigator, the more so as it has been proved by LEHMANN, that in my other cholesteryl-esters, even in the case of the caprinate, *both* or one of the two conditions, treated of here.

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Chemistry. *"The behaviour of the halogens towards each other".*
By Prof. H. W. BAKHUIS ROOZEBOOM.

If the phase-doctrine in its first period was concerned mainly with the question whether two or more substances in the solid condition give rise to chemical compounds, or mixed crystals, or remain unchanged in the presence of each other, lately it has commenced to draw conclusions from the form of the melting point lines of the solid mixtures, both for the nature of those solid mixtures and of the liquid mixtures into which they pass, namely whether, and to what extent, compounds occur therein:

Likewise, the same questions may be answered in regard to liquid and vapour from the equilibrium lines for those two phases, namely boiling point lines or vapour pressure lines.

The three systems of the best known halogens having now been investigated their mutual behaviour may be surveyed.

As regards chlorine and iodine, STORTENBEKER had proved in 1888 that no other compounds occur in the solid condition but ICl_3 and ICl. He also showed that it is probable that ICl, on melting, liquefies to a very large extent without dissociation, whilst on the other hand ICl_3 is almost entirely dissociated into $ICl + Cl_2$.

Miss KARSTEN has now added to this research by the determination of the boiling point lines. This showed that the liquid and the vapour line approach each other so closely in the vicinity of the composition ICl [1]), that the conclusion must be drawn that the dissociation of ICl is also exceedingly small in the vapour, it being already known that it is very large in the case of ICl_3.

From the investigation of MEERUM TERWOGT [2]) it has been shown that Br and I form only one compound BrI which in the solid state forms mixed crystals both with Br and I and which on account of the form of the vapour pressure and boiling point lines is largely dissociated in the liquid and gaseous states.

Finally it now appears from an investigation by Miss KARSTEN that Chlorine and Bromine only give mixed crystals on cooling and that in a connected series, whilst, in agreement with this no indication for the existence of the compound in the liquid or vapour could be deduced from the form of the boiling point line.

We, therefore come to the conclusion that ICl_3 is a feeble and ICl a strong compound. IBr is also a feeble compound and no compound exists between Cl and Br. The combining power is, therefore,

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[1]) Still closer than represented in Fig. 7, p. 540. These proceedings [VIII] 1904.

[2]) These proceedings VI, p. 331.

greatest in the most distant elements and greater in Br + I than in Br + Cl.

From the researches of MOISSAN and others it follows that Fluorine yields the compound IF_5 which is stable even in the vapour-condition. With Bromine, the compound BrF_3 is formed but no compound is formed with Chlorine. This, also, is in harmony with the above result.

As, however, the compounds with Fluorine have not been studied from the standpoint of the phase-doctrine, there does not exist as yet a reasonable certainty as to their number or their stability.

Mathematics. — *"Second communication on the* PLÜCKER *equivalents of a cyclic point of a twisted curve."* By Dr. W. A. VERSLUYS. (Communicated by Prof. P. H. SCHOUTE).

§ 1. If the origin of coordinates is a cyclic point (n, r, m) of a twisted curve C the coordinates of a point of C lying in the vicinity of the origin on a branch passing through the origin can be represented as follows:

$$x = a\,t^n,$$
$$y = b_0\,t^{n+r} + b_1\,t^{n+r+1} + b_2\,t^{n+r+2} + \text{etc.},$$
$$z = c_0\,t^{n+r+m} + c_1\,t^{n+r+m+1} + c_2\,t^{n+r+m+2} + \text{etc.}$$

Let q_1 be the greatest common divisor of n and r, let q_2 be that of r and m, q_3 that of m and $n+r$ and finally q_4 that of n and $r+m$.

If $q_1 = q_2 = q_3 = q_4 = 1$ the PLÜCKER equivalents depend only on n, r and m. In a preceding communication[1]) I gave the PLÜCKER equivalents for this special case[2]).

§ 2. If the 4 G. C. Divisors q are not all unity, the PLÜCKER equivalents of the cyclic point (n, r, m) depend on the values of the coefficients b and c, just as in general for a cyclic point of a plane curve given by the developments:

$$x = t^n,$$
$$y = t^{n+m} + d_1\,t^{n+m+1} + d_2\,t^{n+m+2} + \text{etc.},$$

the vanishing of coefficients d influences the number of nodal points and double tangents equivalent to the cyclic point (n, m)[3]).

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[1]) Proceedings Royal Acad. Amsterdam, Nov. 1905.

[2]) The deduction of these equivalents is to be found among others in my treatise: "*Points sing. des courbes gauches données par les équations:* $x = t^n$, $y = t^{n+r}$, $z = t^{n+r+m}$," inserted in "*Archives du Musée Teyler*", série II, t. X, 1906.

[3]) A. BRILL and M. NOETHER. Die Entwicklung der Theorie der algebraischen Functionen, p. 400. *Jahresbericht der Deutschen Mathematiker-Vereinigung*, III, 1892—93.

If the coefficients c and b are not zero, if no special relations exist between these coefficients and if besides n, r and m are greater than *one*, the cyclic point (n, r, m) is equivalent to

$n - 1$ stationary points β and to
$\{(n-1)(n+r-3)+q_1-1\}:2$ nodes H.

The osculating plane of the curve C in the cyclic point (n, r, m) is equivalent to

$m - 1$ stationary planes α and to
$\{(m-1)(r+m-3)+q_2-1\}:2$ double planes G.

The tangent of the curve C in the cyclic point (n, r, m) is equivalent to

$r - 1$ stationary tangents θ, to
$\{(r-1)(n+r-3)+q_1-1\}:2$ double tangents ω and to
$\{(r-1)(r+m-3)+q_2-1\}:2$ double generatrices ω' of the developable O formed by the tangents of the curve C.

§ 3. The cyclic point (n, r, m) of the curve C is an $n+r$-fold point of the developable O of which C is the cuspidal curve.

The cyclic point (n, r, m) counts for

$$(n+r-2)(n+r+m)$$

points of intersection of the cuspidal curve C with the second polar surface of O for an arbitrary point.

Through the cyclic point (n, r, m) of the cuspidal curve C pass

$$\{n(n+2r+m-4)+q_3-q_2\}:2$$

branches of the nodal curve of the developable O.

All these nodal branches touch in the cyclic point (n, r, m) the tangent of the cuspidal curve C (the x-axis).

They have with this common tangent in the point of contact

$$\{(n+r)(n+2r+m-4)+q_4-q_2\}:2$$

points in common.

The nodal branches passing through the cyclic point (n, r, m) all have in this point as osculating plane the osculating plane $z=0$ of the cuspidal curve C.

These nodal branches have with their osculating plane $z=0$ in the cyclic point (n, r, m)

$$\{(n+r+m)(n+2r+m-4)+q_1-q_2\}:2$$

points in common.

§ 4. The case of an ordinary stationary plane α, the point of contact of which is a cyclic point $(1, 1, 2)$, shows that through a cyclic point branches of the nodal curve can pass not touching in this point the cuspidal curve.

These intersecting nodal branches exist only when $q_3 > 1$. If $r > 1$ the coefficients b and c must satisfy special conditions. If $r = 1$ then through the cyclic point (n, r, m) of the cuspidal curve pass either $q_3 : 2$, or $(q_3 - 1) : 2$ of these nodal intersecting branches. All intersecting nodal branches have a common tangent in the plane $z = 0$ if $r = 1$.

§ 5. The case of an ordinary stationary point β $(2, 1, 1)$ shows that through a cyclic point of the cuspidal curve nodal branches can pass which have the same tangent, but not the same osculating plane as the cuspidal curve. These particular nodal branches exist only when $q_4 > 1$. If $q_4 > 1$ and $m = 1$ these particular nodal branches are always present. If $q_4 > 1$ and also $m > 1$ the coefficients b and c must satisfy special conditions. These particular nodal branches have in the cyclic point (n, r, m) a common osculating plane (differing from the plane $z = 0$) if $m = 1$.

§ 6. The tangent to C in the cyclic point (n, r, m) is an r-fold generatrix g on the developable O. The r sheets of the surface O passing through the generatrix g all touch the osculating plane $z = 0$ of C in the point (n, r, m).

The generatrix g moreover meets in $\varrho - (n + 2r + m)$ points R a sheet of the surface O, when O is of order ϱ.

In every point R the generatrix g meets r branches of the nodal curve. These r branches form, when $m > r$ a singularity $(r, r, m - r)$ and the osculating plane of these nodal branches is the tangent plane of O along g.

If $m < r$ these r nodal branches form a singularity $(r, m, r - m)$ and the osculating plane of these r nodal branches is the tangent plane of O along the generatrix intersecting g in R.

If $r = m$ these r nodal branches form a singularity $(r, r, 1)$.

§ 7. In general the singular generatrix g will meet only nodal branches in the cyclic point (n, r, m) and in the points R. If $q_2 > 1$ the generatrix g may meet moreover nodal branches arising from the fact that some of the r sheets, which touch each other along g penetrate each other. These nodal branches meet g in the same point Q. If $q_2 > 1$ and $n = 1$ there is always such a point of intersection Q. If $q_2 > 1$ and $n > 1$ the coefficients b and c must satisfy some special conditions if the sheets passing through g are to penetrate each other.

Physics. — *"On the measurement of very low temperatures.* XIII. *Determinations with the hydrogen thermometer."* By Prof. H. Kamerlingh Onnes and C. Braak. (Communication N° 95^e from the Physical Laboratory of Leiden).

§ 1. *Introduction.*

The results of determinations of low temperatures made with the hydrogen thermometer, which was described in Comm. N°. 27 (June 1896) and more fully discussed in Comm. N°. 60 (September 1900), have already frequently been used, but no further particulars have as yet been given about these determinations themselves. We give them now in connection with a series of observations made in 1905 and 1906. They have served for the investigations described in Comm. Nos 95^a and 95^c (June 1906) and further for determinations of isotherms of hydrogen at low temperatures, which will be discussed in a following communication. Comprising also measurements on liquid hydrogen, they extend over the whole of the accessible area of the lower temperatures. All the precautions which proved necessary in former years, have been taken. The temperature of the bath, in which the thermometer was immerged, could be kept constant to 0°.01 at all temperatures. It was therefore to be expected, that the accuracy and reliability aimed at in the arrangement of the thermometers, might to a great extent be reached.[1]) In how far this is really the case, the following data may show.

§ 2. *Arrangement of the thermometer.*

There is little to add to Comm. N°. 60. The steel capillary connecting the thermometer bulb and the manometer, was protected from breaking by passing a steel wire along it, the ends of which are soldered to copper hoods, which may be slidden on the steel pieces *c* and *e* (Plate II, Comm. N°. 27) at the end of the capillary. The dimensions of the thermometer reservoir of Comm. N°. 60 (80 c.M^3.) did not present any difficulty in our measurements, the bath in the cryostats (see Comm. Nos. 83, 94^c, 94^d and 94^f (May and June 1905 and June 1906)) offering sufficient room besides for the thermometer and other measuring apparatus, for the stirring apparatus, which works so thoroughly, that no variation of tempe-

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[1]) A complete example of the determination of very low temperatures with the hydrogen thermometer was as yet not found in the literature. Such an example follows here.

rature could be found [1]) at least with the thermo-element [2]). The section of the glass capillary forming the stem of the thermometer was 0,0779 mM^2. With regard to the temperature correction (see § 4, conclusion), it is desirable that this section is small. It appears both from calculation and from observation [3]), that the equilibrium of pressure between the space near the steelpoint and reservoir is still very quickly reached with these dimensions of the capillary [4]), much more quickly than the equilibrium of the mercury in the two legs of the manometer, which is inter alia also confirmed by the rapidity with which the thermometer follows fluctuations in the temperature of the bath[5]).

The determination of the pressure which is exerted on the gas, may, when the determination applies to very low temperatures, be simplified and facilitated by following the example of CHAPPUIS [6]) and making the manometer tube serve at the same time as barometer tube. The modification applied for this purpose to the arrangement according to Comm. N°. 60 Pl. VI, is represented on Pl. I, which must be substituted for part of Pl. VI belonging to Comm. N°. 60. By means of an india-rubber tube and a T-piece l_0 the thermometer (a, b, c, d, e, h, k) is connected on one side with the manometer l_1, to which (see Pl. VI Comm. N°. 60) at m_1 the reservoir at constant temperature is attached and at m_2 the barometer, on the other side with the barometer tube (n_0, n_1 (airtrap) n_2). Besides from the manometer and the barometer joined at m_2, the pressure can now also immediately be read from the difference in level of the mercury in n_2 and in g. We have not availed ourselves of this means for the determinations discussed in this Communication.

§ 3. *The hydrogen.*

The filling took place in two different ways:

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[1]) TRAVERS, SENTER and JAQUEROD, (Phil. Trans. Series A, Vol. 200, Part. II, § 6) who met with greater difficulties when trying to keep the temperature constant in their measurements, had to prefer a smaller reservoir.

[2]) A resistance thermometer is more sensible (Cf. Comm. Nos. 95^a and 95^c). As soon as one of suitable dimensions will be ready, the experiment will be repeated.

[3]) Calculation teaches that for reducing a pressure difference of 1 c.M. to one of 0.01 m.M., the gas flowing through the capillary requires 0.1 sec., the mercury in the manometer 4 sec. Experiment gives for this time 25 sec. This higher amount must be due to the influence of the narrowing at the glass cock k.

[4]) We must be very careful that no narrowings occur.

[5]) A great deal of time must be given to exhausting the reservoir with the mercury airpump when filling it, as the equilibrium of reservoir and pump is established much more slowly than that between dead space and reservoir.

[6]) Travaux et Mémoires du Bureau International, Tome VI.

a. By means of hydrogen prepared in the apparatus of Comm. N°. 27 with the improvements described in Comm. N°. 94^e (June 1905) § 2. After having beforehand ascertained whether all junctures of the apparatus closed perfectly, we maintained moreover all the time an excess of pressure in the generator, in order to exclude any impurity from the gas. The expulsion of the air originally present in the apparatus was continued till it could be present in the gas at the utmost to an amount of 0.000001.

b. By means of hydrogen prepared as described in Comm. N°. 94^f XIV. In order to apply this more effective mode of preparation, we must have liquid hydrogen at our disposal. [1]) In § 7 the equivalence of the first method with the last is demonstrated for measurements down to — 217°. It is still to be examined whether systematic errors may result from the application of the first method of filling, in measurements on liquid hydrogen by the deposition of impurities, less volatile than hydrogen. [2])

§ 4. *The measurements.*

The zero point of the thermometer is determined before and after every set of observations. Both for the zero point and for every determination of temperature, an average value is derived from three or four observations. Each of these observations consists of a reading of the barometer, preceded and followed by a reading of the manometer. The thermometers, indicating the temperature of the mercury, of the scale and of the gas in the manometer spaces are read at the beginning and at the end of every observation. The temperature of the room is kept as constant and uniform as possible.

The temperature of the thermometer reservoir is taken equal to that of the bath. This is permissible for the cryostats described in Comm. N°. 94^d and Comm. N°. 94^f and the treatment given there.

The temperature of the bath is kept constant by means of the resistance thermometer, described in Comm. N°. 95^c. In order to facilitate the survey of the observations, the resistance was adjusted as accurately to the same value as possible, and by means of signals the pressure in the cryostat was regulated in such a way, that in the very sensible galvanometer the mirror made only slight oscillations about

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[1]) The hydrogen in the vacuum glass *B* (see Comm. N°. 94^f XIV, fig. 4) proved to evaporate so slowly, that a period of two hours was left for filling and exhausting the thermometer again, which previously had been kept exhausted for a long time, being heated during part of the time (cf. footnote 5 § 2).

[2]) In a former set of observations deviations were found, which in conjunction with each other prove that the hydrogen must have been mixed with air.

its position of equilibrium. So far as it proved necessary, a correction curve was plotted of these oscillations (see Plate III Comm. N°. 83, December 1902). As a rule, however, these deviations were so slight, that they could be neglected.

Part of the capillary glass stem of the thermometer has the same temperature as the liquid bath. The length of this part is derived from the indications of a float [1]) in the cryostat, which is omitted in the drawings, not to render them indistinct. In order to find the distribution of temperature in the other parts of the capillary within the cryostat, special determinations are made, viz. *a.* by means of a resistance thermometer placed by the side of the capillary, (see Comm. N°. 83 Plate II [2])), *b.* with the aid of a thermoelement, whose place of contact was put at different heights in the cryostat, the distribution of temperature in the cryostat was examined for the case that liquid air, liquid ethylene or liquid hydrogen was used as bath, and finally *c.* the distribution at other temperatures of the bath was derived from this distribution. This may be deemed sufficient, as the volume, the temperature of which is determined, amounts only to $\frac{1}{3000}$ of the reservoir, and as an error of 50° in the mean temperature of the capillary corresponds to only 0°.01 in the temperature of the bath, while the agreement of the observations sub *a* and *b* show that an error of more than 20° is excluded.

§ 5. *Calculation of the temperatures.*

The calculation of the zero point is made by reducing the observed pressure of the gas to that under fixed circumstances, the same as taken in Comm. N°. 60. Put:

V_0 the volume of the reservoir at 0°.

u_1 the volume of that part of the glass capillary that has the same temperature t as the reservoir. As such is considered the part immerged in the liquid bath, to which is added 2 cm. of the part immediately above it.

u_2' and u_2'' the volumes of the parts of the glass capillary in the cryostat outside the bath at temperatures t_2' and t_2''.

u_3 the volume of the part of the glass capillary outside the cryostat (u_2''') and of the steel capillary at the temperature t_3.

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[1]) For determinations on liquid hydrogen no float was used. The level of the liquid in the bath was derived from the volume of the evaporated gas.

[2]) The lowest part from ζ_{11} to ζ_{12} with close windings is 9 cm., the part where the windings are farther apart (about 20 cm.) reaches up to in the top of the cryostat.

u_4 the volume at the steel point of the volumenometer.

β_1 and β_2 the variation of the volume V_0 caused by the pressure of the gas.

If H_T is the observed pressure, and H_0 and u have the same meaning as in Comm. N°. 60, the temperature is found from the formula:

$$H_T\left[\frac{V_0(1+k_1t+k_2t^2)+\beta_1+u_1}{1+at}+\frac{u_2'}{1+at_2'}+\frac{u_2''}{1+at_2''}+\frac{u_3}{1+at_3}+\frac{u_4}{1+at_4}\right]=$$

$$=H_0\left[V_0+\beta_2+u_1+u_2'+u_2''+u'''_2+\frac{u}{1+15a}\right]\quad .\quad .\quad (1)$$

The change of volume of the glass stem caused by the change of temperature need not be taken into account, as little as that of u. That of the thermometer reservoir has been calculated by means of a quadratic formula, of which the coefficients k_1 and k_2 have the following values: $k_1 = 23.43 \times 10^{-6}$, $k_2 = 0.0272 \times 10^{-6}$ [1]).

Put

$$\left.\begin{aligned}\frac{u'_2}{1+at'_2}+\frac{u''_2}{1+at''_2}+\frac{u_3}{1+at_3}+\frac{u_4}{1+at_4}&=\Sigma\frac{u}{1+at}\\ H_0\left[v_0+\beta_2+u_1+u'_2+u''_2+u'''_2+\frac{u}{1+15a}\right]&=A,\end{aligned}\right\}\quad .\quad (2)$$

then follows from the above for the temperature:

$$t=\frac{V_0+\beta_1+u_1-\dfrac{A}{H_T}+\Sigma\dfrac{u}{1+at}+V_0\,k_2\,t^2}{\left\{\dfrac{A}{H_T}-\Sigma\dfrac{u}{1+at}\right\}a-V_0\,k_1}\quad .\quad .\quad .\quad (3)$$

If the term with t^2 is omitted, we find an approximate value for the temperature. Now t may be calculated again, while in the term with t^2 this value is substituted. This approximate calculation is quite sufficient.

§ 6. *Survey of a measurement.*

The observations communicated in this §, yielded the temperature corresponding to the electromotive force of the thermoelement determined in Table IV and V of Comm. 95^a and corresponding to the resistance measured in the observation given in Table I of Comm. N°. 95^c (in the last case even almost simultaneous).

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[1]) These values have been derived from Comm. N°. 95^b. They refer to the determinations made in 1903 on the expansion of glass. If we calculate the temperatures by means of the quadratic and cubic formula derived in the same Comm. from the observations of 1905, we find but slight differences, which amount respectively to — 0°.014 and — 0°.016 at — 100°, and remain always below 0°.01 at — 200° and lower.

The tables I and II are analogous to those of Comm. N°. 60, only column *K* has been added to the former, in which the readings from the kathetometer scale are noted down. In every measurement they are always determined, in order to be used, if necessary, as a control for the readings by means of the standard scale, in connection with the collimation differences of the telescopes.

TABLE I.

DETERMINATION IN A BATH OF LIQUID HYDROGEN. (ABOUT — 253°). READINGS.

May 5, '06, 3.10-3.30		*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*K*
	Point	14.75	7.9	974	20.17	9.1				
				975	17.86	8.1				
Manometer	lower top	23.00	9.0	297	22.02	9.3	15.5	15.5	15.4	
	meniscus rim	26.01	9.0	298	19.90	10.3		15.6	15.1	21.926
							15.5	14.3		
	higher top	15.10	7.9	974	20.17	9.1				
	meniscus rim	18.43	7.9	975	17.86	8.1	15.5			89.294
Barometer	lower top	21.03	8.7	297	22.02	9.3	15.5			
	meniscus rim	22.70	8.6	298	19.90	10.3	15.5			
	higher top	25.82	9.6	1058	28.07	11.3	15.7			103.279
	meniscus rim	27.98	10.0	1059	25.43	11.0	15.7			
Manometer	lower top	22.98	9.3	297	22.02	9.3	15.4	15.5	15.4	
	meniscus rim	25.99	9.3	298	19.90	10.3		15.4	15.2	
							15.3	14.3		
	higher top	15.06	7.9	974	20.17	9.1				
	meniscus rim	18.42	8.0	975	17.86	8.1	15.5			
	Point	14.76	8.0	974	20.17	9.1				
				975	17.86	8.1				

TABLE II.

DETERMINATION IN A BATH OF LIQUID HYDROGEN (ABOUT — 253°). CORRECTED AND CALCULATED DATA OF THE OBSERVATION.

		A'	B'	C'	D'	E'	F'
Manometer	lower meniscus	296.55	296.70	14.8	14.9		
	height	1.39		14.9	14.8		
	higher meniscus	976.21	976.37	14.9	13.8	81.53	0.14
	height	1.46					
Barometer	lower meniscus	297.46	297.48	14.8			
	height	0.77					
	higher meniscus	1058.87	1058.90	15.0			
	height	0.83					

The correction was applied for the difference in level of barometer and manometer (cf. also Comm. N°. 60). In this way we find H_T, the pressure of the gas in the thermometer.

TABLE III.

DETERMINATION IN A BATH OF LIQUID HYDROGEN. (ABOUT —253°). DATA FOR THE CALCULATION,

$u_1 = 0.0105$ cm^3	
$u_2' = 0.0126$ »	$t'_2 = -162°$
$u_2'' = 0.0140$ »	$t''_2 = 0°$
$u_3 = 0.6990$ »	$t_3 = 14°.5$
$u_4 = 0.2320$ »	$t_4 = 14°.9$
$u_2''' = 0.1141$ »	

$H_T = 81.53$ m.m.

$V_0 = 82.265$ cm^3

$\beta_1 = -0.0041$ » , $\beta_2 = +0.0021$ cm^3

$H_0 = 1091.88$ mm.

$u = 0.7991$ cm^3

From the indication of the float the value of u_1 is found. u_2' and u_2'' are chosen such that the circumstances are as closely as possible equal to those for which the distribution of temperature in the cryostat is determined. We get now the table III, in which H_0 is the zero point pressure.

From these data with formula (3), where the value 0,0036627 of Comm. N°. 60 [1]) was assumed for a, follows for the approximate value of the temperature:

$$t = -252°.964$$

and after application of the correction for the quadratic term:

$$t = -252°.964 + 0°.035 = -252°.93.$$

§ 7. *Accuracy of the determinations of the temperature.*

In order to arrive at an opinion about the error of the observations with the hydrogen thermometer, we determine the differences of the hydrogen temperatures found in different observations in which the resistance was adjusted to the same value, reduction having been applied for small differences left.

The mean error of a single determination derived from the differences of the readings of the thermometer, which succeed each other immediately, is on an average ± 0°.0074, from which we derive for the mean error of a temperature ± 0°.0043, assuming that on an average 3 observations have served to determine a temperature. As a rule no greater deviations than 0°.02 were found between the separate readings of one determination. Only once, on Oct. 27th '05 (cf. Comm. N°. 95^c Tab. I) a difference of 0°.04 occurred. Even at the lowest temperatures only slight deviations occur. Thus on May 5th '06 two of the observations in the neighbourhood of the boiling point of hydrogen (cf. Comm. 95^a Tab. VI,, observation N°. 30, and Comm. N°. 95^c Tab. I) yielded:

$3^u20'$	— 252°.926
$3^u58'$	— 252°.929

the two others with another resistance:

$2^u35'$	— 252°.875
$3^u\ 7'$	— 252°.866 [2])

Determinations of one and the same temperature on different days

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[1]) From the values of α found by Chappuis at different pressures and from Berthelot's calculations follows by extrapolation from Chappuis' value for $p = 1000$ m M. $\alpha = 0.00366262$ for $p = 1090$ m.M., from Travers' value of α for 700 m.M. with the same data $\alpha = 0.00366288$ for $p = 1090$ m.M.

[2]) At both these temperatures the indications of the resistance thermometer were not made use of, but only the pressure in the cryostat was kept constant. That in spite of this the readings of the thermometer differ so little is owing to the great purity of the liquid hydrogen in the bath.

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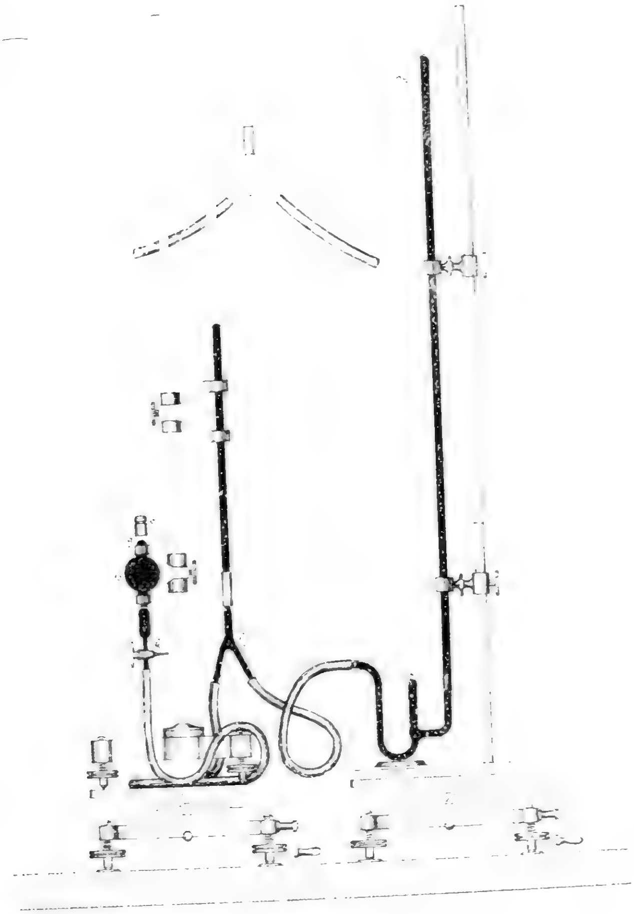
Plate I.



with the same filling of the thermometer yielded the following results: (cf. Comm, N°. 95^a Tab. VI and N°. 95^c Tab. I) 1)

July 7th, '05	— 139°.867
Oct. 26th, '05	— 139°.873
July 6th, '05	— 217°.416
March 3rd, '06	— 217°.424
June 30th, '06	— 182°.730
July 6th, '06	— 182°.728

For the deviation of the determinations on one day from the mean of the determinations on the two days follows resp.:

0°.003, 0°.004 and 0°.001 so mean 0°.0027,

which harmonizes very well with the mean error derived above for a single observation 2), from which appears at the same time that different systematic errors are excluded. This justifies at the same time the supposition from which we started, that the error in the resistance thermometer may be neglected.

Determinations with different fillings agree very well.

The determinations made on July 6th, '05 and March 3rd, '06 with the thermometer filled with electrolytic hydrogen (see § 3) and those made on June 30th, '06 with the thermometer filled with distilled hydrogen, give:

mean of July 6th, '05 and March 3rd, '06 — 217°.420

$$\text{June } 30^{\text{th}}\text{, '06}\quad \left.\begin{array}{l} 5^u50' \;\; -217^\circ.327 \\ 6^u\;\,5' \;\; -217^\circ.362 \\ 6^u25' \;\; -217^\circ.347 \end{array}\right\} \text{ mean } -217^\circ.345.$$

If the last temperature is reduced to the same resistance as the first, we find — 217°.400, hence the difference of these values is 0°.020, from which, only one determination being made, we must conclude, that also with regard to the filling systematic errors are pretty well excluded down to — 217°.

§ 8. *Results.*

It appears from the foregoing that with our hydrogen thermometer determinations of temperature, even at the lowest temperatures,

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1) The temperature for June 30th '06 given here differs slightly from that given in Table I of Comm. N°. 95^c, though both refer to the same resistance. This difference is due to the fact that in Comm. N°. 95^c the result of one reading has been used, and here the mean has been given of more readings.

2) It gives namely for the probable error 0°.0029, so only a trifling difference with the above.

may without difficulty be effected accurate to $\frac{1^\circ}{50}$ if the requisite precautions are taken. Though it is not certain that the determinations in liquid hydrogen of the last series come up to this accuracy, as there a systematic error caused by the filling may show its influence, which does not yet make its appearance at —217°, yet it lies to hand to suppose, that, at least with the thermometer filled with distilled hydrogen, also these temperatures may be determined with the same degree of accuracy.

§ 9. *Vapour tension of liquid hydrogen at the melting point.*

By sufficiently lowering the pressure over the bath of liquid hydrogen the temperature was reached at which the hydrogen in the bath becomes solid. This temperature indicates the limit below which accurate determinations are no longer possible by the method discussed in this Communication.

It could be accurately determined by a sudden change in the sound which the valves of the stirrer in the bath bring about. (See Comm. N°. 94*f*, XII § 3).

It appeared from the indication of the resistance thermometer that the gas in the hydrogen thermometer had partly deposited. Hence the pressure in the hydrogen thermometer gives the vapour tension of liquid hydrogen near the melting point. For this we found:

$$H_{Sm} = 53.82 \text{ m.m.}^{1})$$

§ 10. *Reduction on the absolute scale.*

The reduction of the readings of the hydrogen thermometer on the absolute scale by means of the results of determinations of the isotherms will be discussed in a following Communication.

§ 11. *Variations of the zero point pressure of the thermometer.*

It is noteworthy that the pressure in the thermometer in determinations of the zero point slowly decreases. This change is strongest when the thermometer has just been put together and becomes less in course of time. This is very evident when the results of the determinations made at the beginning of every new period of observation are compared, so after the thermometer has been left unused for some time under excess of pressure.

Thus on the fifth of July '05 shortly after the thermometer had

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1) For this TRAVERS, SENTER and JAQUEROD (loc. cit., p. 170) find a value lying between 49 and 50 m.m. The great difference is probably owing to the inferior accuracy of these last determinations.

been put together we found:

$$H_0 = 1093.10 \text{ mm.}$$

whereas at the beginning of the two following periods of observation was found:

on Oct. 13th '05 $H_0 = 1092.11$ mm.
on Febr. 26th '06 $H_0 = 1091.93$ mm.

The determinations before and after every period of observation give but slight differences when compared. As a rule the pressure decreases slightly as in the second of the above-mentioned periods of observation (March 7th '06, $H_0 = 1091.83$ mm.), sometimes there is a slight increase, as in the first period of observation (Nov. 2nd '05, $H_0 = 1092.23$ mm.) after observations under low pressure. Before and after the last series of observations, when shortly after the thermometer had been filled with distilled hydrogen, determinations were made at — 183° and — 217°, this difference was particularly large. The zero point pressure after the measurements was then 0.33 mm. larger than before them.

From earlier observations made with another thermometer the same thing appeared.

Thus on Nov. 19th '02

$$H_0 = 1056.04 \text{ mm.}$$

was found, and the pressure on June 8th '04 was

$$H_0 = 1055.43 \text{ mm.}$$

while during further measurements up to July 7th '04 the pressure retained a value which within the limits of the errors of observation remained equal to this.

CHAPPUIS[1]) found a similar decrease viz. 0.1 mm. in three months with a zero point pressure of 1 M. of mercury.

Finally a decrease of the normal volume was observed by KUENEN and ROBSON and by KEESOM also with the air manometer (see Comm. N°. 88 (Oct. 1903) III § 3). The same phenomenon was recently observed with the auxiliary manometer filled with hydrogen mentioned in Comm. N°. 78 (March 1902), when it was again compared with the open standard manometer. This comparison will be discussed in a following Communication.

The possibility of there being a leak is excluded by the fact that a final condition is reached with the thermometer.

It lies to hand to attribute the variations of the zero point to an

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[1]) Nouvelles études sur les thermomètres à gaz, Travaux et Mémoires du Bureau International. T. XIII p. 32.

absorption which comforms slowly to the pressure. As to the absorption of the gas in the mercury, its adsorption to the wall and the interchange of gas with a thin layer between the wall and the mercury they (and especially the last) may be left out of account, though they are not rigorously zero. For with manometers, where no influences but these can exert themselves, the pressure of the gas is sometimes considerably raised during a long time, and notwithstanding the variations of the normal volume are much slighter than with the thermometers.

Consequently we shall rather have to think of a slow dissolving in and evaporating from the layer of glue, which is applied between the steel caps and the glass.

ERRATA.

p. 193	l. 1 from top	for: deviation, read: value of the deviations.
	l. 2 from top	for: largest deviation, read: of the largest deviations.
p. 195	l. 8 from bottom	and l. 2 from bottom for: values read: quantities.
p. 196	l. 7 from top	for: from, read: for.
	l. 9 from top	for: and are combined, read: and these are given.
p. 198	l. 19 from top	for: agree, read: correspond.
	l. 6 from bottom	in note, for: calculations, read: calculation of the formulae we used.
	l. 6 from top	must be omitted: "are used"
p. 211	l. 16 from top	for: with, read: containing also.

(November 22, 1906).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday November 24, 1906.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 24 November 1906, Dl. XV).

CONTENTS.

Zoology. — *"On the placentation of Sciurus vulgaris."* By Dr. F. Muller. (Communicated by Prof. A. A. W. Hubrecht).

(Communicated in the meeting of September 29, 1906).

I. The very earliest stages. The ovule of Sciurus undergoes its first developmental stages in the oviduct. Meanwhile the bicornuate uterus has prepared itself for the reception of the ovule: underneath the single layer of epithelium the mucosa, which mesometrially remains very thin, has become very strongly thickened, so that an excentrical T-shaped slit is left open, the transverse part of which lies closest to the mesometrium. A special arrangement for the attachment of the ovules can nowhere be detected; a subepithelial zone is found to be richer in nuclei, however, than the loose connective tissue, separating this layer from the muscularis.

II. Pre-placentary stages (From the arrival of the ovule in the uterus until the first formation of the allantoid placenta).

The ovules fix themselves in varying numbers, to the right generally more than to the left, at about equal distances on the anti-mesometral (i.e. anti-placentary) uterine wall; they are fixed with their vegetative poles. A pellucid zone is absent, on the other hand the ovule becomes surrounded by a mass, formed from glandular secretions of cellular origin from the uterine wall.

The ovules grow pretty quickly, for the greater part by dilatation of the umbilical vesicle, which in these stages still forms the principal part of the ovule. It is remarkable that the area vasculosa remains so small, so that only entoderm and trophoblast form the wall of the germinal vesicle over the greater part of the umbilical vesicle.

The uterine wall shows intense activity during this stage. Many processes take place here in rapid succession and simultaneously. They all start from the spot where the ovule has settled, and from this point extend in all directions, successively reaching the spaces of the uterine horn, left open between the fixations of the ovules, as also the mesometrally situated parts; all these processes begin sub-epithelially, gradually penetrating deeper and deeper. These successive processes thus gradually give rise to dish-shaped layers of varying structure, surrounding the ovule at the anti-mesometral side and the character of which is most sharply pronounced in the points that are at the greatest distance from the mesometrium. By the extension of the anti-mesometral part of the long end of the

T-shaped slit, a broadening is brought about here, which, progressing more and more in the mesometral direction, finally produces a space, the cross-section of which presents a shape like that of a cone, truncated mesometrally by the old transverse part of the T, and bordered anti-mesometrally by a circular segment corresponding to the umbilical vesicle. The ovular chambers, formed in this way, have originated as the result of growth and extension of the anti-mesometral uterine wall, as a consequence of which the parts of the horn that connect them, are implanted at the mesometral side of the foetal chambers and at the same time are bent in this direction. The proliferation in the stroma tissue, beginning in the sub-epithelial layer, squeezes the mouths of the glands asunder. Later the epithelium in these latter degenerates, the walls agglutinate, finally only remnants of glands are found in the more normal stroma under the muscularis.

The processes by which the first formation of dish-shaped layers takes place (the existence of which is always of a relatively short duration, however) are the oedematous imbibition of the tissue and disintegration of cell-elements, accompanying the proliferation of the sub-epithelial multinuclear zone, the final result being a system of cavities, separated by thin cell-partitions and filled with the products of oedema and disintegration of tissue. This layer is externally surrounded by layers which form the transition to the still normal, although proliferating tissue, while at the opening they are more and more separated by products of a later process.

Very remarkable is the appearance at this time of "giant cells", plasma-lumps of different size, which assume a dark colour and contain many giant nuclei with a large nucleolus. Continuous layers or more isolated groups are found as individual differences, apparently. They lie mostly superficially, often connected with the trophoblast, not with the vessels. At first sight one would feel inclined to regard them as the foetal "suction roots" of the trophoblast, described for Spermophilus by Rejsek. Since all transitions are found between the mucosa tissue and these elements (in some cases even the transition having been followed up); since, moreover, they are found on the ovule, in course of being dissolved in the surrounding mass; since, on the other hand, in no case an origin from the trophoblast could be made probable, the giant cells are for this and other reasons in my opinion to be considered as a degenerative maternal formation, as a symplasm. They cannot be identified with the "monster cells" of Minot, Schoenfeld and others, described for the rabbit, since these elements are also found in Sciurus, only much later. Finally comparative anatomical considerations plead for my opinion (see below). The uterine epithelium gradually disappears in all places where the germinal vesicle is in contact with it. There is never question of proliferation now.

Relatively soon already (even with a very extensive material the transitions are difficult to follow) a second stage sets in, in which by proliferation of the stroma cells, beginning from the surface, a dish is formed of cubical cells with granulated plasm (decidua), which extends more and more, while the above described cavities disappear, probably by resorption under influence of the pressure. In the mean time the decidua cells at the surface undergo further alterations and are resorbed (very likely by the umbilical vesicle, since in this and in the cells of the wall a similar substance can be found), so that a fine meshy texture is formed by the peripheral part of the cells remaining; by the pressure this meshy texture is compressed to a thin layer of lamellar structure, which in its youngest parts still shows the meshes. Vessels are not or scarcely found in the decidua. The separation between the decidua and the little or not changed subdecidual tissue outside it, is the limit to which the differentiating processes in the wall have progressed, at the same time approximately the limit, marking how far the agglutination of the germinal vesicle with the wall has advanced; it may therefore be called "differentiation limit".

At this time the above described giant cells become fewer and fewer in number, have an increasingly degenerate appearance and soon disappear altogether. At the mesometral side especially by proliferation of the epithelium an increase in number and size of crypts takes place (not of glands).

A second period in these pre-placentary stages is characterised for the ovule by the origin of the amnion etc. The growing embryo seeks place in an impression of the upper part of the umbilical vesicle, which becomes more and more accentuated. At the umbilical vesicle begins, starting again at the part that is most distant from the embryo, an outgrowth of the trophoblast cells with their nuclei, which process also continually advances towards the embryonic pole.

Characteristic for this stage are different processes beginning on the ovule as well as on the uterus in equatorial bands above the differentiation limit, and from here also proceeding mesometrally on all sides. For the ovule these processes consist in a proliferation of the trophoblast which will later cover the outer layer of the amnion fold; irregularly placed, dark, polygonal cells with distinct borders appear; on the surface of the trophoblast small cell-heaps rise everywhere. On the corresponding spot of the uterine wall a progressive process sets in; first: formation of crypts by proliferation of epithelium, at the same time thickening of the intermediate stroma; later by this process a ring has been formed, which everywhere projects a little into the lumen above the differentiation limit, dividing the cavity of the foetal chamber into a mesometrally situated placentary part, and an omphaloid part situated below it, while by this arrangement the meanwhile completed diplotrophoblast (chorion) with its very strongly thickened layer of trophoblast bulges out. The hyperplastic stroma of the projecting ring is everywhere well provided with crypts.

In the meantime this proliferation process has been closely followed by a regressive one; the epithelium begins to degenerate, first at the surface, later deeper and deeper in the formed crypts; plasm and nuclei become darker, more homogeneous, smaller; later the pycnotic nuclei dissolve in the plasm and a mass is formed, epithelial symplasm, in which finally greater and smaller vacuoles are evenly distributed. Everywhere short ramifications of epithelium have penetrated into the stroma, which soon degenerate. Also the stroma itself undergoes similar alterations later.

Wherever this degeneration has somewhat advanced, a third process sets in, likewise extending as a band: the thickened trophoblast penetrates with its ramifications some distance into the crypts, later also between these into the degenerated mass. Here and there the foetal mass thereby changes, after its elements have become enlarged and paler, into a syncytium, the nuclei of which contrast well with those of the maternal symplasm. In this connecting ring the syncytium soon disappears again; extension causes the trophoblast with its hollow ramifications, penetrating into the crypts, to become a single layer once more; exactly here the area vasculosa still remains for a time in connection with the trophoblast: everything pleads, in my opinion, for the hypothesis that this has to be considered as a rudiment, namely of an omphaloid placentation (Sorex, which among the Insectivora stands nearest the Rodents, shows a distinct omphaloid placentation).

The products of the crypts and glands, transsudates and symplasm masses, are shed over the cupola of the diplotrophoblast and probably are resorbed by this latter.

The vessels in the meantime proliferate strongly in the wall of the mesometral part of the foetal chamber between the crypts, which has remained unchanged yet; their wall consists as before of simple endothelium, without a perivascular sheath.

III. Placentary stages (After the beginning of the formation of the allantoid placenta). In the omphaloid part of the foetal cavity the wall is more and more attenuated by extension and resorption of tissue, although the layers may be recognised as before. The increase in size of the trophoblast cells of the umbilical vesicle, which had set in formerly, now leads to the formation of true "monster cells", the cellular body of which often shows concentric rings and other peculiarities, while the big nucleus often lies like a crescent round a vacuole. This process comes nearer and nearer the mesometrally situated formations. The entoderm, covering these monster cells, is very narrow and small-celled; where it covers the area vasculosa, it consists on the other hand of cubical, strong cells. In the umbilical vesicle a coagulated mass is always present. The large embryo more and more invaginates the upper part of the umbilical vesicle. Between the monstercells and the entoderm a sort of cuticle develops.

The processes, extending in equatorial bands, continally advance towards the mesometral pole of the foetal chamber, also in the partitions of the foetal chambers, so that they are more and more incorporated by these latter. In this manner extremely complicated pictures are formed, especially in cross-sections.

The dilatation now affects very strongly as well the placentary part of the foetal chambers as their mutual connecting pieces, so that the omphaloid part becomes smaller and smaller, while the formerly existing comb-shaped division between them disappears.

The progressive process finally reaches the mesometral pole of the placentary space and continually advances further into the connecting pieces of the foetal chambers: the still intact part of the wall, which at first had the shape of a cupola, later assumes the form of an 8, finally reduced to two round planes, which by the proliferation are more and more limited to the connecting pieces. The progressive process now forms crypts, which in other places are narrow and deep, but in the place of the placenta are broad and wide by dilatation and excessive proliferation of the stroma. The epithelium has many layers, its surface still rises everywhere in papillae. In the stroma not all the cells reach their full development as decidua cells simultaneously, so that a peculiar reticulated aspect is produced. Also the vessels increase.

In this soil now the degenerative process occurs, again advancing centripetally towards the mesometral pole. The epithelium becomes a symplasm, exactly like that described above, but this time more abundant and, everywhere covering the trophoblast. In the stroma a conjunctival symplasm is formed, and, as was the case in the hyperplastic process, not everywhere simultaneously, so that small partitions of symplasm still surround more healthy groups. Outside the placentary trophoblast all this goes on until a single mass of epithelial and conjunctival symplasm is formed; within reach of the placentary trophoblast, however, the trophoblast has already penetrated before that time. During this degeneration also vessels are opened, so that extravasates are not rare now and altered blood is found against the trophoblast.

The third process by which the trophoblast is connected with the uterine wall, consists in the formation of hollow, one-layered invaginations in the crypts, which trophablast papillae are covered by caps of symplasm; between the crypts the trophoblast is extremely thin by extension, often irrecognisable, also when later the formation of giant cells had advanced thus far: these latter are then very long and narrow.

Finally the placentary trophoblast (which now forms if it were the keystone of the cupola of the diplotrophoblast and consists of a distinct basal layer of cells of one cell thickness and an often 20 cells thick layer above it) now lays itself everywhere against the papillae of the mesometral cupola of the placentary foetal chamber cavity, which papillae are in progress of being degenerated; the trophoblast papillae are likewise still covered by the symplasm, when between them this has already been resorbed.

Next comes the formation of a foetal syncytium from the superficial layers of the thickened placentary trophoblast, the process beginning above and centrally and proceeding centrifugally downwards; the nuclei which at first were dark and small, become larger and clearer, contain one big nucleolus and are clearly distinct from all maternal elements. This syncytium everywhere penetrates into the maternal tissue in strands, so that an intimate interweaving of maternal and foetal tissue results, proceeding centripetally into the papilla. Then everywhere "vacuoles" are formed in this mass (probably now for the first time at the expense of maternal tissue), which, when they become larger, bend the basal trophoblast layer (cytotrophoblast) inwards and finally fill with maternal blood. The allantois has meanwhile penetrated into the trophoblast papillae and is divided into small lobes by the growth of pairs of bulges of the cytotrophoblast. Foetal vessels soon penetrate freely into each lobule.

The primordium of the placenta as a whole has no round shape, the edges facing the connecting pieces of the foetal chambers are concave to these sides, corresponding to the shape of the surface, here occupied by the progressive and regressive processes.

Gradually all the maternal tissue is replaced by foetal, so that finally the papillae which at first were entirely maternal, have become entirely foetal. Now the "vacuoles", surrounded by foetal syncytium dilate further (also grow at the expense of a foetal symplasm which now forms everywhere) and subdivide, a process, accompanied by constantly increasing separation of the allantoic villi by these cavities, containing maternal blood; the final result is that papilla-shaped lobes with secondary lateral lobules are formed, all separated by allantois-strands with foetal vessels; these are surrounded by the cytotrophoblast, which in its turn surrounds the "vacuoles" (now identical with cavities, containing maternal blood), enclosed by a layer of syncytium which at first is broad, later becomes gradually narrower. The placenta, originated in this way rests on a substructure of maternal tissue, composed of the same elements as formerly (decidua, etc.); the decidua-cells often grow out strongly, while the border between foetal and maternal tissue is in many places marked by a narrow streak of symplasm. The formation of trophoblastic giant cells gradually reaches also the supra-placentary parts, so that here also the enormous cells (later often free) lie in the maternal tissue.

Outside the placenta a stage soon is reached in which the progressive and regressive processes, described above, have attained their extreme limit. Superficially all has been changed into symplasm, only in the depth decidua-cells still exist, which meanwhile, since the degeneration does not reach to this depth, have become pretty large. The parts of the mucosa spared by these processes, are only the mucous membrane of the dilated connecting pieces, now entirely incorporated in the foetal chambers and whose mucosa, attenuated by extension, only possesses crypts still, that are squeezed flat, and a rather thick epithelium which for a part turns into symplasm. Against all these extra-placentary parts lies the extra-placentary trophoblast, now consisting entirely of giant cells which at present often get loose and then lie freely amid the decidua.

The embryo has, during its further growth, found place in the umbilical vesicle which gradually has become entirely invaginated and whose walls almost touch each other. The edges of the bowl, thus originated and containing the embryo, are not formed by the sinus terminalis; this latter lies further down in the inner wall. The small space in the umbilical vesicle is still filled with coagulating masses, while the entoderm, covering the area vasculosa, which now often forms papillae, has still a very healthy appearance. The outer wall of this bowl never disappears. In its further growth the placenta reaches the edges of the bowl of the umbilical vesicle, later still it grows into it and coalesces with the inner wall: the sinus terminalis then lies halfway the thickness of the placenta, while a fold of the endoderm seems to have been incorporated into it.

In the last period of pregnancy, from the above described parts, left free by the progressive and regressive processes, epithelium grows between the degenerated and the normal part of the mucosa, perhaps joins with the meanwhile proliferating glandular remains in the depth: the umbilical vesicle is lifted off from the mucosa. Somewhat later this begins also all round the placenta, so that at the end of pregnancy this organ is more or less stalked and after parturition the greater part of the uterine wall is already provided with a new epithelium.

Comparative considerations. Among Rodents the investigation of the times at which various processes and organs of the ovule (not of the foetus) are found, leads to the following series: Sciurus — Lepus — Arvicola — Meriones — Mus — Cavia, in which the first has retained the most primitive forms, Lepus in many respects forms a transition to the last, in which more and more by new processes coming to the fore, the old, primitive ones are supplanted, mixed up and altered, in a word become nearly irrecognisable. Of this latter fact the study of the literature on the relation of ovule and uterus in Rodents, gives sufficient evidence; it also appears here how great a support is afforded by a comparative anatomical investigation; even, that various problems cannot be solved without its assistance.

The progression appears clearly in the pecularities of the umbilical vesicle in the various animals: in all the upper part is invaginated into the lower, with Sciurus not until late, with Cavia the process is among the first; the distal wall always remains with Sciurus, with Lepus it disappears late, with Cavia already quite at the beginning; the endoderm covers the inner wall already very early in Sciurus, very late in Mus, never entirely in Cavia.

In the same order the antimesometral fixation and the allantoid placenta occur earlier and together with these the trophoblast thickening, which causes them. It is exactly the remarkable pre-placentary processes which have been so carefully studied with Mus and Cavia, which by this replacing present the greatest difficulties.

With all Rodents the vegetative ovular pole becomes connected with the anti-mesometral wall of the uterus. This connection only ends in Sciurus towards parturition, in Mus and Cavia already very early, in Lepus at an intermediate stage, by epithelium being pushed underneath from the connecting pieces of the foetal chambers.

In this fixation the umbilical vesicle is surrounded by proliferating mucosa tissue which later degenerates and is dissolved and resorbed by the ovule. The epithelium soon disappears after slight progressive changes, the stroma changes into decidua by very strong proliferation which in Mus, Cavia, etc. rises as reflexa round the ovule, corresponding with the smallness of the umbilical vesicle and consequently of the ovule. In accordance with an existing inclination, in the order of the above mentioned series, to replace nutrition by stroma products by maternal blood, the vascularisation of the decidua is very small in the squirrel, very strong in Cavia and correspondingly the extravasates, surrounding the ovule are very rare in Sciurus, common and abundant in Mus and Cavia.

In these processes in Sciurus maternal giant cells appear (symplasm) and later foetal ones, when the former have disappeared. In Lepus SCHOENFELD and others found the foetal giant cells (monster cells) already in earlier stages, in accordance with our series; all the cells then occurring are by him considered as foetal; probably, however, the maternal cells occur at the same stage and part of the described cells are of maternal, symplasmatic origin. With Mus both were found and distinguished by JENKINSON at much earlier stages, KOLSTER did not see the foetal ones, DUVAL not the maternal ones. So they must occur still earlier in Cavia; the foetal ones are then probably the proliferating "Gegenpolcellen" of v. SPEE, which perforate the zone at the vegetative pole; the maternal ones correspond to the products of the processes in the "Implantationshof" of v. SPEE. Also the disappearance of these formations takes place at an increasing rate (By all this it becomes clearer still that the comparison of Cavia and man by v. SPEE, which already from a phylogenetic point of view is hazardous, must be received with caution).

In the light of the comparative investigation these foetal "monster cells" may be considered as rudiments of an organ which was strongly developed in the ancestors of the Rodents.

In Sciurus the mass surrounding the ovule ("coagulum") consists especially of tissue products; these become less prominent in the order of the series and are replaced by blood.

Of the omphaloid placentation, which in Sciurus is already rudimentary, not much can be expected in the other members, although the study (until now neglected) of the morpho logy of the extra-placentary parts of the foetal chamber might perhaps shed light on this subject.

The now following appearance of the allantoid placenta is found latest in Sciurus, earliest in Cavia. The tendency, increasing in the well-known order, to bring about as much as possible a nutrition without tissue products of the mucosa of the uterus and an allantoidean-placentary exchange between foetal and maternal blood, causes the processes, playing a part in placentation, to change: in Sciurus we still have a very strong hyperplasia of stroma-epithelium, later degeneration, disintegration and resorption with penetration of the trophoblast into this mass, all temporarily clearly distinct and relatively slow, in Cavia we find almost exclusively vascular proliferation, while proliferation and degeneration go hand in hand and the invasion of the trophoblast follows closely on these, this latter process not proceeding far and being soon finished (since the object: amener une hémorrhagie maternelle a être circonscrite par des tissus foetaux (DUVAL), is sooner reached). In the other animals all intermediate stages are found.

The later processes in the development of the placenta are in all different, although they are alike in principle: subdivision of cavities respectively vessels, containing maternal and foetal blood. The allantois remains passive, the foetal mass grows further and further round the allantois-ramifications, as it penetrates further into the cavity of the foetal chamber.

The formation of foetal giant cells proceeds with all Rodents over the whole trophoblast from the vegetative to the placentary pole; also the decidual cells become larger, so that also the giant cells, which in all have been found supra-placentary (as JENKINSON already stated for the Mouse), are partly of maternal, partly of foetal origin; with Sciurus the two always remain easy to distinguish.

The more or less isolated place, which according to the statements of authors, Lepus would in some respects occupy, will perhaps disappear, when the until now somewhat neglected study of the pre-placentary period will have been more extensively carried out (also in regard to the morphology of the foetal chamber).

Finally I have not become convinced that also for the morphology of the foetal chamber cavities the unity in the structural plan goes for all Rodents as far as is claimed by FLEISCHMANN; the difference in the statements I met with, will however perhaps disappear when all this has been studied with the aid of a more extensive material, although FLEISCHMANN's conceptions, for similar reasons, are certainly incorrect in their present shape.

Botany. — *"On the influence of the nectaries and other sugar-containing tissues in the flower on the opening of the anthers."* By Dr. W. Burck. (Communicated by Prof. F. A. F. C. Went.)

(Communicated in the meeting of September 29, 1906).

The consideration that the opening of the anthers is preceded by a very considerable loss of water [1]) and that with very many plants, e.g. *Compositae, Papilionaceae, Lobeliaceae, Antirrhineae, Rhinanthaceae, Fumariaceae* and further with all plants, chasmogamous as well as cleistogamous, which fertilise in the bud, this opening takes place within a closed flower and consequently cannot be caused by transpiration to the air, gave rise to the question whether perhaps the nectaries or other sugar-containing tissues in the flower, which do not secrete nectar outwardly, have influence on the withdrawal of water from the anthers.

My surmise that also among the plants whose anthers only burst after the opening of the flower, some would be found in which this process is independent of the hygroscopic condition of the air, was found to be correct. If the flowers are placed under a glass bell-jar, the air in which is saturated with water-vapour, the anthers of many plants burst at about the same time as those of flowers which are put outside the moist space in the open air.

This led me to arranging some experiments, yielding the following results:

1. If in a flower of *Diervilla* (*Weigelia*) *rosea* or *floribunda*, which is in progress of unfolding itself, one of the stamens is squeezed by means of a pair of pincers, so that the drainage of water from the stamen downwards is disturbed, the four anthers whose stamens have remained intact, spring open, but the fifth remains closed. With this plant it is not necessary to place the flower in a moist space; the same result is generally obtained if the flower remains attached to the plant.

If a flower is placed in the moist space together with the loose

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[1]) This loss of water amounts e.g. with *Fritillaria imperialis* to 90 % of the weight of the anthers, with *Ornithogalum umbellatum* to 86 %, with *Diervilla floribunda* to 87 %, with *Aesculus Hippocastanum* to 88 %, with *Pyrus japonica* to 80 %, with different cultivated tulips 59—68 %. etc. With plants whose anthers burst in the flower, the loss is smaller; the anthers and the pollen remain moist then. With *Oenothera Lamarckiana* the loss amounts to 41 %, with *Canna hybrida grandiflora* to 56 %, with *Lathyrus latifolius* to 24 %.

anthers of another flower, those which are attached to the flower spring open; the loose ones don't. If only the corolla with the stamens attached to it is placed in the moist space, the anthers open as well as those of the complete flower. Consequently the nectary which is found in the middle of the flower at the side of the ovary, exerts no direct influence on the bursting of the anthers. If further a stamen is prepared in its full length and placed in the moist space together with some loose anthers, the anthers of the stamen burst, whereas the loose anthers remain closed.

From these experiments we infer that the anthers open under the influence of the stamen whether or not connected with the corolla. Now an investigation with FEHLING's solution shows that as well the stamen as the whole corolla and even the corollar slips, show the well-known reaction, indicating glucose.

Of *Digitalis purpurea* two of the anthers of a flower in the moist chamber, were separated from the corolla by an incision. The uncut anthers burst open, but the other two remained closed. A stamen prepared free over its full length causes the anther to burst in the moist chamber; loose anthers, on the other hand, remain closed.

An investigation with FEHLING's solution showed that here also the corolla contains glucose everywhere, but in especially large quantities where the stamens have coalesced with the corolla. Also the stamens are particularly rich in sugar over their entire length.

Of *Oenothera Lamarckiana,* the anthers of which burst already in the bud, a flower-bud was deprived of sepals and petals. One of the stamens was taken away from the flower in full length; of another stamen only the anther was removed. These three objects were placed together in the moist chamber. The anthers of the stamens which had remained connected with the tube of the calyx and those of the loose stamen sprang open; the loose anther, however, remained closed. An examination with FEHLING's solution gave the same result as was found above with *Digitalis.*

Similar experiments were made with the flowers of *Antirrhinum majus* L., *Lamium album* L., *Glechoma hederacea* L., *Salvia argentea* L., *Nicotiana affinis* Hort. and *sylvestris* Comes., and *Symphytum officinale* L., which all gave the same results, while with the flowers of *Ajuga reptans* L., *Stachys sylvatica* L., *Scrophularia nodosa* L., *Cynoglossum officinale* L., *Anchusa officinalis* L., *Echium vulgare* L., *Calceolaria pinnata, Hibiscus esculentus, Anoda lavateroides, Malva vulgaris* Tr., *Torenia asiatica, Corydalis lutea* Dc., *Colchicum autumnale* L., *Lysimachia vulgaris* L., *Atropa Belladona* L. and *Rhinanthus major* Ehrh. the experiments were restricted to showing that with all of them the anthers spring open in a space, saturated with water-vapour. With all these plants the corolla and stamens react very strongly with FEHLING's solution.

These experiments indicate that the water is withdrawn from the anthers by an osmotic action, having its origin in the glucose-containing tissue.

I remark here that the presence of glucose — in so far as we may infer it from the precipitate of cuprous oxide after treatment with FEHLING's solution — in other parts of the flower than the nectaries proper and especially in the corolla, is a *very common* phenomenon (to which I hope to return later) and that it is not restricted to those flowers in which stamens and corolla have coalesced. There is rather question here of a quantitative difference than of a special property, peculiar to these flowers.

2. With *Stellaria media* the epipetalous stamens are mostly abortive, while of the episepalous ones only three have remained, as a rule. These three stamens bear at the base on the outside, a gland, secreting nectar.

If a flower is placed in the moist chamber and one of the stamens is injured with the pincers, the anthers of the uninjured stamens will afterwards burst, but the other remains closed. And when loose anthers from the flower are placed in the moist chamber, together with an intact flower, the loose anthers remain closed, while the anthers of the flower open. As well the petals as the stamens precipitate cuprous oxide from FEHLING's solution; also the tissue at the base of the sepals reacts with it. But the bursting of the anthers stands in no relation to this; if the petals are removed, this has no influence on the result of the just mentioned experiment.

The experiment indicates that the water is withdrawn from the anthers by the osmotic action, proceeding from the nectary.

In this connection it deserves notice that the nectaries of the epipetalous whorl and also those of the missing stamens of the episepalous whorl are abortive together with the stamens. The same is observed with *Cerastium semidecandrum* L., *C. erectum* L. and *Holosteum umbellatum* L.; here also the nectaries of the missing stamens have disappeared as a rule.

With the *Papilionaceae*, of which I investigated *Lupinus luteus L., Lupinus grandifolius L., Lathyrus odoratus L., Lathyrus latifolius L.* and *Vicia Faba L.*, the anthers are known to open already in the closed flower. The petals precipitate cuprous oxide from FEHLING's solution, but exert no influence on the opening of the anthers. Flower buds of *Lathyrus latifolius* and *Lathyrus odoratus* were deprived of their petals and placed in the moist chamber together with loose anthers. The loose anthers remained closed, but the others burst open.

In the same way as the flowers of *Stellaria media* and the mentioned *Papilionaceae,* behave with respect to the opening of the anthers in a space, saturated with water-vapour:

Stellaria Holostea L., St. graminea L., Cerastium Biebersteinii C. arvense L., Cochlearia danica L., Sisymbrium Alliaria Scop., Crambe hispanica L., Bunias orientalis L., Capsella Bursa pastoris Mnch., Hesperis violacea L., H. matronalis L., Thlaspi arvense L., Alyssum maritimum Lam., and further *Lychnis diurna Sibth., Silene inflata* Sm. *Galium Mollugo L., Asperula ciliata Rochl., Campanula media L., C. latifolia L.*

With all these plants the bursting of the anthers must, in my opinion, be ascribed to the influence of the nectaries.

With *Hesperis* two large nectaries are found at the inner side of the base of the two short stamens and between these and the four long stamens. If a flower of *Hesperis violacea* or *H. matronalis L.*, after being deprived of its petals and sepals, is placed in the moist chamber, nearly always the four long stamens only burst; the other two remain closed.

It has been repeatedly observed that the secretion of nectar begins as soon as the stamens open.

In connection with what was stated above, one would be inclined to infer from this that flow of water from the anther causes the secretion of nectar. If, however, with *Stellaria media,* the anthers are removed before they have discharged water to the nectaries, one finds all the same the nectaries amply provided with honey, when the flower opens. The same may be observed in the male flowers of *Aesculus Hippocastanum.* In the still nearly closed flowerbud the nectary is dry yet. When the flower continues to open small drops of liquid are seen to appear on the surface of the nectary, still before the anthers extend halfway from the bud. These droplets increase in size as the anthers approach the moment in which they open. By weighing it may be proved that the anthers have already lost part of their original weight when the first droplets of nectar appear on the surface of the nectary. From this circumstance also one would be inclined to infer that the water of the anthers comes out again as nectar. When, however, from very young buds, whose nectary is not moist yet, the anthers are removed, yet at a later stage of development of the bud, secretion of nectar is found in them as in buds that have kept their anthers.

With *Fritillaria imperialis* I found the same; but here the secretion of nectar was not so abundant as in buds, the anthers of which had not been removed. In my opinion these observations indicate that the sugar, stored up in the nectaries or other sugar-containing tissues of the flower, at the moment when it begins to exert its osmotic action, attracts water not only from the anthers but also from other parts of its surroundings.

3. With the following plants the anthers remain closed in a space, saturated with water-vapour. In so far as they possess nectaries, these latter appeared to exert no influence on the bursting of the anthers.

Ranunculus acris L., R. bulbosus L., Aquilegia vulgaris L., Clematis Vitalba L., Chelidonium majus L., Brassica oleracea L., Geranium molle L., G. Robertianum L., G. macrorhizum L., Geum urbanum L., Rubus caesius L., Philadelphus coronarius L., Heracleum Sphondylium L., H. lanatum Michx, Aegopodium Podagraria Spr., Carum Carvi L., Pimpinella magna L., Valeriana officinalis L., Ligustrum vulgare L. Majanthemum bifolium Dc., and *Iris Pseudacorus L.*

It is remarkable that *Brassica oleracea L.* forms an exception to what is otherwise generally observed with the Cruciferae; the position of the stamens with respect to the nectaries which secrete honey abundantly, would make us expect that in a moist chamber they would behave like the others. The same remark holds for the species of *Geranium.*

The secretion of nectar in the flower attracted the attention of various investigators many years before Sprengel published his view of the matter. Also after Sprengel, in the first half of the preceding century, it has many times been the object of investigation. All these investigators agreed in being convinced that, apart from the significance of the honey-secretion for the fertilisation of the flowers by the intervention of insects, to which Sprengel had drawn attention, the sugar-containing tissues and the secreted liquid were still in another respect useful to the plant.

After Darwin had in 1859 brought to the front again Sprengel's observations on the biological significance of the various properties of the flower — which observations were falling more and more into oblivion — and had accepted their consequences by bringing them into relation on one hand with his conceptions about the necessity of cross-fertilisation for the maintenance of the vital energy of the species, on the other hand with the theory of natural selection, the investigation of still another significance of the nectaries for the plant was for a long period entirely abandoned.

Not until 1878 this subject was again broached by BONNIER [1]) who, in his extensive paper on the nectaries, in which as well the anatomical as the physiological side of the problem were submitted to a very extensive investigation, proved that sugar-containing tissues in the flower and especially in the immediate vicinity of the ovary are not only found with plants which regularly secrete nectar during the flowering, but also with such plants as under normal conditions never secrete such a liquid. With these plants, which in the literature on flower biology are called "pollen flowers", since the insects find no nectar in them, he found as well sugar-containing tissues as in the so-called "insect flowers". Even with anemophilous plants he found "nectaires sans nectar", e. g. with *Avena sativa, Triticum sativum* and *Hordeum murinum.* A number of plants which under ordinary conditions of life contain no nectar, he could induce to nectar-secretion by placing them under conditions, favourable for this purpose.

At the end of his paper he reminds us that an accumulation of reserve materials, wherever a temporary stagnation in the development exists, may be considered a very general and well characterised phenomenon. When a plant stops its further development at the end of its growing period, it has stored up reserve material in its subterranean, parts and when the seed has finished its development, it has accumulated nourishing substances in the endosperm or in the cotyledons of the embryo. These reserve materials, turned into assimilable compounds, then serve for the first nutrition of the newly formed parts.

He then arrives at the conclusion that in the vicinity of the ovary saccharose is stored up, and that this reserve substance after fertilisation and in the same proportion as the fruit develops, passes partly or entirely into the tissue of the fruit and into the seed, after having first been changed, under the influence of a soluble ferment, into assimilable compounds.

Investigation showed me also that the accumulation of saccharose as a reserve substance in the flower is a very common phenomenon [2]).

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[1]) GASTON BONNIER. Les nectaires. Étude critique, anatomique et physiologique. Annales des sciences naturelles. Tome VIII. 1878.

[2]) On this point see also: PAUL KNUTH, Über den Nachweis von Nektarien auf chemischem Wege. Bot. Centralbl. LXXVI. Band, 1898, p. 76 and ROB. STÄGER, chemischer Nachweis von Nektarien bei Pollenblumen und Anemophilen. Beihefte zum Bot. Centralbl. Band XII. 1901, p. 34.

But besides the function, discovered by Bonnier and the significance of the secreted nectar for the fertilisation, it has become clear to me that as well the glucose, formed from saccharose, as the outwardly secreted nectar, are also in other respects of great importance to the plant. The observations, here communicated, point already to one very important function, i. e. *to enable the stamens to bring their pollen to the surface at the right time, independent of the hygroscopic condition of the air.*

I hope before long to be able to point out still another function.

The secretion of nectar now appears in another light. The view that it must be considered as an excretion of "a waste product of chemical changes in the sap" [1]), which in the course of time has become more marked through natural selection, as a useful adaptation for promoting cross-fertilisation, since this liquid was eagerly taken away by insects, has to give way to the conception that, preceding any adaptation, it has in its further development kept pace with the sexual organs.

Anatomy. — "*On the relation of the genital ducts to the genital gland in marsupials.*" By A. J. P. v. d. Broek. (Communicated by Prof. L. Bolk).

(Communicated in the meeting of October 27, 1906).

In the following communication the changes will be shortly described which the cranial extremities of the genital ducts in marsupials undergo during the development and their relations in regard to the genital gland. In more than one respect the ontogenetic development differs in these animals from what can be observed in other mammals.

It is especially a series of young marsupials of Dasyurus viverrinus in successive stadia of development from which the observations are derived. The preparations of other investigated forms (Didelphys, Sminthopsis crassicaudata, Phascologale pincillata, Trichosurus vulpecula, Macropus ruficollis) correspond however completely with the conditions we meet in Dasyurus.

In our description we start from a stadium schematically represented in figure 1 that still prevails for both sexes, (Dasyurus, Didelphys, Macropus). The genital gland (Figure 1 *k*) is situated at the medial

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[1]) Ch. Darwin. Origin of species. Sixth Edition. 1872. Chap. IV, p. 73 and The effects of Cross and Selffertilisation. Edition 1876. Chap. X, p. 402.

side of the mesonephros and is attached to it by a narrow band (afterwards the mesorchium or mesovarium) (Fig. 1 *m*). The genital ducts are developed on their whole length. The Wolffian duct (*w.g.*) joins transversal mesonephridial tubules in the mesonephros but has no connection whatever as yet with the genital gland. The Müllerian duct (Figure 1 *m. g.*) commences with an ostium abdominale (*o. a.*) and runs as far as the region of the mesonephros is concerned at the lateral side of the Wolffian duct.

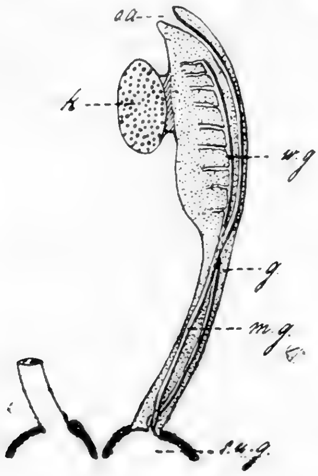

Fig. 1.

. relation of the genital gland and genital ducts in an indifferent stadium.

k.	genital gland.
o.a.	Ostium abdominale tubae.
g.s.	genital cord.
w.g.	Wolffian duct.
m.g.	Müllerian duct.
s.u.g.	Sinus uro-genitalis.

We firstly will follow the transformations, which appear in the female sex. The first change is a reduction in the cranial part of the mesonephros. Here nothing is to be observed that points to a transformation of the mesonephridial tubules by renovation of the epithelium. The Wolffian duct meanwhile grows cranially, remains situated near the Müllerian duct, and moves then, passing archwise through the mesovarium, to the ovarium, penetrates in it and there ends blind (Figure 2 *w. g.*). The condition which issues from this I have demonstrated in Figure 2 (Dasyurus 40 m.m.).

Only now the reduction of the Wolffian duct begins. This occurs in such a way, that the medial part disappears; both at the cranial and at the caudal extremity, a remnant of the duct remains.

The cranial rudiment of the Wolffian duct is then found as a little tubule blind at both ends, which commences in the ovarium and can be traced till in the mesovarium. Figure 3 points out this little tubule as I have found it in several animals (Dasyurus, Sminthopsis) (Fig. 3 *w. g.*).

In how far the remnant of the Wolffian duct has relation to the little tubules which I described and represented in the mesovarium of a fullgrown Petrogale penicillata, remains out of discussion here [1]).

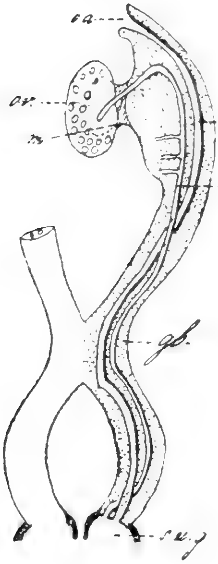

Fig. 2.

Relation of the genital ducts to the ovarium.

ov.	Ovarium.
m.	Mesovarium.
o. a.	Ostium abdominale tubae.
m. g.	Müllerian duct.
w. g.	Wolffian duct.
tr. c.	Transversal combination of both the genital cords.
s. u. g.	Sinus uro-genitalis.

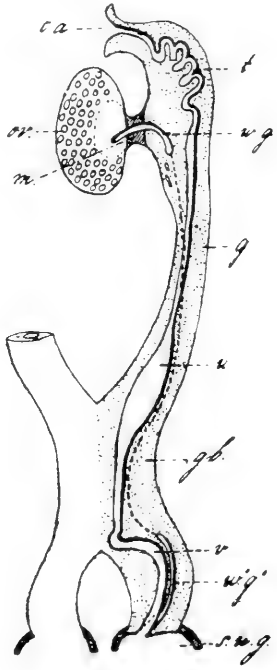

Fig. 3.

Relation of the genital ducts to the ovarium.

ov.	Ovarium.
m.	Mesovarium.
o. a.	Ostium abdominale tubae.
t.	Tuba Falloppie.
u.	Uterus.
v.	Vagina.
w.g.	Remnant of the Wolffian ducts.
w'.g'.	„ „ „ „ „
g. s.	genital cord.
tr. c.	Transversal combination of both the genital cords.
s. u. g.	Sinus uro-genitalis.

In the male sex the Wolffian duct shows in the development of its cranial extremity, very much resemblance to that of the female sex. (Fig. 4 and 5).

During the reduction of the mesonephros the cranial extremity of

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[1] v. d. Broek, Untersuchungen über die weiblichen Geschlechtsorgane der Beuteltiere. Petrus Camper III.

the Wolffian duct grows forth and takes its course archwise through the mesorchium in the testicle. (Fig. 4 *w. g.*). Here is brought about in one place (Dasyurus) a connection with the future spermatic tubes, which are still present in the stadium of solid cords of cells.

The mesonephridial tubules disappear almost quite, so that at a certain stadium (Dasyurus viverrinus 53 m.m.) the Woffian duct, strongly grown forth in length, runs twisting through the mass of tissue, which must be considered as the epididymis, without any appearance of tubules in the form of the coni vasculosi.

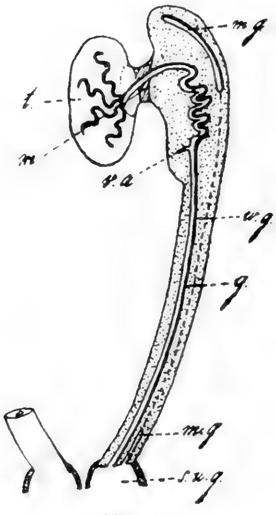

Fig. 4.

Relation of the genital ducts to the testicle.

t.	Testicle.
m.	Mesorchium.
m.g.	Remnants of the Müllerian duct.
w.g.	Wolffian duct (vas deferens).
g.s.	Genital cord.
s.u.g.	Sinus uro-genitalis.
v.a.	Vas aberrans.

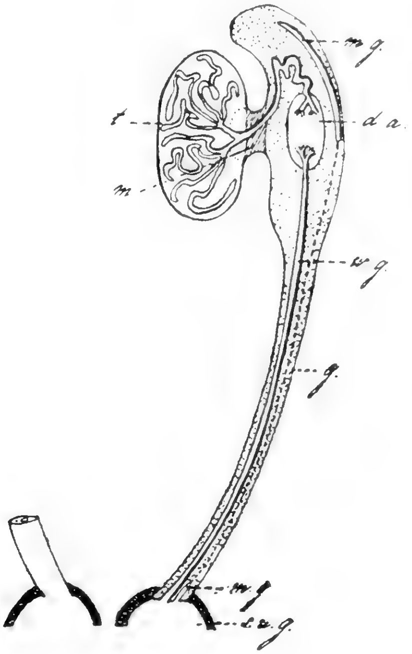

Fig. 5.

Relation of the genital duct to the testicle.

t.	Testicle.
m.	Mesorchium.
m.g.	Remnants of the Müllerian duct.
d.a.	Glandule part in the epididymis.
w.g.	Wolffian duct (vas deferens).
g.s.	Genital cord.
s.u.g.	Sinus uro-genitalis.

Meanwhile the Müllerian duct is for the greater part reduced. The cranial extremity remains as a remnant of the duct either beginning with an ostium abdominale or not, and ending caudally blind in the epididymis tissue.

The change following on this consists therein that the spermatic tubes obtain a lumen and combine in one or two places (Didelphys) with the Wolffian duct grown into the testicle. In the epididymis a great many cell cords have meanwhile appeared in the course of the Wolffian duct (Vas epididymidis), out of which cell cords the little tubules of the epididymis will develop.

Of the Müllerian duct a rest has remained in the tissue of the epididymis, I have not observed rests of this duct in the form of hydatids. Neither did I find them mentioned in literature.

In the genital gland of the full grown animal I found that the connection of the testicle and epididymis is formed by a mesorchium, in which evidently a single tube forms the communication between the two parts (Didelphys, Halmaturus). Probably the same holds true for Hypsiprymnus, where, according to DISSELHORST [1]), the epididymis is a spindle shaped swelling in the course of the vas deferens.

About the microscopic structure of the testicle and epididymis I found in DISSELHORST the communication that it agrees with that of other animals. As on this immediately follows: "die Spermatogenese war in vollem Gange", it seems to me that this communication relates more to the structure of epithels of the tubules than to the nature of the connection of testicle and epididymis.

A comparison with what we find in other mammals shows us the following.

There now and then is to be observed in the female sex (at least in man) an excrescence of the cranial extremity of the Wolffian duct, which then becomes the tubo-parovarian tube, which was first described by ROTH [2]) and recognised by MIHALKOVICS [3]) as a part of the Wolffian duct. Where however in Marsupials the Wolffian duct penetrates into the genital gland, the tubo-parovarian tube of man remains in the Ligamentum latum.

For the male sex the following holds true.

A rete testis, whether it has to be considered as tubules, which have appeared afterwards, and must be considered as a second generation of tubuli seminiferi (COERT)[4]) or as homologa of the

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[1]) R. DISSELHORST. Die männlichen Geschlechtsorgane der Monotremen und einiger Marsupialen.

SEMON's Zoölogische Forschungsreisen in Australiën und den Malayischen Archipel. 1904. p. 121.

[2]) Quoted by MIHALKOVICS.

[3]) MIHALKOVICS, Untersuchungen über die Entwickelungsgeschichte der Uro-genitalorgane der Cranioten.

Internat. Zeitschrift für Anatomie und Histologie. Bd. 2.

[4]) COERT, Over de ontwikkeling der geslachtsklier bij de z ogdieren. Diss. Leiden 1898.

"Markstränge" of the ovarium (Mihalkovics), or as tubules of the mesonephros grown into the tissue of the testicle (Kollmann) [1]) is not found in marsupials. If, during further development a network resembling the rete testis, arises in the marsupial testicle, it must be considered as a part which appears quite secondary.

The connection of the testicle and epididymis is not caused by a number of tubules of the mesonephros, transformed to vasa efferentia, but by a single tube which must be considered as a part of the Wolffian duct. For the conception that the connecting tube really is the Wolffian duct, the phenomena of development in the female sex can be cited together with those in the male animals. In the marsupials all the tubules of the mesonephros are reduced to minimal rests (vasa aberrantia). In the mass of tissue, which represents the so-called epididymis of these animals, a great number of tubes arise secondary, which afterwards probably possess as epididymis tubules the same function as the coni vasculosi in the epididymis of other mammals.

To explain the differences in the connection of the testicle and epididymis in marsupials and in other mammals, the following considerations seem to me to be of importance.

About the changes, which the mesonephros undergoes, by its connection with the testis, which connection furnishes the later vasa efferentia testis, we read the following in the extensive investigations of Coert [2]): In the proximal part of the Wolffian body where the Malpighian bodies are connected with the blastem of the rete testis, we see the glomeruli and the inner epithelium of the capsules disappearing gradually; after which the outer walls of these capsules form the blind extremities the mesonephridial tubules. The epithelium of the mesonephridial tubules also begins to have another aspect. Two kinds of processes occur here together: a number of epithelium cells are pushed out into the lumen and are destroyed, while on the other hand many new cells are formed (mitosis). With this the cells get another appearance both as concerns the nucleus and the protoplasm. The result is that at last the tubules of the menonephros are surrounded all over their extent, which formerly was not the case, by an uniform epithelium, formed by cylindrical cells, the nuclei ranged regularly at the basis of the cells. Whether the connection of these tubes with the Wolffian duct always remains unchanged during those transformations or is perhaps broken off and afterwards re-established in another place I have not been able to investigate.

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[1]) Kollmann, Lehrbuch der Entwickelungsgeschichte des Menschen.

[2]) l.c. p. 96.

My opinion is that these investigations show that the vasa efferentia testis must not be considered as simple tubules of the mesonephros, but newly formed tubules, which use quite or for the greater part the way given to them by the tubules of the mesonephros. And that they are able to use this way finds its cause in this, that, according to FELIX and BÜHLER [1]) there is most probably no idea of a functioning of the mesonephros in monodelphic mammals, even not in the pig, where it is so strongly developed.

Not so in the didelphic mammals. Here the mesonephros does not only function embryonally, as is known, but still during the first period of the individual life. A separation of the mesonephros in two parts as is found in reptilia does not come about here.

The connection of the genital gland, especially of the testicle and its duct, the Wolffiian duct, could not, it may be supposed, in the stadium in which this connection will come about in other animals, be established in marsupials with the help of tubules of the mesonephros, because these had still to fulfill their excretory function.

Instead of this the connection could be established in such a way that the Wolffian duct grews out cranially and brings about itself the connection between the gland and its excretory duct.

At last the tubes, which occur secondary and independently ot the tubules of the mesonephros in the tissue of the epididymis, might be explained in the same way, i.e. as tubules which have the same signification as the coni vasculosi, but for the same reason do not originate on the bottom of tubules of the mesonephros but are separated from them both locally and temporarily.

Another view may be, that the tube which encroached in the genital gland, might not be the Wolffian duct but the most cranial tubule of the mesonephros so that in other words the so-called sexual part of the mesonephros in marsupials should be reduced. I do not believe that this conception is true, firstly because no separation between the tubules can be observed, and secondly because at the reduction of the mesonephros, as is mentioned above, in marsupials, nothing can be observed, as far as my preparations are concerned, of differences between the tubules of the mesonephros, what must surely be the case at a transformation of a tubule of the mesonephros to a connecting duct.

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[1]) FÉLIX und BÜHLER, Die Entwickelung der Harn und Geschlechtsorgane in HERTWIG's Handbuch der vergleichenden und experimentellen Entwickelungsgeschichte der Wirbeltiere.

Physics. — "*Supplement to Communication N°. 95^a from the Physical Laboratory of Leiden, on the comparison of the thermo-element constantin-steel with the hydrogen thermometer*". By Prof. H. KAMERLINGH ONNES and C. A. CROMMELIN.

§ 14. *Corrected representation of the observations by a five term formula.*

As appears from note 1 the calculations in § 12 were made with not perfectly accurate values of the temperature at — 182° and in the same way the mean errors were derived from the assumption of those less accurate values. [1])

If the correct values of those temperatures for the calculations of the deviations $W—R_1$, $W—R_2$, $W—R_3$, $W—R_4$ in Table VIII, are used, the mean errors in microvolts become:

for formula (BI) ± 3.0
(BII) ± 3.4
(BIII) ± 2.8 (2.5 without — 217°)
(BIV) ± 2.1

instead of

(BI) ± 2.8
(BII) ± 3.2
(BIII) ± 2.6 (2.1 without — 217°)
(BIV) ± 1.8

which would also have been obtained if the observations at — 182° were excluded.

Now it was necessary to examine whether a repetition of the adjustment would diminish these mean errors. It appeared convincingly that this was not possible to an appreciable degree for (BI), (BII), (BIII). It appeared possible for (BIV) to distribute the errors more equally. However, this only reduced the sum of squares from 26,57 to 26,14.

Instead of the coefficients a_4, b_4, c_4, e_4 and f_4 (see § 12) we get then

$a'_4 = + 4.32513$ $e'_4 = + 0.023276$
$b'_4 = + 0.409153$ $f'_4 = — 0.0025269$
$c'_4 = + 0.0015563$

The deviations are given in Table IX under $W—R'_4$.

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[1]) The correction amounted to 0°,081 in temperature or to 1.7 microvolt. in electromotive force.

§ 15. *Representation of the observations by means of a four term formula.*

We have now quite carried out the calculation of a formula of the form

$$E = a\left(\frac{t}{100}\right) + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + e\left(\frac{t}{100}\right)^4 \quad . \quad . \quad . \quad (C)$$

announced in note 2 of § 11, by the method of E. F. v. d. SANDE BAKHUYZEN, which proved to facilitate matters greatly again.

Four solutions (C) were found, viz. $(C\,\mathrm{I})$, $(C\,\mathrm{II})$, $(C\,\mathrm{III})$ representing the observations down to — 253°, whereas in $(C\,\mathrm{IV})$ only agreement down to — 217° has been sought for.

The coefficients in millivolts are the following:

	1	2	3	4
a	+ 4.30192	+ 4.30571	+ 4.30398	+ 4.33031
b	+ 0.357902	+ 0.366351	+ 0.363681	+ 0.421271
c	— 0.0250934	— 0.0192565	— 0.020071	+ 0.018683
e	+ 0.0257462	+ 0.0270158	+ 0.0270044	+ 0.035268

The residuals have been given in tenth parts of microvolts in Table IX under $W\!-\!R_{C\,I}$, $W\!-\!R_{C\,II}$, $W\!-\!R_{C\,III}$, $W\!-\!R_{C\,IV}$.

Just as with the five term formula, the residual at — 182° appeared also now greater than the others.

In calculation 3 it was tried to distribute the errors more equally, but the sum of squares appeared now to have increased.

The mean errors are if we include the observations down to — 253° for $(C\,\mathrm{I})$, $(C\,\mathrm{II})$, $(C\,\mathrm{III})$, and only those down to — 217° for $(C\,\mathrm{IV})$, for

$(C\,\mathrm{I})$	± 3.0
$(C\,\mathrm{II})$	± 2.9
$(C\,\mathrm{III})$	± 3.0
$(C\,\mathrm{IV})$	± 2.3

If — 182° is excluded, they become:

$(C\,\mathrm{I})$	± 2.7
$(C\,\mathrm{II})$	± 2.6
$(C\,\mathrm{IV})$	± 1.8

The mean errors of $(C\,\mathrm{I})$, $(C\,\mathrm{II})$, $(C\,\mathrm{III})$ must be compared with those of $(B\,\mathrm{I})$ and $(B\,\mathrm{III})$, those of $(C\,\mathrm{IV})$ with those of $(B\,\mathrm{IV})$.

This comparison teaches that the four term formula for the representation of the observations may be considered to be almost equivalent to the five term formula, and that therefore (this remark is in harmony with note 2 of § 13) for the calibration to — 217° the lowest number of temperatures for which observations are required, amounts to *four*. That three are not sufficient was already proved in § 11. This appears also clearly, when the mean error is determined, which rises to ± 7.6 microvolts for the three term formula.

TABLE IX.

DEVIATIONS OF THE CALIBRATION-FORMULAE FOR THE THERMO-ELEMENT CONSTANTIN-STEEL.

I	II	III	IV	V	VI	VII
N⁰.	t	$W-R_4'$	$W-R_{CI}$	$W-R_{CII}$	$W-R_{CIII}$	$W-R_{CIV}$
22	— 29°.82	— 12	+ 20	+ 15	+ 18	— 19
24 and 20	— 58.75	+ 16	+ 30	+ 26	+ 29	+ 4
21 and 23	— 88.15	+ 14	+ 1	+ 1	+ 1	+ 1
1 and 17	— 103.70	— 6	— 29	— 28	— 30	— 20
16 and 18	— 139.86	+ 1	— 26	— 24	— 31	— 17
19	— 158.83	— 10	— 10	— 10	— 18	— 10
3, 11 and 5	[— 182.73]	+ 26	+ 46	+ 44	+ 35	+ 34
4, 28 and 6	— 195.19	+ 2	+ 23	+ 21	+ 12	+ 11
12, 27 and 7	— 204.70	— 20	— 9	— 11	— 19	— 18
26, 14, 13 and 8	— 212.85	+ 24	+ 21	+ 21	+ 13	+ 21
29, 15 and 25	— 217.55	— 15	— 30	— 29	— 37	— 23
30	— 252.93	+ 280	0	+ 20	+ 20	+ 150
31	— 259.24	+ 485	+ 115	+ 141	+ 143	+ 313

Mathematics. — *"On a special class of homogeneous linear differential equations of the second order"*. By Prof. W. KAPTEYN.

The differential equation of LEGENDRE

$$(1-x^2)\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + n(n+1)\,y = 0$$

is satisfied by a polynomium $P_n(x)$ of the n^{th} degree and by a function $Q_n(x)$ which may be reduced to the form

$$Q_n(x) = \int_{-1}^{1} \frac{P_n(z)\,dz}{x-z}$$

This function however is not determined for real values of the variable in the interval -1 to $+1$, the difference on both sides of this line being $2i\pi\, P_n(x)$.

In analogy to this we have examined the question: to determine all homogeneous linear differential equations of the second order of the form

$$R(x)\frac{d^2y}{dx^2} + S(x)\frac{dy}{dx} + T(x)y = 0$$

where the coefficients are polynomia in x, which possess the property that $y_1(x)$ being a first particular integral, the second integral may be written

$$y_2(x) = \int_{\alpha}^{\beta} \frac{y_1(z)\,dr}{x-z}$$

where α and β represent two real values, supposing moreover that this integral has a meaning everywhere except on the line of discontinuity.

Let

$$R(x) = \sum_0^{\lambda} r_p\, x^p \quad , \quad S(x) = \sum_0^{\lambda} s_p\, x^p \quad , \quad T(x) = \sum_0^{\lambda} t_p\, x^p$$

then we obtain firstly the conditions

$$R(x) = (x-\alpha)(x-\beta)\,r(x) = (x-\alpha)(x-\beta)\sum_0^{\lambda-2} \varrho_p\, x^p$$

$$S(x) = R'(x) + (x-\alpha)(x-\beta)\sum_0^{\lambda-2} h_p\, x^p.$$

If now we put

$$G_p'' = \int_{\alpha}^{\beta} z^p\, y_1''(z)\,dz \quad , \quad G_p' = \int_{\alpha}^{\beta} z^p\, y_1'(z)\,dz \quad , \quad G_p = \int_{\alpha}^{\beta} z^p\, y_1(z)\,dz$$

and

$$\begin{aligned} M &= -\, G_0'' \\ N &= (\alpha+\beta)\, G_0'' - G_1'' - 2G_0' \\ m &= -\, G_0' \\ n &= (\alpha+\beta)\, G_0' - G_1' - G_0 \end{aligned}$$

the further necessary conditions may be deduced from the equation

$$I + J = 0$$

where I and J represent the following polynomia of degree $\lambda-1$

$$\begin{aligned} I = & \sum_{p=0}^{\lambda-1} (\varrho_p N + \varrho_{p-1} M)\, x^p \\ & + \sum_{p=0}^{\lambda-1} [\{h_p + (p+1)\, \varrho_{p+1}\}\, n + \{h_{p-1} + p\varrho_p\}\, m]\, x^p \\ J = & \sum_{p=0}^{\lambda-1} (r_{p+1}\, G_p'' + s_{p+1}\, G_p' + t_{p+1}\, G_p) \\ & + x \sum_{p=0}^{\lambda-2} (r_{p+2}\, G_p'' + s_{p+2}\, G_p' + t_{p+2}\, G_p) \\ & + \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \\ & + x^{\lambda-2} \sum_{p=0}^{1} (r_{p+\lambda-1}\, G_p'' + s_{p+\lambda-1}\, G_p' + t_{p+\lambda-1}\, G_p) \\ & + x^{\lambda-1} \sum_{p=0} (r_{p+\lambda}\, G_p'' + s_{p+\lambda}\, G_p' + t_{p+\lambda}\, G_p). \end{aligned}$$

From this we may easily deduce that if $\lambda = 2$, the most general differential equation of the second order possessing the property in question is

$$(x-\alpha)\,(x-\beta)\,\frac{d^2y}{dx^2} + [t_1\,(x-\alpha)\,(x-\beta) + 2x - \alpha - \beta]\,\frac{dy}{dx} + (t_0 + t_1 x)\, y = 0$$

where α, β, t_0 and t_1 are arbitrary constants.

When $\lambda = 3$ the most general equation may be written

$$(x-\alpha)\,(x-\beta)\,(\varrho_1 x + \varrho_0)\,\frac{d^2y}{dx^2} + (t_2 x^3 + s_2 x^2 + s_1 x + s_0)\,\frac{dy}{dx} + \\ + (t_2 x^2 + t_1 x + t_0)\, y = 0$$

Here however the ten constants must satisfy the following three conditions

$$\begin{aligned} & s_1 + (\alpha+\beta)\, s_2 + (\alpha^2 + \alpha\beta + \beta^2)\, t_2 = 2\varrho_0 + (\alpha+\beta)\, \varrho_1 \\ & s_0 - \alpha\beta s_2 - \alpha\beta\,(\alpha+\beta)\, t_2 = -\,(\alpha+\beta)\, \varrho_0 - 2\alpha\beta\varrho_1 \\ & (t_1 - s_2 + 2\varrho_1)\, G_0 - t_2\, G_1 = 0. \end{aligned}$$

Mathematics. — *"Some formulae concerning the integers less than n and prime to n."* By Prof. J. C. KLUYVER.

The number $\varphi(n)$ of the integers ν less than n and prime to n can be expressed by means of the divisors d.

We have

$$\varphi(n) = \sum_{d/n} \mu(d)\, d', \qquad (dd' = n)$$

if we denote by $\mu(q)$ the arithmetical function, which equals 0 if q be divisible by a square, and otherwise equals $+1$ or -1, according to q being a product of an even or of an odd number of prime numbers.

This equation is a particular case of a more general one, by means of which certain symmetrical functions of the integers ν are expressible as a function of the divisors d.

This general relation may be written as follows [1])

$$\sum_{\nu} f(\nu) = \sum_{d/n} \mu(d) \sum_{k=1}^{k=d'} f(k\,d).$$

For the proof we have to observe that, supposing $(m, n) \sim D$, the term $f(m)$ occurs at the righthand side as often as d in a divisor of D. Hence the total coefficient of the term $f(m)$ becomes

$$\sum_{d/D} \mu(d),$$

that is zero if D be greater than unity, and 1 when m is equal to one of the integers ν.

We will consider some simple cases of KRONECKER's equation.

First, let

$$f(y) = e^{xy}.$$

The equation becomes

$$\sum_{\nu} e^{x\nu} = \sum_{d/n} \mu(d) \sum_{k=1}^{k=d'} e^{xkd} = \sum_{d/n} \mu(d)\, e^{xd} \frac{e^{xn} - 1}{e^{xd} - 1},$$

or because of

$$\sum_{d/n} \mu(d) = 0,$$

$$\sum_{\nu} e^{x\nu} = \sum_{d/n} \mu(d) \frac{e^{xn} - 1}{e^{xd} - d}.$$

If we write

$$\sum_{\nu} \frac{x e^{x\nu}}{e^{xn} - 1} = \sum_{d/n} \mu(d) \frac{x}{e^{xd} - 1},$$

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[1]) KRONECKER, Vorlesungen über Zahlentheorie. I, p. 251.

we may introduce the BERNOULLIAN functions $f_k(\theta)$, defined by the equation

$$\frac{e^{\theta x}-1}{e^x-1}=\theta+\sum_{k=1}^{k=\infty}x^k f_k(\theta),$$

and hence show that

$$\sum_{\nu}\left\{\frac{1}{n}+\sum_{k=1}^{k=\infty}x^k n^{k-1}f'_k\left(\frac{v}{n}\right)\right\}=\sum_{d/n}\frac{\mu(d)}{d}\left\{1-\tfrac{1}{2}xd+\frac{B_1}{2\,!}x^2d^2-\frac{B_2}{4\,!}x^4d^4+\dots\right\}.$$

By equating the corresponding terms on the two sides we get

$$\sum_{\nu}f'_{2m}\left(\frac{v}{n}\right)=(-1)^{m-1}\frac{B_m}{2m\,!}\sum_{d/n}\mu(d)d'^{-2m+1}$$

as a first generalisation of the relation

$$\sum_{\nu}v^0=\sum_{d/n}\mu(d)d'.$$

Observing that we have

$$\sum_{d/n}\mu(d)d'^{-2m+1}=\frac{1}{n^{2m-1}}\sum_{d/n}\mu(d)d^{2m-1},$$

there follows for two integers n and n', both having the same set of prime factors,

$$\frac{\sum_{\nu}f'_{2m}\left(\frac{v}{n}\right)}{\sum_{\nu'}f'_{2m}\left(\frac{v'}{n'}\right)}=\left(\frac{n'}{n}\right)^{2m-1}.$$

In the same way an expression for the sum of the k^{th} powers of the integers v may be obtained. Expanding both sides of the equation

$$\sum_{\nu}e^{x\nu}=\sum_{d/n}\mu(d)\frac{e^{xn}-1}{e^{xd}-1}$$

we find

$$\frac{1}{k\,!}\sum_{\nu}v^k=\sum_{d/n}\mu(d)d^kf_k(d').$$

Other relations of the same kind, containing trigonometrical functions are deduced by changing x into $2\pi ix$.

From

$$\sum_{\nu}e^{2\pi ix\nu}=\sum_{d/n}\mu\,(d)\frac{e^{2\pi ixn}-1}{e^{2\pi ixd}-1}$$

we find by separating the real and imaginary parts

$$\sum_{\nu}\cos 2\pi xv=\tfrac{1}{2}\sin 2\pi xn\sum_{d/n}\mu\,(d)\cot\pi xd,$$

$$\sum_{\nu}\sin 2\pi xv=\quad\sin^2\pi xn\sum_{d/n}\mu\,(d)\cot\pi xd.$$

In particular the first of these equations gives a simple result if we put $x = \frac{1}{n} + \varepsilon$, where ε is a vanishing quantity. As the factor $\sin 2\,\pi x n$ tends to zero with ε the whole right-hand side is annulled but for the term in which $d = n$.

So it follows that

$$\sum_{\nu} \cos \frac{2\pi\nu}{n} = \mu\,(n),$$

and we have $\mu\,(n)$, originally depending upon the prime factors of n, expressed as a function of the integers prime to n.

Similarly we may put in the second equation $x = \frac{1}{2n}$ and write

$$\sum_{\nu} \frac{\sin \pi\nu}{n} = \sum_{d/n} \mu\,(d) \cot \frac{\pi d}{2n}\,.$$

Still another trigonometrical formula may be obtained by the substitution $x = \frac{q}{n} + \varepsilon$. Let D be the greatest common divisor of the integers n and q, so that

$$n = n_0 D \quad , \quad q = q_0 D;$$

then as ε vanishes, we have to retain at the right-hand side only those terms in which qd is divisible by n, or what is the same the terms for which the complementary divisor d' divides D.

Hence, we find

$$\sum_{\nu} \cos \frac{2\pi q\nu}{n} = \sum_{d'/D} \mu \left(\frac{n}{d'}\right) d' = D \sum_{d/D} \mu\,(n_0 d)\,\frac{1}{d}\,. \qquad (dd' = D)$$

Instead of extending the summation over all divisors d of D, it suffices to take into account only those divisors δ of n, that are prime to n_0. In this way we find

$$D \sum_{d/D} \mu\,(n_0 d)\,\frac{1}{d} = \mu\,(n_0)\,D \sum_{\delta} \mu\,(\delta)\,\frac{1}{\delta}\,,$$

and as the second side is readily reduced to

$$\mu(n_0)\,\frac{\varphi(n)}{\varphi(n_0)} = \mu\left(\frac{u}{D}\right) \frac{\varphi(n)}{\varphi\left(\frac{n}{D}\right)}\,,$$

we obtain for any integer q, for which we have $(n\,,q) \sim D$,

$$\sum_{\nu} \cos \frac{2\pi q\nu}{n} = \mu\left(\frac{u}{D}\right) \frac{\varphi(n)}{\varphi\left(\frac{n}{D}\right)}\,.$$

Concerning the result

$$\sum_{\nu} \cos \frac{2\pi\nu}{n} = \mu\,(n)$$

a slight remark may be made. To each integer ν a second $\nu' = n - \nu$ is conjugated; hence denoting by ϱ_n an irreducible fraction $< \frac{1}{2}$ with the denominator n, we may write

$$2\Sigma \cos 2\pi\varrho_n = \mu(n),$$

and also

$$2\sum_{n \leqq g} \cos 2\pi\varrho_n = \sum_{n \leqq g} \mu(n).$$

Now for large values of g the fractions ϱ_n will spread themselves not homogeneously, but still with some regularity more or less all over the interval $0 - \frac{1}{2}$ and there is some reason to expect, that in the main the positive and the negative terms of the sum $\sum\limits_{n \leqq g} \cos 2\pi\varrho_n$ will annul each other, hence the equation

$$2\sum_{n \leqq g} \cos 2\pi\varrho_n = \sum_{n \leqq g} \mu(n)$$

is quite consistent with the supposition of VON STERNECK, that as g takes larger and larger values the absolute value of $\sum\limits_{n \leqq g} \mu(n)$ does not exceed $\sqrt{g}$.

Another set of formulae will be obtained by substituting in KRONECKER's equation

$$f(y) = \log\left(e^{\frac{2\pi ix}{n}} - e^{\frac{2\pi iy}{n}}\right).$$

Thus we get

$$\sum_{\nu} \log\left(e^{\frac{2\pi ix}{n}} - e^{\frac{2\pi i\nu}{n}}\right) = \sum_{d/n} \mu\,(d) \sum_{k=1}^{k=d'} \log\left(e^{\frac{2\pi ix}{n}} - e^{\frac{2\pi ikd}{n}}\right),$$

or

$$\sum_{\nu} \log\left(e^{\frac{2\pi ix}{n}} - e^{\frac{2\pi i\nu}{n}}\right) = \sum_{d/n} \mu(d) \log\left(e^{\frac{2\pi ixd'}{n}} - 1\right)$$

and after some reductions

$$\sum_{\nu} \log 2 \sin \frac{\pi}{n}(\nu - x) = \sum_{d/n} \mu(d) \log 2 \sin \frac{\pi x}{d}.$$

By repeated differentiations with respect to x we may derive from this equation further analogies to the formula

$$\varphi\,(n) = \sum_{d/n} \mu\,(d)\, d'.$$

So for instance we obtain bij differentiating two times

$$\sum_{\nu} \frac{1}{\sin^2 \frac{\pi\nu}{n}} = \frac{1}{3} \sum_{d/n} \mu(d)\, d'^2$$

and by repeating the process

$$-\sum_{\nu} \left[\frac{d^{2m}}{dy^{2m}} \log \sin y\right]_{y=\frac{\pi\nu}{n}} = \frac{B_m\, 2^{2m}}{2m} \sum_{d/n} \mu(d)\, d'^{2m},$$

a result included in the still somewhat more general relation

$$n^s \sum_{\nu} \sum_{k=1}^{k=\infty} \frac{1}{(nk-\nu)^s} = \zeta(s) \sum_{d/n} \mu(d)\, d'^s,$$

which is self evident from.

Returning to the equation

$$\sum_{\nu} \log 2 \sin y \frac{\pi}{n} (\nu - x) = \sum_{d/n} \mu(d) \log 2 \sin \frac{\pi x}{d},$$

we obtain as x tends to zero

$$\sum_{\nu} \log 2 \sin \frac{\pi\nu}{n} = -\sum_{d/n} \mu(d) \log d.$$

In order to evaluate the right-hand side, we observe that for $n = p_1^{\alpha_1}\, p_2^{\alpha_2} \dots$ we have

$$-\sum_{d/n} \mu(d) \log d = -\left[\frac{d}{dy} (1 - e^{y \log p_1})(1 - e^{y \log p_2}) \dots\right]_{y=0}.$$

So it is seen that, putting

$$-\sum_{d/n} \mu(d) \log d = \gamma(n),$$

the function $\gamma(n)$ is equal to zero for all integers n having distinct prime factors, and that it takes the value $\log p$, when n is any power of the prime number p.

Hence we may write

$$\Pi_{\nu}\, 2 \sin \frac{\pi\nu}{n} = e^{\gamma(n)},$$

a result in a different way deduced by KRONECKER [1]).

Again in the equation

$$\Pi_{\nu}\, 2 \sin \frac{\pi}{n} (\nu - x) = \Pi_{d/n} \left(2 \sin \frac{\pi x}{d}\right)^{\mu(d)}$$

we will make x tend to $-\frac{n}{2}$.

If n be odd, all divisors d and d' are odd also and we have at once

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[1]) KRONECKER, Vorlesungen über Zahlentheorie. I, p. 296,

$$\mathop{\Pi}_{\nu} 2\cos\frac{\pi\nu}{n} = \mathop{\Pi}_{d/n}(-1)^{\frac{d'-1}{2}\mu(d)} = (-1)^{\frac{1}{2}\varphi(n)}.$$

If $n=2m$ and m be odd, we shall have $\varphi(m)=\varphi(n)$. Half the numbers $\varkappa$ prime to m and less than m will be equal to some integer ν, the other half will be of the form $\nu - m$.

Hence we have

$$\mathop{\Pi}_{\nu} 2\sin\frac{2\pi\nu}{n} = (-1)^{\frac{1}{2}\varphi(n)} \mathop{\Pi}_{\varkappa} 2\sin\frac{2\pi\varkappa}{n} = (-1)^{\frac{1}{2}\varphi(n)} \mathop{\Pi}_{\varkappa} 2\sin\frac{\pi\varkappa}{m},$$

and therefore

$$\mathop{\Pi}_{\nu} 2\cos\frac{\pi\nu}{n} = (-1)^{\frac{1}{2}\varphi(n)} \frac{\mathop{\Pi}\limits_{\varkappa} 2\sin\frac{\pi\varkappa}{m}}{\mathop{\Pi}\limits_{\nu} 2\sin\frac{\pi\nu}{n}} = (-1)^{\frac{1}{2}\varphi(n)} e^{\gamma\left(\frac{n}{2}\right)-\gamma(n)}$$

Lastly, if $n=2m$, and m be even, we shall have $\varphi(m)=\frac{1}{2}\varphi(n)$. Now each of the numbers $\varkappa$ prime to m and less than m at the same time will be equal to some integer ν and to one of the differences $\nu - m$. Reasoning as before we have in this case

$$\mathop{\Pi}_{\nu} 2\sin\frac{2\pi\nu}{n} = (-1)^{\frac{1}{2}\varphi(u)} \mathop{\Pi}_{\varkappa}\left(2\sin\frac{2\pi\varkappa}{n}\right)^2 = (-1)^{\frac{1}{2}\varphi(n)} \mathop{\Pi}_{\varkappa}\left(2\sin\frac{\pi\varkappa}{m}\right)^2.$$

and therefore

$$\mathop{\Pi}_{\nu} 2\cos\frac{\pi\nu}{n} = (-1)^{\frac{1}{2}\varphi(n)} \frac{\mathop{\Pi}\limits_{\varkappa}\left(2\sin\frac{\pi\varkappa}{m}\right)}{\mathop{\Pi}\limits_{\nu} 2\sin\frac{\pi\nu}{n}} = (-1)^{\frac{1}{2}\varphi(n)} e^{2\gamma\left(\frac{n}{2}\right)-\gamma(n)}.$$

From the foregoing we may conclude as follows. If we put

$$\mathop{\Pi}_{\nu} 2\cos\frac{\pi\nu}{n} = (-1)^{\frac{1}{2}\varphi(n)} e^{\lambda(n)},$$

the arithmetical function $\lambda(n)$ is different from zero only when n is double the power of any prime number p, in which case we have $\lambda(n) = \log p$.

Again we introduce here the irreducible fractions ϱ_n less than $\frac{1}{2}$ with the denominator n; then denoting by $M(q)$ the least common multiple of all the integers not surpassing q we may write

$$2\sum_{n\leqq g} \log 2\sin\pi\varrho_n = \sum_{n\leqq g}\gamma(n) = \log M(g),$$

$$2\sum_{n\leqq g} \log 2\cos\pi\varrho_n = \sum_{n\leqq g}\lambda(n) = \log M\left(\frac{g}{2}\right).$$

If we consider the quotient $\log M(g) : \log g$ as an approximate (but always too small) value of the number $A(g)$ of prime numbers less than g, to KRONECKER's result

$$A(g) = \frac{2}{\log g} \sum_{n \leqq g} \log 2 \sin \pi \varrho_n$$

we may add

$$A\left(\frac{g}{2}\right) = \frac{2}{\log \frac{g}{2}} \sum_{n \leqq g} \log 2 \cos \pi \varrho_n \,.$$

Astronomy. — "*Researches on the orbit of the periodic comet Holmes and on the perturbations of its elliptic motion.* IV." By Dr. H. J. ZWIERS. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

At the meeting of the Academy on the 27 January of 1906, a communication was made of my preliminary researches on the perturbations of the comet Holmes, during the period of its invisibility from January 1900 till January 1906, and also of an ephemeris of its apparent places from the 1st of May till the 31st of December 1906. This time again this computation led to its rediscovery. Owing to its large distance from the earth and the resulting faintness of its light, there seemed to be only a small chance for its observation during the first months. This proved to be true, as not before the 30th of August of this year, the Leiden observatory received a telegram, that the comet was found by prof. MAX WOLF at the observatory Koenigstuhl near Heidelberg, on a photograph taken in the night of the 28th of August of a part of the heavens where according to the ephemeris it ought to be found. The roughly measured place

$$\alpha = 61^\circ\ 51' \qquad \delta = +\ 42^\circ\ 28'$$

for $13^h\,52^m1$ local time, appeared to be in sufficient agreement with the calculation.

Afterwards the place of the comet has been twice photographically determined: on the 25th of September and on the 10th of October, and each time prof. WOLF was so kind, to communicate immediately to me the places as they had been obtained, after carefully measuring the plates. Although WOLF declared in a note to the observed position of the 25th of September[1]) that the brightness had increased sufficiently, to make the comet visible in a powerful telescope, till now I did not hear, that any visual observation of the comet has been made. The three Heidelberg plates are therefore the only material that can be used for testing the elements and ephemeris given before.

I communicate here the results as I had the pleasure to receive them from prof. **Wolf.**

1. "Den Kometen Holmes habe ich auf der Platte von 28 August rechtwinklig an die 4 Sterne

A.G. Bonn 3456, 3462, 3472, 3493

angeschlossen, und die Messungen nach der Turner'schen Methode reduziert. Ich finde für 1906.0 :

$$\alpha = 4^h\ 7^m\ 34^s84 \qquad \delta = +\ 42°\ 30'\ 59''9$$

für die Aufnahmezeit: 1906 Aug. 28, 13h 52m1 Kgst. Das äusserst schwache zentrale Kernchen wurde dabei eingestellt. Die Messung und Rechnung bezieht sich auf die mittleren Orte der 4 Sterne für 1906; sonst ist gar nichts angebracht."

(Note of the 5th of September 1906).

2. "Ich habe Ihren Kometen nochmals am 25 aufgenommen und finde ihn entschieden etwas heller. Den Ort nach Turner mit 3 Sternen (A.G. Bonn 3710, 3760, 3778) fand ich

1906 Sept. 25: 12h 46m0 M.Z. Kgst.

$$\alpha_{1906.0} = 4^h\ 32^m\ 10^s02 \qquad \delta_{1906.0} = +\ 47°\ 34'\ 54''6$$

Ich habe auch den letzten Ort (viz. of Aug. 28) mit nur 3 Sternen nochmals gerechnet (weil ein Stern sehr ungünstig war) und fand für 1906 August 28: 13h 52m1 Kgst.:

$$\alpha_{1906.0} = 4^h\ 7^m\ 35^s00 \qquad \delta_{1906.0} = +\ 42°\ 30'\ 58''3$$

Ich bin nicht sicher, ob diese Bestimmung aus 3 Sternen besser ist als die erst mitgeteilte."

(Note of the 29th of September 1906).

3. "Herr Dr. **Kopff** hat gestern den Ort einer Aufnahme vom 10 Okt. 1906 des Kometen Holmes ausgemessen . . . . .

1906 Okt. 10: 9h 1m0 Kgst.

$$\alpha_{1906.0} = 4^h\ 34^m\ 48^s94 \qquad \delta_{1906.0} = +\ 49°\ 54'\ 59''2$$

Sterne: A.G. Bonn 3759, 3768, 3777 . . . . . Der Komet war

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[1] *Astron. Nachr.*, N°. 4123, S. 302.

diesmal schon recht schwach, wahrnehmbar schwächer als im September. Die Messung ist deshalb auch wohl etwas unsicherer."

(Note of the 13th of October 1906).

Concerning the observation on the 28th of August I preferred the position obtained from 3 reference stars.

For the reduction to the apparent place, I used as before in the ephemeris the constants of the Nautical Almanac, where the short period terms are omitted. Assuming for the parallax of the sun 8"80, I find for the Heidelberg Observatory the following constants:

$$\lambda = -0^h 34^m 54^s 8$$

$$tg\,\varphi' = 0.06404$$

$$A = 9.58267$$

$$D = 0.82425$$

which are used for the computation of the parallax of the comet. The following table gives an account of the reduced observations.

TABLE I.

N⁰.	Red. on app. pl.		Parallax		Apparent geoc. place.	
	$\Delta\alpha$	$\Delta\delta$	$\Delta\alpha$	$\Delta\delta$	α	δ
	s	"	s	"	h m s	° ' "
1	+ 1.888	—8.55	— 0.191	+1.24	4 7 36.697	+42 30 50.99
2	+ 2.929	—8.57	— 0.217	+0.92	4 32 12.732	+47 34 46.95
3	+ 3.593	—7.51	— 0.298	+2.35	4 34 52.235	+49 54 54.04

I used for comparison with the ephemeris my original computations, which contained in α as well as in δ one decimal place more than the published values. The computed places and their comparison with the observed positions, are given in the following table.

TABLE II.

Local time	Aberration-time.	Comp. apparent place		Observ.—Comp.	
		α	δ	α	δ
	d	h m s	° ' "	s	"
Aug. 28.553602	0.013211	4 7 29.753	+42 30 24.28	+6.94	+26.7
Sept. 25.507699	.012005	4 32 4.255	+47 34 29.94	+8.48	+17.0
Oct. 10.351449	.011462	4 34 43.017	+49 54 43.02	+9.22	+11.0

Together with the ephemeris I communicated a table containing the variations of the right ascension and the declination by a variation of the perihelion passage of $+ 4$ or $- 4$ days. In comparing the above given values $O—C$ with the numbers of that table, it is evident that by a small negative variation of the perihelion passage, the agreement between observation and computation may be nearly attained, at least in α. The deviations in δ cannot be used so well for that purpose, as the variations of δ, resulting from a variation of T, are always much smaller than those of α, and this is especially the case in the period during which these observations are made. Yet we may conclude from the table for $\Delta T = - 4$ days that the positive errors in δ will not entirely disappear by a variation of T.

By means of a rough interpolation I derived from the 3 differences $O—C$ in right ascension the following corrections for the time of perihelion passage:

Observ. of	Aug. 28 :	$\Delta T = - 0.0900$ day
„ „	Sept. 25 :	$- 0.0916$ „
„ „	Oct. 10 :	$- 0.0896$ „

In the average $\Delta T = - 0.0904$ day, which at the rate of a mean daily motion of 517″448 corresponds to an increase of the mean anomalies of 46″8.

As a first step to correct the adopted elements of the orbit, I therefore computed the 3 places, in the supposition of an increase of the mean anomalies: 1° by 40″, 2° by 50″. I interpolated the following sun's co-ordinates (with reference to the mean equinox of 1906.0) from the Naut. Almanac.

TABLE III.

1906	X	Y	Z
Aug. 28.540391	$- 0.9134887$	$+ 0.3947635$	$+ 0.1712510$
Sept. 25.495694	$- 1.0018399$	$- 0.0318699$	$- 0.0138250$
Oct. 10.339987	$- 0.9565810$	$- 0.2616405$	$- 0.1135029$

For the reduction to the apparent places I added to the mean α of the comet: $f + g \sin (G + \alpha) \operatorname{tg} \delta$, to its mean δ: $g \cos (G + \alpha)$. The following table contains the computed apparent places in the two suppositions.

TABLE IV.

N⁰.	$\Delta M = +40''$		$\Delta M = +50''$	
	α	δ	α	δ
	h m s	° ′ ″	h m s	° ′ ″
1	4 7 35.758	+ 42 30 34.72	4 7 37.266	+ 42 30 37.38
2	4 32 11.451	+ 47 34 31.46	4 32 13.248	+ 47 34 31.85
3	4 34 51.050	+ 49 54 42.20	4 34 53.060	+ 49 54 41.99

A sufficient control is obtained here by comparing the values for $\Delta M = 0''$ (ephemeris), $\Delta M = +40''$ and $\Delta M = +50''$.

In comparing with the observed apparent places we obtain the following differences $O - C$:

TABLE V.

N⁰.	$\Delta M = +40''$		$\Delta M = +50''$	
	$\Delta\alpha$	$\Delta\delta$	$\Delta\alpha$	$\Delta\delta$
	s	″	s	″
1	+ 0.939	+ 16.27	− 0.569	+ 13.61
2	+ 1.281	+ 15.49	− 0.516	+ 15.10
3	+ 1.185	+ 11.84	− 0.825	+ 12.05

By means of interpolation between the values of $\Delta\alpha$ we find as resulting value for $\Delta M + 46''412$, leaving the following errors:

N⁰.	$\Delta\alpha$	$\Delta\delta$
	s	″
1	− 0.03	+ 14.7
2	+ 0.13	+ 15.2
3	− 0.10	+ 11.9

From this follows that by a variation of M alone, the differences $O - C$ in α can be reduced to very small quantities, but this is not the case with the differences in δ. It could be seen beforehand that no further improvement could be expected from alterations in π, φ or μ; at the end I will add a few words on these elements. So we must try to bring it about by variations in the position of the plane of the orbit, viz. of i and ☊, and for this reason I determined the relation between those elements and the computed places of the comet. As from the two suppositions $\Delta M = +50''$ seems to be nearer to the truth, I computed the apparent places of the comet: for $\Delta M = +50''$ $\Delta i = +10''$ and Δ☊ $= 0$ and also for $\Delta M = +50''$ $\Delta i = 0$ Δ☊ $= -10''$. Probably a somewhat larger value of Δ☊ had been more convenient. The following table gives the variations of α and δ in the two cases.

TABLE VI.

N°.	$\Delta i = +10''$		Δ☊ $= -10''$	
	$\Delta\alpha$	$\Delta\delta$	$\Delta\alpha$	$\Delta\delta$
	s	$''$	s	$''$
1	− 0.149	+ 10.00	+ 0.040	+ 1.26
2	− 0.108	+ 11.95	+ 0.067	+ 0.83
3	− 0.111	+ 12.88	+ 0.080	+ 0.56

The numbers from the tables V and VI give the following values of the differential quotients of α and δ with respect to M, i and ☊, which will be used as coefficients in the equations of condition.

	Aug. 28	Sept. 25	Oct. 10
$\frac{\partial\alpha}{\partial M}$	+ 0.1508	+ 0.1797	+ 0.2010
$\frac{\partial\delta}{\partial M}$	+ 0.266	+ 0.039	− 0.021
$\frac{\partial\alpha}{\partial i}$	− 0.0149	− 0.0108	− 0.0111
$\frac{\partial\delta}{\partial i}$	+ 1.000	+ 1.195	+ 1.288
$\frac{\partial\alpha}{\partial}$☊	− 0.0040	− 0.0067	− 0.0080
$\frac{\partial\delta}{\partial}$☊	− 0.126	− 0.083	− 0 056

For α the second of time and for the others quantities the second of arc have been adopted as unities. I multiplied the equations of condition for α by $15 \cos \delta$, and instead of $\Delta\,\Omega$ I introduced $\dfrac{\Delta\Omega}{10}$ as unknown quantity.

Equations of condition.

a. From the Right ascensions:

$$\begin{array}{llllllll}
0.22202 & \Delta M & + 9.21681_n & \Delta i & + 9.64568_n & \dfrac{\Delta\Omega}{10} & = & 0.79873_n \\
0.25966 & ,, & + 9.03853_n & ,, & + 9.83118_n & ,, & = & 0.71776_n \\
0.28811 & ,, & + 9.03023_n & ,, & + 9.88800_n & ,, & = & 0.90136_n
\end{array}$$

b. From the Declinations:

$$\begin{array}{llllllll}
9.42488 & \Delta M & + 0.00000 & \Delta i & + 0.10037_n & \dfrac{\Delta\Omega}{10} & = & 1.13386 \\
8.59106 & ,, & + 0.07737 & ,, & + 9.91908_n & ,, & = & 1.17898 \\
8.32222_n & ,, & + 0.10992 & ,, & + 9.74819_n & ,, & = & 1.08099
\end{array}$$

The coefficients are written logarithmically; the second members are taken from column 4 and 5 of table V, and therefore to ΔM, found from these equations, the correction $+ 50''$ has still to be applied.

From the above equations of condition we derive in the ordinary way the following normal equations:

$$\begin{array}{llllllll}
+ 9.9278 & \Delta M & - 0.39596 & \Delta i & - 3.8260 & \dfrac{\Delta\Omega}{10} & = & - 31.495 \\
- 0.39596 & ,, & + 4.1375 & ,, & - 2.7434 & ,, & = & + 49.637 \\
- 3.8260 & ,, & - 2.7434 & ,, & + 3.8423 & ,, & = & - 23.951
\end{array}$$

These equations are much simpler if we introduce besides ΔM, only one of the two unknown quantities. If we try e.g. to represent the observations only through variations of M and i we have not only $\Delta\Omega = 0$ but the third equation falls out entirely.

1. *Solution for* $\Delta\Omega = 0$.

The results are:

$$\begin{aligned} \Delta M &= - 2''\,7042 \\ \Delta i &= + 11.74 \end{aligned}$$

and the remaining errors:

$$\begin{array}{lll}
1. & \Delta\alpha = + 0^s014 & \Delta\delta = + 2''59 \\
2. & = + 0.097 & + 1.18 \\
3. & = - 0.151 & - 3.13
\end{array}$$

2. *Solution for* $\Delta i = 0$.

In this case we find:

$$\begin{aligned} \Delta M &= - 9''0461 \\ \Delta \Omega &= - 2'32''41 \end{aligned}$$

and for the remaining errors:

$$\begin{array}{llr} 1. & \Delta\alpha = + 0^s185 & \Delta\delta = - 3''18 \\ 2. & + 0.089 & + 2.80 \\ 3. & - 0.226 & + 3.32 \end{array}$$

3. *Solution with* 3 *unknown quantities:*

The results are:

$$\begin{aligned} \Delta M &= - 5''3045 \\ \Delta i &= + 7.32 \\ \Delta \Omega &= - 1'\,2.90 \end{aligned}$$

and according to the equations of condition there remain the following differences Obs.—Comp.

$$\begin{array}{llr} 1. & \Delta\alpha = + 0^s088 & \Delta\delta = - 0''23 \\ 2. & + 0.095 & + 1.34 \\ 3 & - 0.181 & - 1.01 \end{array}$$

As we see the solution with $\Delta\Omega = 0$ and that with $\Delta i = 0$ satisfy the observations fairly well, the first one somewhat better, especially in right ascension. Stili we cannot deny that in the values Obs.—Comp. of δ in both solutions, there exists a systematic variation. On account of that I prefer for the present the solution with 3 unknown quantities, where such a systematic variation doesnot appear. I therefore take the following elements as the most probable for the return in 1906:

Epoch 1906 January 16.0 M.T. Greenw.

$$\begin{aligned} M_0 &= 1266456''838 \\ &= 351°47'36''838 \\ \mu &= 517''447665 \\ \log a &= 0.5574268 \\ T &= 1906 \text{ March } 14.09401 \\ \varphi &= 24°20'25''55 \\ e &= 0.4121574 \end{aligned}$$

$$\left.\begin{aligned} i &= 20°49'\ 0''62 \\ \pi &= 346\ \ 2\ 31.63 \\ \Omega &= 331\ 44\ 37.85 \end{aligned}\right\}\ 1906.0$$

Yet it is evident that the accuracy of these elements is not equal to the accuracy of those I could derive for previous returns of the comet. In the first place the observations include only a period of 43 days, in which the heliocentric motion of the comet with its large perihelion distance was not even 12°. Secondly three observations with their inevitable errors are in general only sufficient to obtain a mere approximate idea of the orbit. We must admire the ability and accuracy of the Heidelberg astronomers, who, from measurements on a short focal photographic plate taken of a still wholly invisible nebula, could deduce the position of the comet with an accuracy that could be compared to that of micrometer measurements of objects several hundred times brighter. Still we must bear in mind that the rejection of only one of the 4 reference stars on the plate of the 28th of August, had an influence of 0^s16 in α and $1''6$ in declination, or of $2''39$ in arc of a great circle.

As a test to my calculations, I derived the 3 places finally by direct computation from the obtained elements.

Heliocentric aequatorial co-ordinates:

$$x = [9.993\ 7648.63]\ \sin\,(v + 77°37'28''36)$$
$$y = [9.876\ 2140.59]\ \sin\,(v - 20\ 58\ 46.82)$$
$$z = [9.832\ 7020.56]\ \sin\,(v - \ \ 1\ 46\ 46.76)$$

The following table contains the computed apparent places of the comet and the differences Obs.—Comp.

TABLE VII.

N⁰.	α	δ	$\Delta\alpha$	$\Delta\delta$
	h m s	° ′ ″	s	″
1	4 7 36.602	+ 42 30 51.32	+ 0.095	— 0.33
2	4 32 12.633	+ 47 34 45.69	+ 0.099	+ 1.26
3	4 34 52.412	+ 49 54 55.19	— 0.177	— 1.15

The agreement between these differences found directly, and the quantities obtained by substitution in the equations of condition forms a sufficient control on the whole computation.

The elements μ, π and φ.

The elements from which the ephemeris for 1906 has been derived are those given in "Système VII" p. 78 of my Deuxième Mémoire, reduced to 1906 by applying the perturbations, arising from the action of Jupiter. The mean error of the obtained value for μ is so small, that although not absolutely impossible, it is hardly probable that the correction obtained for the mean anomaly should have been caused totally or for the greater part by an error in μ. Taking the obtained ΔM for the 25th of Sept. we get:

$$\Delta\mu = + \frac{44''\,6955}{2662.50} = + 0''\,016787$$

and thus the real error of μ should be 67 times the mean one. Adopting this correction of μ, the mean anomalies for the 28th of August and the 10th of October would be only 0″ 469 smaller and 0″ 249 greater than the adopted ones.

It is more probable that the correction of M arises from neglected perturbations of that element by Saturn. This perturbation is given by the formula

$$\Delta M = \int_{t_0}^{t} \frac{dM}{dt}\, dt + \int\!\!\int_{t_0}^{t} \frac{d\mu}{dt}\, dt^2.$$

Even if instead of the sum of the values each term was known separately it would be equally impossible to conclude from the value of the double integral, the final value of $\int \frac{d\mu}{dt}\, dt$, or the correction of μ for 1906. Observations during a much longer period can only decide in this case.

Something like this holds for π and φ. During the short period of the observations, we may even substitute for a part of the correction ΔM corresponding variations of π and φ. If we keep to the plane of the orbit, the apparent place, except for small variations in the radius-vector (of little influence near the opposition), depends wholly on the longitude in the orbit, or on

$$l = \pi + v.$$

So we can apply small variations to the elements without varying perceptibly the computed positions, if only

$$\Delta l = \Delta\pi + \Delta v = 0$$

or

$$\Delta\pi = - \Delta v.$$

This relation provides us with the means to throw a part of the correction found for M on π or on φ or on both together. In the first case we have to satisfy the equation

$$\Delta\pi = - \frac{\partial v}{\partial M}\, \Delta M.$$

We can derive the values of $\frac{\partial v}{\partial M}$ directly from the comparison of the two former computations with $\Delta M = +40''$ and $\Delta M = +50''$. And so I find for the three dates of the observations:

$$\begin{aligned}\Delta M = & -0.506\,\Delta\pi \\ & -0.549\,\Delta\pi \\ & -0.573\,\Delta\pi\end{aligned}$$

If we keep π constant and want to substitute a part of the correction of M by a variation of φ, we must satisfy the relation

$$\Delta v = 0$$

or

$$\Delta M = \left(\frac{\partial M}{\partial \varphi}\right)_{v\ \mathrm{const.}} \Delta\varphi.$$

I derived the values of $\left(\frac{\partial M}{\partial \varphi}\right)_{v\ \mathrm{const.}}$ by computing from the three values of v, with a varied excentricity, the corresponding values of the mean anomaly. Hence I got for the three observations:

$$\begin{aligned}\Delta M = & -1.040\,\Delta\varphi \\ & -1.186\,\Delta\varphi \\ & -1.260\,\Delta\varphi\end{aligned}$$

Although the coefficients as well those of $\Delta\pi$ as of $\Delta\varphi$ show a small variation in the influence of the corrections of the elements on the three positions, practically this influence differs too little from that of a constant variation of M to allow a determination of ΔM, $\Delta\varphi$ and $\Delta\pi$ separately from the three observations.

Leiden, November 1906.

Mathematics. "*On the locus of the pairs of common points and the envelope of the common chords of the curves of three pencils.*" (1st part). By Dr. F. SCHUH. (Communicated by Prof. P. H. SCHOUTE).

1. *Given three pencils* (C_r), (C_s), (C_t) *of plane curves of degree* r, s, t. *To find the locus* L *of the pairs of points through which passes a curve of each of those pencils.*

Let P and P' be the points of such a pair. When determining the locus we shall notice but those points P and P' which are for each couple of pencils *movable* points of intersection (i. e. points not necessarily coinciding with the basepoints), a distinction to be made only when the pencils have common basepoints. The locus L arrived at in this way we shall call the *locus proper*, to distinguish it from the *total locus* to be arrived at by allowing one of the points P and P' to be a fixed point of intersection of two of the pencils.

Suppose the pencils (C_s) and (C_t) show α fixed points of intersection and that this number amounts to β for the pencils (C_t) and (C_r) and to γ for the pencils (C_r) and (C_s).

The degree n of L is determined from its points of intersection with an arbitrary straight line l. On l we take an arbitrary point Q_{rs} and through Q_{rs} we let a C_r and a C_s pass, which cut each other besides in the basepoints and in Q_{rs} still in $rs - \gamma - 1$ points. Through each of these points we let a curve C_t pass. These $rs - \gamma - 1$ curves C_t cut l in $t(rs - \gamma - 1)$ points Q_t, which we make to correspond to the point Q_{rs}. To find reversely how many points Q_{rs} correspond to a given point Q_t of l we take on l an arbitrary point Q_r through which we allow a C_r to pass cutting the C_t through Q_t in $rt - \beta$ points differing from the basepoints. Through each of those points we allow a C_s to pass, of which the points of intersection with l shall be called Q_s. To a point Q_r now correspond $s(rt - \beta)$ points Q_s and to a point Q_s correspond $r(st - \alpha)$ points Q_r. The $2rst - \alpha r - \beta s$ coincidences $Q_r Q_s$ are the t points of intersection of l with the C_t passing through Q_t and the points Q_{rs} corresponding to Q_t, whose number therefore amounts to $2\,rst - \alpha r - \beta s - t$.

So between the points Q_{rs} and Q_t of l we have a $(rst - \gamma t - t,\ 2\,rst - \alpha r - \beta s - t)$-correspondence. The $3\,rst - \alpha r - \beta s - \gamma t - 2t$ coincidences are the points of intersection of l with L and the points of intersection of l with the curve of contact of the pencils (C_r) and (C_s), i. e. the locus of the points of contact of the curves C_r and C_s touching each other. If there are two systems of curves (μ_1, ν_1) and (μ_2, ν_2) [1]), the order of that curve of contact is

$$\mu_1\nu_2 + \mu_2\nu_1 + \mu_1\mu_2\ ^{2)}.$$

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[1]) A system of curves (μ, ν) is a simply infinite system of curves, of which μ pass through an arbitrarily given point and ν touch an arbitrarily given straight line.

[2]) This order is found by counting the points of intersection with an arbitrary line l. To this end we consider the envelope of the tangents of the curves of the system (μ_1, ν_1) in its points of intersection with l; this envelope is of class $\mu_1 + \nu_1$, the tangents of that envelope passing through an arbitrary point Q of l being the tangents in Q to the μ_1 curves of the system through Q and the line l counting ν_1 times. In like manner does the system (μ_2, ν_2) give an envelope of class $\mu_2 + \nu_2$. The $(\mu_1 + \nu_1)(\mu_2 + \nu_2)$ common tangents of both envelopes are the line l counting $\nu_1\nu_2$ times and $\mu_1\mu_2 + \mu_1\nu_2 + \mu_2\nu_1$ other lines whose points of intersection with l indicate the points of intersection of l with the curve of contact. For a deduction with the aid of the symbolism of conditions see SCHUBERT, "Kalkül der abzählenden Geometrie", p. 51—52.

If we take for the systems the two pencils (C_r) and (C_s) then $\mu_1 = \mu_2 = 1$ and (as ensues immediately from the principle of correspondence) $\nu_1 = 2(r-1)$, $\nu_2 = 2(s-1)$. So the order of the curve of contact is

$$2r + 2s - 3.$$

For the number of points of intersection of l with L remains

$$3rst - \alpha r - \beta s - \gamma t - 2t - (2r + 2s - 3) = 3(rst+1) - 2(r+s+t) - (\alpha r + \beta s + \gamma t).$$

So we find:

The locus L of the pairs consisting of two movable points by which a curve of each of the pencils is possible is of order

$$n = 3(rst + 1) - 2(r + s + t) - (\alpha r + \beta s + \gamma t);$$

here α is the number of fixed points of intersection of the pencils (C_s) and (C_t), β that of the pencils (C_t) and (C_r) and γ that of (C_r) and (C_s).

2. Whilst the preceding considerations remain accurate when of the basepoints of one and the same pencil some coincide, we shall suppose in the following that the pencils (C_r), (C_s) and (C_t) have respectively r^2, s^2 and t^2 different basepoints, so that we can only allow the basepoints of one pencil to coincide in part with those of an other pencil. Then α is the number of common basepoints of the pencils (C_s) and (C_t) (which can however also belong to (C_r)), etc. If the pencils have no common basepoints ($\alpha = \beta = \gamma = 0$), the order of the locus becomes

$$3(rst + 1) - 2(r + s + t).$$

This is also in the case of common basepoints the order of the *total* locus as long as that is definite, i. e. as long as there are no basepoints common to the three pencils. If there is such a point, this furnishes together with an entirely arbitrary point a pair of points PP through which a curve of each of the pencils is possible; of this pair of points however only one is movable. The locus proper however is still definite then.

A basepoint of the pencil (C_r) only we call A_r, a common basepoint of the pencils (C_s) and (C_t) which is not a basepoint of the pencil (C_r) we call A_{st} and a common basepoint of the three pencils we call A_{rst}. If δ is the number of points A_{rst} then the number of points A_{st} amounts to $\alpha' = \alpha - \delta$, that of the points A_{rt} to $\beta' = \beta - \delta$ and that of the points A_{rs} to $\gamma' = \gamma - \delta$, whilst the number of points A_r is equal to $r^2 - \beta' - \gamma' - \delta$, etc. By introduction of α', β', γ' and δ the order n of this locus proper becomes

$$n = 3\,(r\,s\,t + 1) - 2\,(r + s + t) - (\alpha' r + \beta' s + \gamma' t) - \delta\,(r + s + t).$$

From this we see that the order of the locus proper is lowered by r on account of a common basepoint A_{st}. If there are no points A_{rst} ($\delta = 0$) one can easily account for that lowering of order by noticing that from the total locus the C_r passing through A_{st} separates itself, as not belonging to the locus proper. The point A_{st} furnishes namely together with an arbitrary point of that C_r a pair of points satisfying the question; of which points however only the latter is movable [1]). Farthermore we see that a point A_{rst} diminishes the order of L by $r + s + t$, a fact one cannot account for by separation, the total locus becoming indefinite [2]).

3. The locus proper L has in the basepoints of the three pencils multiple points, the multiplicities of which are easy to determine.

A basepoint A_r of the pencil (C_r) only is an ($st - \alpha - 1$)-fold point of L. In fact, the curves C_s and C_t passing through A_r have, A_r and the basepoints excepted, still $st - \alpha - 1$ points of intersection each of which combined with A_r furnishes a pair of points satisfying the question. The tangents in A_r to the curves C_r passing through the $st - \alpha - 1$ mentioned points of intersection are the tangents of L in the multiple point.

To determine the multiplicity of a point A_{st} we remark that to obtain a pair of points satisfying the question and of which one of the movable points coincides with A_{st}, it is necessary for C_r to pass through A_{st} (by which it is determined), whilst C_s and C_t which always pass through A_{st} must present a movable point of intersection in A_{st}, thus must touch each other in A_{st}. The question now rises: How often do two curves C_s and C_t touching each other in A_{st} intersect each other again on the curve C_r passing through A_{st}? To answer this question we introduce an arbitrary C_s intersecting the above mentioned C_r in $rs - \gamma - 1$ points differing from the basepoints. Through each of these points we allow a C_t to pass which gives rise to a correspondence between the curves C_s and C_t (so likewise between its tangents in A_{st}) where $rs - \gamma - 1$ curves C_t correspond to a C_s and $rt - \beta - 1$ curves C_s to a C_t. Thus for the curves C_s and C_t touching each other in A_{st} it happens ($rs + rt - \beta - \gamma - 2$)

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[1]) If A_{st} counts for ε fixed points of intersection of the curves C_s and C_t, the C_r passing through A_{st} separates itself ε times by which the degree of L is lowered by εr.

[2]) If A_{rst} counts for ε fixed points of intersection of C_s and C_t, for ζ fixed points of intersection of C_r and C_t and for η fixed points of intersection of C_r and C_s, then A_{rst} diminishes the order of L by $\varepsilon\, r + \zeta\, s + \eta\, t$; this holds for a point A_{st} too, but then we must regard ζ and η as being zero.

times that C_s and C_r have besides A_{st} another movable point of intersection, being at the same time movable point of intersection of C_t and C_r. Here is included the case in which this second point of intersection coincides with A_{st}, thus where the curves C_s and C_t touch C_r in A_{st}; then only one movable point of intersection of C_s and C_t still coincides with A_{st}, whilst there need be no other movable point of intersection lying on C_r, so that in this way we get no pair of points furnishing a branch of L passing through A_{st}. So the point A_{st} is an $(rs + rt - \beta - \gamma - 3)$-fold point of L.

To determine the multiplicity of a point A_{rst} we have to consider how many times three curves C_r, C_s and C_t touching each other in A_{rst} pass once more through a same point. To this end we consider an arbitrary C_r and the C_s which touches this C_r in A_{rst}. Through each of the $rs - \gamma - 1$ points of intersection of these C_r and C_s, differing from the basepoints, we allow a C_t to pass. Then the question arises how many times this C_t touches C_r and C_s in A_{rst}. Let us call l_{rs} the common tangent in A_{rst} of C_r and C_s and l_t the tangent of C_t in that point. To l_{rs} correspond $rs-\gamma-1$ lines l_t. To find reversely how many lines l_{rs} correspond to an arbitrary line l_t we consider an arbitrary C_r intersecting the C determined by l_t in $rt-\beta$ points differing from the basepoints. Through each of those points of intersection we imagine a C_s. If l_r and l are the tangents in A_{rst} of C_r and C_s then $rt-\beta$ lines l_s correspond to l_r and $st-\alpha$ lines l_r to l_s. The $rt + st - \alpha - \beta$ rays of coincidence indicate the lines l_{rs} corresponding to l_t; to those rays of coincidence however belongs the line l_t itself, which must not be counted, so that $rt+st-\alpha-\beta-1$ lines l_{rs} corresponding to l_t remain. So between the lines l_{rs} and l_t exists an $(rs-\gamma-1, rt + st-\alpha-\beta-1)$-correspondence.

The required lines l_{rst} are indicated by the $st+tr+rs-(\alpha+\beta+\gamma)-2$ rays of coincidence of this correspondence of which however three must not be counted. When namely the contact in A_{rst} of C_r and C_s becomes a contact of the second order one of the $rs-\gamma-1$ points of intersection differing in general from the basepoints of C_r and C_s coincides with A_{rst}, namely in the direction of l_{rs}. The C_t passing through that point of intersection will touch l_{rs} in A_{rst} in other words l_t coincides with l_{rs}. As however the curves C_r and C_s, but not the curves C_r and C_t, neither the curves C_s, C_t have in A_{rst} a contact of the second order we do not find in this way a pair of points satisfying the question. Now it happens three times with two pencils o curves with a common basepoint, between which a projective correspondence has been in such a way arranged that the curves must touch each other in that basepoint, that this is a contact of the second order, so that from the number of rays of coincidence three must be subtracted to find that of the lines l_{rst} wanted. From this ensues that the multiplicity of the point A_{rst} amounts to $st + tr + rs - (\alpha + \beta + \gamma) - 5$.

So we find:

A basepoint of the pencil (C_r) *only is a*

$$(st - \alpha - 1)\text{-}$$

fold point of the locus proper L. A common basepoint of the pencils (C_s) *and* (C_t) *which is not basepoint of* (C_r) *is a*

$$(rs + rt - \beta - \gamma - 3)\text{-}$$

fold point of L and a common basepoint of the three pencils is a

$$(st + tr + rs - \alpha - \beta - \gamma - 5)\text{-}$$

fold point of L [1]).

4. With the help of the preceding the points of intersection of L with an arbitrary curve of one of the pencils, e.g. a C_r, are easy to indicate. These are:

1. The $r^2 - \beta - \gamma + \delta$ points A_r counting together for

$$(r^2 - \beta - \gamma + \delta)(st - \alpha - 1)$$

points of intersection.

2. The $\beta - \delta$ points A_{rt} counting together for

$$(\beta - \delta)(sr + st - \alpha - \gamma - 3)$$

points of intersection.

3. The $\gamma - \delta$ points A_{rs}, giving

$$(\gamma - \delta)(tr + ts - \alpha - \beta - 3)$$

points of intersection.

4. The δ points A_{rst}, giving together

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[1]) If there are no points A_{rst} $(\delta = 0)$ and therefore the total locus is not indefinite, we can also ask after the multiplicities of the points A_r and A_{st} as points of the total locus. Now the improper part of the locus consists of α curves C_r, β curves C_s and γ curves C_t. Of these pass through a point A_r the α curves C_r and through a point A_{st} the β curves C_s, the γ curves C_t and one of the curves C_r. From this ensues:

A point A_r *is an* $(st - 1)$, *a point* A_{st} *an* $(rs + rt - 2)$*-fold point of the total locus.*

So the multiplicity of A_r as a point of the total locus is not changed by the coincidence of the basepoints, whilst the multiplicity of A_{st} is equal to the sum of the multiplicities which this point would have if it were only basepoint of the pencil (C_s) or only basepoint of the pencil (C_t).

$$\delta(st + tr + rs - \alpha - \beta - \gamma - 5)$$

points of intersection.

5. The movable points of intersection of L with C_r; these are those points of intersection which displace themselves when we choose another C_r. These are found as the pairs of common points of the simply infinite linear systems of pointgroups intersect on C_r by the pencils (C_s) and (C_t). The number of these are found from the following theorem:

If there are on a curve of genus p two simply infinite linear systems of pointgroups consisting of a and b points, the number of common pairs of points of those systems is

$$(a - 1)(b - 1) - p.$$

In our case $a = rs - \gamma$, $b = rt - \beta$ and (as C_r is an arbitrary curve of the pencil (C_r)) $p = \frac{1}{2}(r-1)(r-2)$. For the number of pairs of common points we therefore find

$$(rs - \gamma - 1)(rt - \beta - 1) - \tfrac{1}{2}(r - 1)(r - 2),$$

and for the number of movable points of intersection of L and C_r:

$$2(rs - \gamma - 1)(rt - \beta - 1) - (r - 1)(r - 2).$$

So the total number of points of intersection is:

$$r(3rst + 3 - 2r - 2s - 2t - \alpha r - \beta s - \gamma t),$$

in accordance with the formula we have found for the order of L.

5. The pairs of points PP' through which a curve of each of the pencils is possible determine on L an involutory (1,1)-correspondence; in the following we shall indicate P and P' as corresponding points of L.

If P falls into a doublepoint of L differing from the basepoints, then in general two different points P' and P'' will correspond to P according to our regarding P as point of the one or of the other branch of L passing through P. The curves of the pencils passing through P now have two more common points P' and P'', so that we get a triplet of points $P\,P'\,P''$, through which a curve of each of the pencils is possible.

It may however also happen that the points P' and P'' coincide. In that case correspond to the two branches through P two branches through P', so that P' is likewise doublepoint of L. The curves of the pencils passing through P have now but one other common point P', but now the particularity arises that P or P' can be displaced in two ways such that the other common point is retained. So PP' is then to be regarded as a double corresponding pair of points.

If reversely we have a triplet of points $PP'P''$ lying on curves of each of the pencils, then P is a doublepoint of L, for P' as well as P'' corresponds to P, and so it must be possible to displace P in such a way that the corresponding point describes a branch passing through P' and in such a way that a branch passing through P'' is described. The curve L has thus two branches $P1$ and $P2$ passing through P to which the branches $P'1$ and $P'2$ correspond. Through the point P' (which is of course likewise doublepoint of L as well as P'') a second branch $P'3$ passes and through P'' a second branch $P''3$, which branches correspond mutually. If a point Q describes the branch $P1$ the curves C_r, C_s, C_t passing through Q have a second common point describing the branch $P'1$, whilst a third common point P'' appears and again disappears when Q passes the point P. This third common point displaces itself (along the branch $P''2$) when Q describes the other branch passing through P, whilst then the common point coinciding with P' appears and disappears.

Triplets of points $PP'P''$, and therefore doublepoints of L differing from the basepoints, there will be as a triplet of points depends on 6 parameters and it is a 6-fold condition that a curve of each of the pencils must pass through it. So we have:

The curve L has doublepoints, differing from the basepoints of the pencils, belonging in triplets together and forming the triplets of points through which a curve of each of the pencils is possible. To one or other branch through a doublepoint of such a triplet corresponds a branch through the second resp. the third doublepoint of this triplet. Moreover L can however have pairs of doublepoints indicating the double corresponding pairs of points. To the two branches through the doublepoint of such a pair correspond the branches through the other doublepoint of the pair.

6. The number of coincidences of the correspondence between P and P' can be determined as follows. The points P and P' coincide if the curves C_r, C_s and C_t passing through P have in P the same tangent. Then P must lie on the curve of contact R_{rs} of the pencils (C_r) and (C_s) as well as on the curve of contact R_{rt} of (C_r) and (C_t). The number of points of intersection of those curves of contact which are of order $2r+2s-3$ resp. $2r+2t-3$ amounts to

$$(2r+2s-3)(2r+2t-3).$$

Some of these points of intersection however do not lie on the third curve of contact R_{st}, and so they must not be counted. The curve R_{rs} namely passes once through a basepoint A_r or A_s and three times through a common basepoint A_{rs} or A_{rst}; in fact in a point of

R_{rs} two movable points of intersection of C_r and C_s, coincide so that the point A_{rs} as a point of the curve of contact is found when C_r and C_s show in A_{rs} a contact of the second orderwhich takes place three times. Further R_{rs} passes through the doublepoints of the curves C_r and C_s, of which the number for the pencil (C_r) amounts to $3(r-1)^2$ and for the pencil (C_s) to $3(s-1)^2$, which follows immediately from the order of the discriminant.

Each of the $r^2 - \beta' - \gamma' - \delta$ points A_r is a simple point of intersection of R_{rs} and R_{rt} (simple, the tangents in A_r to R_{rs} and R_{rt} being the tangents of the curves C_s and C_t passing through A_r, differing thus in general), but no point of R_{st}. Each of the α' points A_{st} is a double point of intersection of R_{rs} and R_{rt}, as those curves of contact in A_{st} have a simple point with the same tangent, namely that of the C_r passing through A_{st}; these points are also points of R_{st}, namely threefold ones. Each of the β' points A_{rt} is threefold point of intersection of R_{rs} and R_{rt} (it being simple point of R_{rs} and threefold point of R_{rt}) and lies at the same time on R_{st}; the same holds for the γ' points A_{rs}. Each of the δ points A_{rst} which are common basepoints of the three pencils is 9-fold point of intersection of R_{rs} and R_{rt}, being threefold point of each of those curves; moreover it is threefold point of R_{st}. Finally the $3(r-1)^2$ doublepoints of the pencil (C_r) are simple points of intersection of R_{rs} and R_{rt}, but not points of R_{st}; of the curves C_r, C_s and C_t passing through such a doublepoint C_r has an improper contact with C_s and with C_t, without however C_s and C_t touching each other.

From this we see that the curves of contact R_{rs} and R_{rt} have

$$r^2 - \beta' - \gamma' - \delta + 3(r-1)^2 = 4r^2 - 6r + 3 - \beta' - \gamma' - \delta$$

points of intersection which are not points of R_{st}, and so do not furnish coinciding points P, P'. Moreover R_{rs} and R_{rt} have

$$2\alpha' + 3\beta' + 3\gamma' + 9\delta$$

points of intersection coinciding with the common basepoints, which do fall on R_{st}, but which do not give any coinciding points P and P', as for this it is necessary that of three curves C_r, C_s and C_t passing through the same point each pair shows two movable points of intersection coinciding with that point. So for the number of coinciding points P and P' remains:

$$(2r + 2s - 3)(2r + 2t - 3) - (4r^2 - 6r + 3 - \beta' - \gamma' - \delta) -$$
$$- (2\alpha' + 3\beta' + 3\gamma' + 9\delta) =$$
$$= 4(st + tr + rs) - 6(r + s + t) + 6 - 2(\alpha' + \beta' + \gamma' + 4\delta).$$

So we find:

It happens

$$4(st + tr + rs) - 6(r + s + t) + 6 - 2(\alpha + \beta + \gamma + \delta)$$

times that the two points P and P' through which a curve of each of the pencils is possible coincide.

7. With the help of this result the class of the envelope of the lines connecting P and P' can easily be determined. To this end we have to count how many lines PP' pass through an arbitrary point S. We find this number by regarding the correspondence between the rays SP and SP', which we call l and l'. This is an involutory (n, n)-correspondence where n represents the order of the locus L of the points P and P'; for on an arbitrary ray l (or l') lie n points P (or P'), to each of which one point P' (or P) corresponds. So there are $2n$ rays of coincidence which can be furnished either on account of PP' passing through S or of P and P' coinciding.

So for the number of rays of coincidence where PP' passes through S we find:

$$2\,\{3(rst+1)-2\,(r+s+t)-(\alpha r+\beta s+\gamma t)\}-\{4(st+tr+rs)-$$
$$-6(r+s+t)+6-2\,(\alpha+\beta+\gamma+\delta)\}=6rst-4\,(st+tr+rs)+$$
$$+2\,(r+s+t)-2\alpha\,(r-1)-2\beta\,(s-1)-2\gamma\,(t-1)+2\delta.$$

These rays of coincidence however coincide in pairs. For if the line connecting the corresponding points P_1 and P_1' passes through S, then to P_1P_1' regarded as line l correspond n lines l', two of which coincide with P_1P_1', for if point P of l is taken in P_1 or in P_1' the corresponding point P' lies in P_1' resp. P_1. Likewise to P_1P_1 regarded as line l' correspond n lines l, of which also two coincide with P_1P_1', from which ensues that P_1P_1' is a double ray of coincidence[1]). So to find the number of the lines PP' passing through S, thus the class of the envelope, the above found number must still be divided by 2, so that we get:

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[1]) One can easily convince oneself of the accuracy of this conclusion by a representation of the correspondence between the rays SP and SP'. To this end we regard the parameters of the lines SP and SP' as rectangular Cartesian coordinates x and y of a point which is the representation of those two lines. The curve of representation (which is symmetrical with respect to the line $y=x$ on account of the correspondence being involutory) indicates by its points of intersection with the line $y=x$ the rays of coincidence. If B is the point of representation of the rays l and l' coinciding in P_1P_1', the curve of representation is cut in two coinciding points B by a line parallel to the y-axis as well as by a line parallel to the x-axis, on account of P_1P_1' regarded as l or l' corresponding twice to itself regarded as l' resp. l. So B is doublepoint of the curve of representation, so that the line $y=x$ furnishes two points of intersection coinciding with B.

The envelope of the lines connecting pairs of points, through which a curve of each of the pencils is possible, is of class

$$3\,rst - 2\,(st+tr+rs) + (r+s+t) - \alpha(r-1) - \beta\,(s-1) - \gamma\,(t-1) + \delta =$$
$$= 3\,rst - 2\,(st+tr+rs) + (r+s+t) - \alpha'\,(r-1) - \beta'\,(s-1) - \gamma'\,(t-1) -$$
$$- \delta\,(r+s+t-4).$$

8. If the pencils have no common basepoints then the class of the envelope is $3\,rst - 2\,(st + tr + rs) + (r + s + t)$. By a common basepoint A_{st} of the pencils (C_s) and (C_t) that class is lowered with $r - 1$. *This is because point A_{st} has separated itself from the envelope $r-1$ times.* In fact, the curve C_r passing through A_{st} has separated itself from the locus of the points P and P'. If we take P arbitrarily on this C_r, the corresponding point P' coincides with A_{st}. So an arbitrary line passing through A_{st} is to be regarded $(r - 1)$ times as a line connecting P and P', as any of the $r-1$ points of intersection with C_r differing from A_{st} may be chosen for P.

If the three pencils have a common basepoint A_{rst} the total envelope of PP' remains definite (in contrast to the total locus of P and P'). It is true P can be taken quite arbitrarily, but then P' coincides with a point A_{rst}, so that the line PP' passes through that point A_{rst}, and therefore is not quite arbitrary. As the class of the envelope proper is lowered by the point A_{rst} with $r + s + t - 4$ it follows, *that A_{rst} separates itself $(r + s + t - 4)$ times from the envelope.* As one of the points of the pair becomes entirely indefinite, that multiplicity is not easy to explain, as far as I can see.

Physics. — "*On a new empiric spectral formula.*" By E. E. Mogendorff. (Communicated by Prof. P. Zeeman).

By the fundamental investigations of Kayser and Runge and those of Rydberg the existence of spectral series was proved. The formulae of these physicists, however, give in general too great deviations for the first lines of a series. I have tried to improve the formula given by Rydberg:

$$n = A - \frac{N_0}{(m + a)^2}.$$

Particularly noteworthy in Rydberg's formula is the universal constant N_0. From Balmer's formula, which is included as a special case in Rydberg's formula, follows for hydrogen for the observation corrected to vacuo $N_0 = 109675$.

Assuming for a moment that the N_0 was also variable for the different series, I have calculated the constants A, a and N_0 from three of the best observed curves. For N_0 the following values were found:

Principal Series	Lithium	109996
,, ,,	Natrium	107178
,, ,,	Potassium	105638
,, ,,	Rubidium	104723
,, ,,	Caesium	104665
1st associated series	Hydrogen	109704
,, ,,	Helium	109703
,, ,,	Natrium	110262
,, ,,	Potassium	109081
,, ,,	Silver	107162
,, ,,	Magnesium	108695
,, ,,	Zinc	107489
,, ,,	Oxygen	110660
Second ,,	Natrium	107819
,, ,,	Magnesium	105247
,, ,,	Calcium	103702
,, ,,	Zinc	105399
,, ,,	Aluminium	105721

These values have been calculated from wave frequencies not corrected to vacuo.

As appears from these values N_0 is not absolutely constant. As KAYSER [1]) found in another way, we see, however, that relatively

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[1]) KAYSER, Handbuch II. p. 553.

N_0 changes little from element to element [1]. The supposition lies at hand, that a constant of nature will occur in the rational formula. For the first associated series of Aluminium calculation gives a considerable deviation. Calculating from the first terms of this series we find $N_0 = 207620$ calculating from the middle lines $N_0 = 138032$, and from the lines with smaller λ $N_0 = 125048$.

The first asssociated series of aluminium behaves therefore quite abnormally.

In RYDBERG's formula another function than $(m + a)^{-2}$ must be used to get a better harmony, specially with the first terms of a series.

In my thesis for the doctorate, which will shortly appear, I have examined the formula:

$$n = A - \frac{109675}{\left(m + a + \frac{b}{m}\right)^2},$$

in which n represents the wave frequency reduced to vacuo, A, a and b are constants which are to be determined, m passes through the series of the positive integers, starting with $m = 1$. In most cases with this formula a good agreement is obtained, also with the first lines of a series. The associated series converge pretty well to the same limit, while also the law of RYDBERG—SCHUSTER is satisfied in those cases where besides associated series, also a principal series is observed.

A spectral formula has also been proposed by RITZ [2].

In my thesis for the doctorate I have adduced some objections to the formula of RITZ, as it gives rise to highly improbable combinations of lines. Moreover for the metals of the 2nd column of MENDELEJEFF's system his views are not at all in harmony with observation.

In the following tables the observed wavelength in Å. E. is given under λ_w, the limit of error of observation under F, the deviation according to the formula proposed by me under A, the deviation according to the formula of KAYSER and RUNGE under A. K. R. The mark * on the right above a wavelength indicates that these lines were used as a basis for the calculation of the constants A, a and b.

The constants are calculated from the wave frequencies reduced to vacuo [3].

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[1] The B in KAYSER and RUNGE's formula varies within considerably wider limits than the N_0 of RYDBERG's formula.

[2] Ann. d. Phys. Bd. 12, 1903, p. 264. W. RITZ, Zur Theorie der Serienspectren.

[3] Where it was possible, I have always taken these values from the "Index of Spectra" from MARSHALL WATTS.

Lithium.

Principal series: $A = 43480{,}13$; $a = +\,0{,}95182$; $b = +\,0{,}00722$
1st ass. series : $A = 28581{,}8$; $a = +\,1{,}998774$; $b = -\,0{,}000822$
2nd ,, : $A = 28581{,}8$; $a = +\,1{,}59872$; $b = -\,0{,}00321$
3rd ,, ; $A = 28581{,}8$; $a = +\,1{,}95085$; $b = +\,0{,}00404$

The associated series converge here evidently to one limit.

The difference of wave frequency between the limits of principal and associated series is 43480,13—21581,8 = 14898,33. The wave frequency of the 1st line of the principal series is 14902,7. So the formula satisfies the law of RYDBERG-SCHUSTER pretty well.

PRINCIPAL SERIES.

m	λ_W	F	K	A. K. R.
1	6708,2 *	0,20	0	+ 108
2	3232,77*	0,03	0	0
3	2741,39	0,03	— 0,06	0
4	2562,60*	0,03	0	0
5	2475,13	0,10	— 0,22	— 0,2
6	2425,55	0,10	— 0,18	— 0,01
7	2394,54	0,20	— 0,13	+ 0,30
8	2373,9 L. D.	?	+ 0,02	+ 0,75
9	2359,4 L. D.	?	+ 0,17	+ 1,18

FIRST ASSOCIATED SERIES.

m	λ_W	F	A	A. K. R.
1	6103,77*	0,03	0	0
2	4602,37*	0,10	0	0
3	4132,44	0,20	— 0,11	0
4	3915,20*	0,20	0	— 0,20
5	3794,9	5,00	+ 0,09	— 0,35
6	3718.9	5,00	— 1,94	— 2,25
7	3670,6	5,00	— 1,06	— 1,41

SECOND ASSOCIATED SERIES.

m	λ_W	F	A	A. K. R.
1	8127,0* S	0,30	0	— 65
2	4972,11	0,10	— 0,13	0
3	4273,44*	0,20	0	0
4	3985,94	0,20	+ 0,22	0
5	3838,30	3,00	+ 2,40	— 0,2

THIRD ASSOCIATED SERIES.

m	λ_W	F	A	A. K. R.
1	6240,3* S	0,40	0	—
2	4636,3* S	0,40	0	—
3	4148,2 S	1,00	+ 1,6	—
4	3921,8 E H	?	— 0,88	

The capitals after the wavelengths denote the observers: L. D. LIVEING and DEWAR; S. SAUNDERS and E. H. EXNER and HASCHEK. Where no further indication is given, the observation has been made by KAYSER and RUNGE.

Natrium.

Principal series (the lines of the doublets with greatest λ)

$$A = 41447,09; \quad a = 1,147615; \quad b = -0,031484$$

Principal series (lines of the doublets with smallest λ)

$$A = 41445,20; \quad a = 1,148883; \quad b = -0,031908.$$

For the calculation of the limit of the associated series RYDBERG-SCHUSTER'S law has been used. With a view to the constant differences of wave frequencies of the doublets of the associated series, I have only carried out the calculation for the components with small wavelength.

For the 1st ass. series $A = 24491,1$; $a = 1,98259$; $b = +0,00639$
For the 2nd ass. series $A = 24491,1$; $a = 1,65160$; $b = -0,01056$

PRINCIPAL SERIES.

m	λ_W	F	A	A. K. R.
1	5896,16*	—	0	+ 78
1	5890,19*	—	0	+ 86
2	3303,07*	0,03	0	0
2	3302,47*	0,03	0	0
3	2852,91	0,05	— 0,14	0
3	2852,91	0,05	— 0,06	0
4	2680,46*	0,10	0	0
4	2680,46*	0,10	0	0
5	2593,98	0,10	+ 0,03	+ 0,03
5	2593,98	0,10	— 0,02	+ 0,09
6	2543,85 L. D.	0,10	— 0,06	+ 0,10
6	2543,85 L. D.	0,10	— 0,14	+ 0,24
7	2512,23 L. D.	0,20	+ 0,03	+ 0,50
7	2512,23 L. D.	0,20	— 0,10	+ 0,60

FIRST ASSOCIATED SERIES.

m	λ_W	F	A	A. K. R.
1	8184,33* L.	0,2	0	0
2	5682,90	0,15	0,01	0
3	4979,30*	0,20	0	0
4	4665,20	0,50	— 0,13	+ 0,52
5	4494,30	1,00	— 0,28	+ 0,50
6	4390,70 L. D.	?	+ 0,28	+ 1,30
7	4325,70 L. D.	?	+ 4,00	+ 1,76

SECOND ASSOCIATED SERIES.

1	11404	?	+ 1,00	+ 100,--
2	6154,62*	0,10	0	0
3	5149,19*	0,10	0	0
4	4748,36	0,15	+ 0,12	0
5	4542,75	0,20	+ 0,65	+ 1,39
6	4420,20 L. D.	?	+ 0,02	+ 1,55
7	4343,70	?	+ 2,00	— 1,36

Zinc.

For this element I have calculated the formulae of the 1st and 2nd associated series for the components with the greatest wavelength of the triplets.

The limits are determined for the two series separately, for the first associated series the calculation gave 42876,25 and for the second associated series the limit appeared to be 42876,70. A very good agreement.

The formula gives as 1st line of the 1st associated series of Zinc the line 8024,05, which has not been observed. The 8th line of the first associated series 2409,22 has not been observed either. As 9th line of this series 2393,93 was calculated, which is in remarkably good harmony with the intense line 2393,88. As yet this line had not yet been fitted in the series. The great intensity of a curve in the root of the series is certainly strange; an investigation of the magnetic splitting might decide whether it is correct to range this line under the first associated series.

The formula for the 1st associated series is:

$$n = 42876{,}25 - \frac{109675}{\left(m + 0{,}909103 - \dfrac{0{,}007085}{m}\right)^2}$$

and for the 2nd associated series:

$$n = 42876{,}70 - \frac{109675}{\left(m + 1{,}286822 - \dfrac{0{,}058916}{m}\right)^2}$$

FIRST ASSOCIATED SERIES.

m	λ_W	F	A	A. K. R.
1	—	—	—	—
2	3345,13*	0,03	0	— 0,08
3	2801,00*	0,03	0	+ 0,03
4	2608,65*	0,05	0	+ 0,06
5	2516,00	0,20	+ 0,04	— 0,11
6	2463,47	0,20	— 0,14	— 0,39
7	2430,74	0,30	+ 0,22	+ 9,00
8	—	—	—	—
9	2393,88	0,05	— 0,05	—

SECOND ASSOCIATED SERIES.

m	λw	F	A	A. K. R.
1	4810,71*	0,03	0	+ 58
2	3072,19*	0,05	0	0,00
3	2712,60*	0,05	0	+ 0,02
4	2567,99*	0,10	+ 0,11	— 0,01
	2493,67	0,15	+ 0,12	— 0,04
6	2449,76	0,25	— 0,11	— 0,20

Thallium.

The formula for the 1st associated series is:

$$n = 41466{,}4 - \frac{109675}{\left(m + 1{,}90141 - \frac{0{,}00366}{m}\right)}$$

for the satellites:

$$n = 41466{,}4 - \frac{109675}{\left(m + 1{,}88956 - \frac{0{,}00085}{m}\right)^2}$$

and for the second associated series:

$$n = 41466{,}4 - \frac{109675}{\left(m + 1{,}26516 - \frac{0{,}07108}{m}\right)^2}$$

The limit has been calculated from three lines of the 1st associated series; only two more lines were required of the satellites and of the 2nd associated series. So in this spectrum all the constants have been calculated from 7 lines and 31 lines are very well represented by the formula.

FIRST ASSOCIATED SERIES.

m	λw	F	A	A. K. R.
1	3519,39*	0,03	0	—
2	2918,43	0,03	— 0,04	—
3	2709,33*	0,03	0	—
4	2609,08	0,03	+ 0,04	—
5	2552,62*	0,10	0	—
6	2517,50	0,10	— 0,06	— 0,34
7	2494,00	0,10	— 0,03	— 0,19
8	2477,58	0,10	— 0,09	+ 0,06
9	2465,54	0,20	— 0,17	+ 0,24
10	2456,53	0,20	— 0,15	+ 0,47
11	2449,57	0,30	— 0,17	+ 0,68
12	2444,00	0,30	— 0,28	+ 0,79
13	2439,58	0,30	— 0,24	+ 0,95

SATELLITES.

m	λ_W	F	A	A. K. R.
1	3529,58*	0,03	0	+ 0,02
2	2921,63	0,03	+ 0,06	— 0,07
3	2710,77*	0,03	0	+ 0,13
4	2609,86	0,03	— 0,03	— 0,02
5	2553,07	0,10	— 0,05	— 0,12

SECOND ASSOCIATED SERIES.

m	λ_W	F	A	A. K. R.
1	5350,65*	0,03	0	— 168
2	3229,88*	0,03	0	— 21,7
3	2826,27	0,05	— 0,05	— 3,65
4	2665,67	0,05	— 1,32	— 1,69
5	2585,68	0,05	— 0,16	+ 0,01
6	2538,27	0,10	— 0,17	+ 0,04
7	2508,03	0,15	— 0,14	— 0,01
8	2487,57	0,20	— 0,06	+ 0,08
9	2427,65	0,20	— 0,34	— 0,21
10	2462,01	0,30	— 0,20	— 0,03
11	2453,87	0,30	— 0,17	+ 0,07
12	2447,59	0,30	— 0,05	+ 0,22
13	2442,24	0,30	— 0,37	— 0,01

I shall just add a few words on the spectrum of Aluminium. None of the formulae given as yet represents the first associated series of this element at all satisfactorily; nor is a satisfactory result attained with my formula. In the beginning of this paper I have pointed out, that very deviating values for N_0 were calculated from three of the 1st lines of the series.

The formula runs:

$$n = 48287{,}9 - \frac{109675}{\left(m + 0{,}89436 + \dfrac{1{,}038060}{m}\right)^2}$$

The constants have been calculated from the lines 4, 5 and 6.

ALUMINIUM. FIRST ASSOCIATED SERIES.

m	λ_W	F	A	A. K. R.
1	3082,27	0,03	— 268,82	+ 384,8
2	2568,08	0,03	+ 3,46	+ 53,5
3	2367,16	0,03	+ 2,52	+ 6,1
4	2263,83*	0,10	0	+ 0,03
5	2204,73*	0,10	0	+ 0,17
6	2168,87*	0,10	0	— 0,13
7	2145,48	0,20	+ 0,06	— 0,31
8	2129,52	0,20	+ 0,11	— 0,21
9	2118,58	0,20	— 0,28	+ 0,44

The agreement with the first lines (1, 2 and 3), leaves much to be desired. The value of the constant b is here 1,03806, greater than the value of a in that formula; this does not occur with any of the other series.

With 4 constants, so with:

$$n = A - \frac{109675}{\left(m + a + \frac{b}{m} + \frac{c}{m^2}\right)^2}$$

a better result is most likely reached. When the constants b and here probably also the c, are not small with respect to a, then the influence of those constants is very great, particularly for small values of m. The deviation for the first line of the above series (3082,27), however, is so great, that I doubt if this is really the first line of this series.

The behaviour of this Aluminium series is certainly peculiar, and a further investigation is desirable.

For the way in which the constants in the formula were calculated, and for the spectra of Potassium, Rubidium and Calcium, of Magnesium, Calcium, Cadmium and of Helium and Oxygen, I refer to my thesis for the doctorate, which will shortly be published.

Astronomy. — *"Mutual occultations and eclipses of the satellites of Jupiter in* 1908." By Prof. J. A. C. OUDEMANS.

SECOND PART. — ECLIPSES.

(Communicated in the meeting of October 27, 1906).

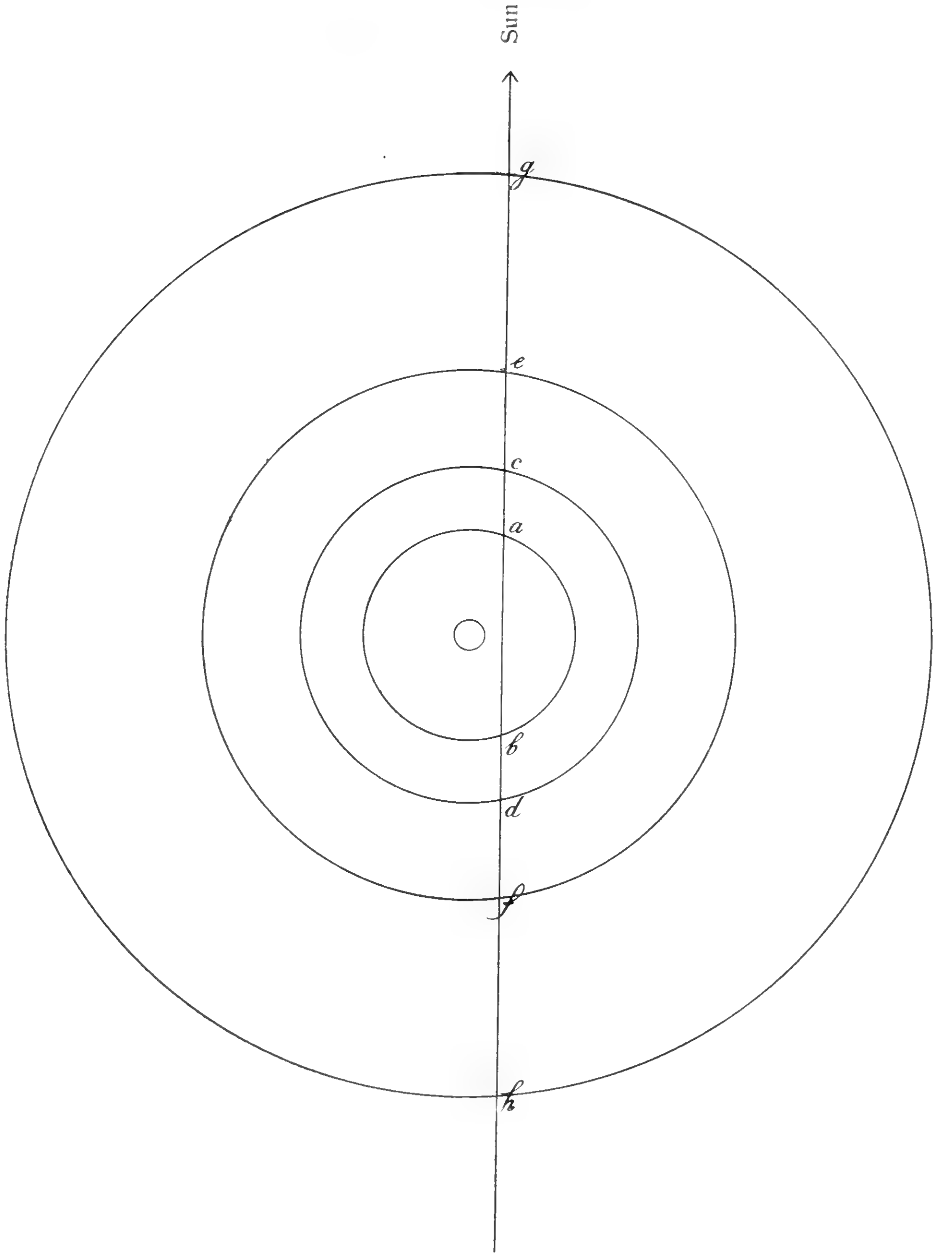
From occultations to eclipses there is but one step.

Between the two phenomena there is this difference that, as has been communicated on p. 305, the occultations have been observed more than once, but that of the eclipses of one satellite by another we have but one, incomplete account given in a private letter of Mr. STANLEY WILLIAMS dated 7 December 1905. In his letter to us he writes: "With regard to the heliocentric conjunctions there does "seem to be one observation of the rare phenomenon of the eclipse "of a satellite in the shadow of another one on record. It occurred "on the 14th August 1891 and was observed by Mr. J. COMAS at "VALLS in Spain and by the writer at HOVE. Mr. COMAS' observation "was published in the FRENCH periodical L'Astronomie, 1891, p. 397 "(read 398) 1). The following is an account of my observation. No "particulars of this have hitherto been published."

" "1891 Aug. 14. $6^1/_2$ inch reflector, power 225. Definition good, " "but interruptions from cloud. Satellite I. transitted on the S. Equa-" "torial belt, (N. component). *Immediately* on its entering the disc " "it became lost to view. At 11^h49^m a minute dark spot was seen " "about in the position which the satellite should have then occupied. " "The shadows of satellites I. and II. were confounded together at " "this time, there seeming to be one very large, slightly oval, black " "spot. At 11^h59^m the two shadows were seen neatly separated, " "thus,  . The preceding shadow must be that of II., the follow-" "ing and *much smaller* one that of I.. At 12^h10^m satellite I. was " "certainly visible as a dark spot, much smaller than the shadow " "of either satellite. It had moved with respect to the shoulder of " "the Red Spot Hollow, so that there could be no doubt of its " "identity. It is on the north band of the north (south) equatorial " "belt 2). Satellite I [this should evidently be II.] shines brightly " "on the disc near the limb. Definition good, but much thin cloud " "about." "

"The foregoing is an almost literal transcript from my observation "book. I take it that when satellite I. entered on the disc of Jupiter, "it was already partly eclipsed by the shadow of II., so that it "became lost to view immediately, instead of shining, as usual, for

J. A. C. **OUDEMANS**. "Mutual occultations and eclipses of the satellites of Jupiter in 1908." Second part: Eclipses.



Scale $\frac{1}{30\,168\,000\,000}$. On this scale the sun's diameter is 0.24 meter and its distance 25.783 m.

"some time as a brillant disc. Also that the minute dark spot seen "at 11^h49^m was produced by the portion of the shadow of II., then "projected on I. Also that the small size of the following shadow "spot at 11^h59^m was due to a part only of the shadow of II. being "projected on the disc of Jupiter, the other part of this shadow "having been intercepted by satellite I. 3)

— — — "But combining Mr. Comas' observation with my own, "there can be no doubt but that satellite I. was actually partially "eclipsed by the shadow of II. on the night of August 14, 1891. "So far as I am aware, this is the only indubitable instance of one "satellite being eclipsed by the shadow of another."....

"P.S. The above times are Greenwich mean times. The Nautical "Almanac time for the transit ingress of satellite I. is 11^h33^m." 4).

Before proceeding to the computation of epochs of such heliocentric conjunctions we have investigated to what extent generally eclipses of one satellite by the shadow of another are possible. That they may occur is proved by the shadows of the satellites on Jupiter itself. The question however is: 1st whether the shadows of the foremost satellite reaches that of the more distant one in *every* heliocentric conjunction and 2nd whether the occurrence of total eclipses is possible in any case. In order to find an answer to these questions we assume that the orbits all lie in a single plane which, being prolonged, passes through the centre of the sun. We further imagine a line in the plane of the orbits starting from the sun and passing Jupiter at a distance equal to its radius, the distance from the centre thus being equal to its diameter (see Plate I). This line cuts the orbits of the four satellites each in two points. Beginning with the point nearest the sun we shall call these points *g*, *e*, *c*, *a*, *b*, *d*, *f* and *h*. For clearness, sake the figure is given below (Plate I).

Now suppose that I is placed either at *a* or at *b*. In both cases the other satellites will be involved in its shadow cone as soon as they come: II_f at *d*, III_f at *f* and IV_f at *h*.

The points of intersection with the orbit of II are *c* and *d*. If II_n is at *c* then I_n may be eclipsed in *a* but also I_f in *b*; III_f at *f* and IV_f at *h*.

But if II_f is in *d* then only III_f and IV_f can be eclipsed, the former at *f* and the latter at *h*.

The points of intersection with the orbit of III are *e* and *f*. If III is at *e* there is the possibility of an eclipse for II_n at *c*, I_n at *a*, I_f at *b*, II_f at *d* and IV_f at *h*. If on the other hand it is in *f* there is such a possibility only for IV_f at *h*.

It is evident that IV can only cause the eclipse of another satellite if it is at the position *g*, one of the other three satellites being then at one of the points of intersection already mentioned.

Each of the satellites might thus produce six different eclipses; if however we compute the radii of the umbra for the positions of the other satellites we are led to a negative value in some of the cases. This means of course that the vertex of the cone of the umbra does not reach the other satellite.

If for the radii of the satellites we adopt the values mentioned in the first part of this communication, diminished however by the amount of the irradiation, it appears that a total eclipse is only possible in two cases. III_n may cause a total eclipse of II_n and I_n; I_f may nearly produce such an eclipse of II_f. If the shadow does not reach the other satellite then an inhabitant of the latter would see an annular eclipse of the Sun.

This case presents itself

for the shadow of I_n in respect to IV_f .
,, II_n ,, ,, ,, III_f and IV_f,
,, III_n ,, ,, ,, IV_f,
,, IV_n ,, ,, ,, II_f and III_f.

In the fifteen remaining cases there may be a partial eclipse.

It need hardly be said that this case can only present itself if, at the time of heliocentric conjunction, the difference of the heliocentric latitudes $(y'-y)$, is smaller than the sum of the radii. In computing however the occultations observed by Messrs Fauth and Nijland it appeared that this difference in latitude, according to the tables of Damoiseau, is sometimes slightly greater. The latitudes found by these tables are therefore not entirely trustworthy. For this reason we included *all* the heliocentric conjunctions between 1 April and 20 May 1908 (both dates inclusive).

The preparation for the computation, *viz* the drawing of the orbits of the satellites is the same as for the computation of the geocentric conjunctions (see 1st part). First however the epochs of the heliocentric superior conjunctions must be derived from the epochs of the *geocentric* superior conjunctions taken from the Nautical Almanac by the aid of the hourly motions of the satellites and of the angle *G*, i.e. the angle Earth—Jupiter—Sun. Furthermore, the jovicentric mean longitudes should be corrected for their equations and perturbations and diminished by S. i. e. the heliocentric longitude of Jupiter, instead of by S—G which is its geocentric longitude.

Of the arguments N°. 3 need not be computed; for this argument only serves, combined with 1, for the computation of the jovicentric latitude of the Earth, which need not be known in the present case. The number of columns in our tables will thus be found to be diminished by one for each of the satellites.

Our results are contained in the annexed table. Between 1 April and 20 May we found 81 heliocentric conjunctions; the last column but one, $(y-y')$, shows that in a very great number of the cases an eclipse is possible.

(1) The account of Mr. José Comas is as follows:

Ombres de deux satellites de Jupiter et éclipse. — Dans la nuit du 14 août, j'ai observé un phénomène bien rare: la coïncidence partielle, sur Jupiter, des ombres de ses deux premiers satellites, et par suite l'éclipse de Soleil pour le satellite I produit par le satellite II.

A 11^h (temps de Barcelone) [1]) l'ombre du satellite II est entrée sur la planète. Près du bord, elle n'était pas noire, mais d'un gris rougeâtre. Comme l'image était fort agitée, j'ai cessé d'observer, mais je suis retourné à l'observation vers 11^h37^m pour observer l'immersion du premier satellite, qui a eu lieu à 11^h42^m (grossissement 100 fois; lunette de 4 pouces). J'ai été surpris de voir disparaître Io [2]) à son entrée sur le disque, ne se détachant pas en blanc, quoiqu'il se projetât sur la bande foncée équatoriale australe.

A 11^h52^m, avec des images plus tranquilles et un grossissement de 160, je remarquai que l'ombre complètement noire que l'on voyait était allongée dans une direction un peu inclinée vers la droite, relativement à l'axe de Jupiter. La phase maxima de l'éclipse du satellite I était déjà passée de quelques minutes. A 11^h56^m je pris le petit dessin que j'ai l'honneur de vous adresser; les deux ombres se touchaient encore [3]). Aussitôt elles se séparèrent et, quoique je n'aie pas pu noter l'instant du dernier contact, je crois être assez près de la vérité, en disant qu'il s'est effectué vers 11^h58^m.

L'empiètement d'une ombre sur l'autre pourrait être de la troisième

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[1]) Barcelone is 2°10' East of Greenwich; mean time at Barcelone is therefore 8^m40^s later than of Greenwich.

[2]) Since a few years the Nautical Almanac mentions the names of the Satellites of Jupiter proposed by Simon Marius: Io, Europa, Ganymedes and Callisto.

[3]) This drawing shows, as seen in an inverting telescope, the right hand (following) part of the well know Red spot in the Southern Hemisphere of Jupiter. Below it, at some distance, a dark band and still further two dark shadows each 4 mm. in diameter, which are not yet separated. The common chord is 2,5 mm. in length; the total length of the two shadows together 7,2mm. The line connecting the centres makes an angle of 40° with the vertical. Meanwhile the motion of the two shadows must have been nearly horizontal.

partie du diamètre. Dans cette supposition la distance minima des centres des deux ombres a dû avoir lieu vers 11^h47^m et le premier contact vers 11^h37^m. Le premier satellite pénétra dans le disque de la planète à 11^h42^m, comme j'ai dit plus haut, donc l'éclipse a commencé quand le satellite se projetait encore dans l'espace, cinq minutes avant l'immersion.

L'invisibilité de l'ombre d'Europe sur Io peut s'expliquer par la mauvaise qualité des images. Toutefois, la pénombre et l'ombre du II satellite ont été suffisantes pour diminuer notablement l'éclat du premier.

(2) The meaning evidently is that, as seen in an *inverting* telescope the dark spot seemed to be situated on the North band of the North belt, but that in reality it was on the South band of the South belt. It is well known that the so-called *Red spot* is there situated.

(3) The author does not refer here to the visibility of a shadow of II on I. This may be explained, in my opinion, by irradiation and diffraction.

(4) According to the tables of Damoiseau, second part, the time of the heliocentric conjunction of the two satellites is 23^h45^m civil time Paris = 11^h36^m Greenwich. In the Nautical Almanac of 1891 we find the following data for 14 August:

II	Shadow.	Ingress	10^h	51^m	M.	T.	Grw.
I	,,	,,	10	59	,,	,,	,,
I	Transit	,,	11	33	,,	,,	,,
II	,,	,,	11	58	,,	,,	,,
I	Shadow.	Egress	13	18	,,	,,	,,
II	,,	,,	13	45	,,	,,	,,
I	Transit	,,	13	51	,,	,,	,,
II	,,	,,	14	49	,,	,,	,,

If from the 1st, 2nd, 5th and 6th line we compute the time at which the shadows must coincide we get 11^h31^m. This result differs by 5^m from that found just now. We have to consider, however, that the two satellites went the same way, and that their relative motion in five minutes, consequently also that of their shadows, was very minute.

Mr. Stanley Williams seems not to have perceived a shadow before 11^h49^m M. T. Greenwich; Mr. Comas already saw an oblong shadow at $11^h43^m20^s$ M. T. Greenwich. For the rest Mr. Stanley

WILLIAMS makes the shadow of II larger than that of I whereas in the estimation of Mr. COMAS they were equal. It seems hardly doubtful but the English observer must be right.

(5) In 1901 SEE repeatedly measured the diameters of the satellites of Jupiter at the 26 inch telescope of Washington. He made use of the filar micrometer but took a special care to eliminate the systematic errors peculiar to this instrument (*Vid.* Astron. Nachr. N°. 3764, 21 Jan. 1902. The communication of SEE is dated 19 Oct. 1901).

During the months May—August (both inclusive) of the year 1901 he measured the diameters in the night. He was then much troubled by the undulation of the limbs caused by the unsteadiness of the air. Afterwards in the months of September and October of the same year he observed a little before and a little after sunset. Artificial illumination was then not needed; and the satellites appeared as quiet discs. Moreover the field and the satellites were coloured greenish yellow by a screen filled with protochloride of copper and picric acid. The results for the diameters turned out to be smaller in every case than those formerly found. The difference was attributed to irradiation.

The results, reduced to the mean distance of Jupiter to the sun (5,2028), are as follows.

Satellite	At night	In daytime	Difference, attributed to irradiation
I	1″,077 ± 0″018	0″834 ± 0″,006	0″243 ± 0″019
II	0 ,976 ± 0 ,043	0 ,747 ± 0 ,007	0 ,229 ± 0 ,0435
III	1 ,604 ± 0 ,038	1 ,265 ± 0 ,009	0 ,339 ± 0 ,039
IV	1 ,441 ± 0 ,018	1 ,169 ± 0 ,006	0 ,372 ± 0 ,019

It is remarkable that the brightest satellite, III, shows also the strongest irradiation. If however we consider the difference insufficiently established, and if therefore we combine the several results obtained for the irradiation, duly taking into account the weights corresponding to the probable errors, we get

$$\text{Irradiation} = 0'',264 \pm 0'',012.$$

This is the irradiation for the whole diameter and we thus get 0″,132 for each of the limbs. This number however holds only for the telescope at Washington for which, owing to its great aperture, the diffraction must be exceedingly small.

It seems worth while to call attention to the differences between the diameters found by the same observer in 1900 and 1901.

	1900	1901	1901—1900
I	0″672 ± 0″098	0″,834 ± 0″,006	+ 0″162
II	0,624 ± 0,078	0 ,747 ± 0 ,007	+ 0,121
III	1,361 ± 0,103	1 ,265 ± 0 ,009	— 0,096
IV	1,277 ± 0,083	1 ,169 ± 0 ,006	— 0,108

Stone, at Oxford, once told me that Airy, in a conversation on the determination of declinations at the meridian circle, remarked to him: "I assure you, Stone, a second is a very small thing".

If we consider the differences just adduced between the results obtained by a single observer in two consecutive years we are led to conclude that, for micrometer observations, even now "a tenth of a second is an exceedingly small thing".

Appendix. *In how far are the tables of* Damoiseau *still reliable?*

In the first part of this paper, pages 319 and 321, we explained why we felt ourselves justified in using the tables of Damoiseau for these computations in advance. We may now add that we also investigated the differences of the eclipses, as observed in some recent years at different observatories, from these tables, or rather from the epochs given by the Nautical Almanac. In these investigations we have been assisted by Mr. Kress, amanuensis at the Observatory of Utrecht, who has carefully searched some volumes of the *Astronomische Nachrichten* and of the *Monthly Notices* for the time of "disappearance and reappearance" of each satellite. He has further combined these times, reduced them to the meridian of Greenwich, and has then compared them with the data of the Nautical Almanac. In order to simplify, we requested him to note only the observation of the last light seen at disappearance and the first light at reappearance[1]). We intended to extend our investigation from 1894 to 1905

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[1]) Delambre in the introduction to his tables, does not state explicitly the *precise* instant to which his tables refer but from some passages we may conclude that he also means the instant *as here defined.* So for instance on page LIII where he says: *"Les demi-dureées ont été un peu diminuées, pour les rapprocher des observations qu'on a faites depuis la découverte des lunettes achromatiques"*.

That Laplace also takes it for granted that such is his real meaning, appears from Ch. VIII, 8th book of the Mécanique Céleste.

or 1906, but after having completed some four years there seemed reason to think that there was hardly need for further information. The general result arrived at was, that the tables were still sufficiently accurate for our purpose, which was no other than to prepare astronomers for the observation of the mutual occultations and eclipses of the satellites.

Now that the work is finished we will not suppress its results though it cannot at all claim to be complete. It never was our intention to make it so, and the journals appearing in France, in America etc. have not been searched.

The following observatories have contributed to our investigation.

	Aperture of the telescopes in m.m.
Greenwich	102, 170, 254, 714.
Utrecht	260
Uccle	150
Jena (Winkler)	162
Halifax (Gledhill)	237
Pola	162
Christiania	74, 190
Kasan	66, 81, 84, 96, 244
Göttingen	161
Windsor (Tebbutt) near Adelaïde	203
Lyon (a single observation)	2

At Greenwich, Christiania and Kasan the eclipses have been often observed by two or more astronomers using telescopes of different aperture. In such cases we have only taken into account the instant observed by means of the telescope of largest aperture. As a rule the observer at this telescope could follow the satellite longer at "disappearance" and he would pick it up earlier at "reappearance". There are however a few exceptions to the rule.

For the eclipses observed during the period of a single opposition of Jupiter the corrections to the data of the Nautical Almanac in no case showed a regular progression. They fluctuated on both sides of the mean in such a way that there could be no objection to adopting their arithmetical mean, a proceeding which still would be perfectly justified, even if there had been a *regularly* increasing or decreasing progression. No further attention was paid to the differences in the aperture of the telescopes. If these apertures exceed a certain amount, for instance 150 mm. we find, theoretically as well as practically that the differences due to the varying apertures are very small.

The results arrived at are as follows:

Corrections to the epochs given in the Nautical Almanac for the eclipses of Jupiter's satellites.

Opposition.	Mean Corr. N.A. Disapp.	Number.	Mean error.	Mean Corr. N.A. Reapp.	Number.	Mean error.	$\frac{1}{2}(D+R)$	Mean error.
I.								
1894/95	+ 37^s	3	±14	— 18^s	25	± 4^s	+ $9^s.5$	± 7^s
1895/96	+ 30	9	8	0	32	4	+ 15	4^5
1897	— 19^5	2	18	— 5	12	6	— 12	9^5
1898	+ 11	15	6	+ 7	13	6	+ 6	4
II.								
9418	— 78	2	±32	0	7	$±11^s$	— 39^s	$±17^s$
1894/95	+ 52	4	22^5	— 42	15	7^5	+ 5	12
1895/96	+ 73	6	18	— 4	19	6^5	+ 34	10
1897	— 72	3	26	+ 11	10	9	— 30	14
1898	— 36	5	20	— 15	9	9^5	— 26	11
III.								
1894	$+151^s$	3	$±22^s$	$—242^s$	3	$±38^s$	— 45^s	$±25^s$
1895	+101	4	19	—127	4	33	— 13	11^5
1895/96	+ 87	9	13	— 50	9	22	+ 19	11^5
1897	+181	4	19	+ 37	9	22	+109	14^5
1898	+266	4	19	+ 10	1	66	+138	34
1899	+361	3	22	—126	4	33	+118	20
IV.								
1895	+ 21^m45^s	3	—	— 17^m 9^s	2		$+138^s$	
. . . .	. . . . .	. . .	. . .	. . . . .	. . .	. . .	. . .	. .
1895/96	+ 3 49	10	±25	— 3 17	7	$±22^s$	+ 16	$±17^s$
1897	— 0 2	2	±57	+ 1 16	1	60	+ 37	—41

Average mean error of a single observation.

	Disappearance	Reappearance	Mean	Delambre *) Introd. p. LIV
I	$\pm 25^s$	$\pm 20^s$	$\pm 22^s5$	17^s5
II	45	29	37	
III	37	66	51, 5	88, 5 72, 5 rejecting the observations deviating more than 3 minutes).
IV	80	60	70	

According to these numbers the complaints about the increased inaccuracy of the tables of DAMOISEAU seem rather exaggerated, at least for the first and second satellites.

Taking into account the mean errors contained in the last column we get the most probable correction at the epoch 1894—98

for I $+ 8^s,0$ with a mean error of $\pm 2^s,6$
similarly „ II $- 3,8$ „ „ „ „ „ $\pm 5,4$.

Both corrections can hardly be vouched for.

For III the case stands otherwise. It is true, the subtractive correction at the reappearances as well as the additive one at the disappearances may be attributable to the use of more powerful telescopes; still there seems to be a progression in the numbers of the last column but one, which calls for a more exhaustive investigation.

In regard to IV, we found great corrections for the year 1895. After some years in which this satellite had not been eclipsed, owing to the fact that at the opposition it passed to the north of the shadow cone of Jupiter, there began a new period of eclipses in this year. In such a case the satellite travels high above the plane of the orbit of Jupiter, and describes only a small chord in the shadow. The consequence is that any small error in the latitude appears strongly magnified in the duration of the eclipse. The observations of Mr. WINKLER at Jena and of the observer at the observatory at Uccle near Brussels, of 8 March 1895 are very suggestive in this regard. The corrections were found to be:

	Jena.	Brussels.	Mean
at disappearance	$+ 19^m 48^s$	$+ 21^m 58^s$	$+ 20^m 53^s$
at reappearance	$- 19\ 36$	$- 18\ 33$	$- 19\ 4,5$

which shows that it is not the mean longitude of this satellite which is mainly in error.

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*) DELAMBRE gives mean *differences*; we have multiplied his numbers by $1^1/_4$ in order to get mean *errors*.

The explanation of these extravagant differences must rather be sought, either in a correction needed by the longitude of the node of the satellite's orbit or in the adopted flattening of Jupiter. It is also possible that for suchlike eclipses the diminution of light is *very slow.*

For the rest, according to the Nautical Almanac, this eclipse would be the fourth after the long period in which no eclipse of this satellite occurred. The data, on pages 450, 452, 454 are as follows:

1895

17 Jan^{y}.	D.	$1^h\,36^m16^s$	M. T. Gr., R.	$2^h\ 8^m17^s$,	duration	$32^m\ 1^s$
2 Feb^{y}.	,,	19 26 12	,, ,, ,, ,,	20 36 58 ,	,,	1^h 10 46
19 ,,	,,	13 24 6	,, ,, ,, ,,	14 59 3 ,	,,	1 34 57
8 March	,,	7 24 14	,, ,, ,, ,,	9 18 28 ,	,,	1 54 14.

Only, according to Scott-Hansen, who, on the North-Polar expedition of Nansen, was in charge of the astronomical observations, the satellite has not been eclipsed at all on the 17th of January [1]).

On the 2nd February 1895 too an eclipse of IV was not observed; (I cannot now call to mind where I saw this negative observation). On the 19th February, however, an observer at Greenwich, using the Sheepbanks equatorial, aperture 120 mm., got a correction of $+\ 23^m30^s$, for the disappearance of IV. This agrees quite well with the preceding results, obtained at Uccle and at Jena on 8th of March.

If we adopt the mean result of the observations at Brussels and at Jena, the duration of the eclipse on that day was

$$1^h44^m14^s - 39^m57^s,5 = 1^h14^m16^s,5,$$

The number might be of some use for the correction of the elements of IV.

The difference here found cannot be attributed to a too small value of the adopted flattening, for Damoiseau's value $\frac{1}{13,49}$ exceeds already that found by direct measurement by most observers. Taking into account however the results obtained by De Sitter, as communicated at the meeting of the Section (Proceedings Vol. VIII p. 777), it appears that the longitude of the ascending node of the 4th satellite must be increased by about + 10°, whereas for the inclination on

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[1]) The Norwegian North Polar Expedition 1894 – 1896. Scientific Results, edited by Fridtjof Nansen. VI. Astronomical Observations, arranged and reduced under the supervision of H. Geelmuyden, p. XXIV.

the fixed plane is found the value $= 0^\circ{,}2504 = 15'\,2''4$, which exceeds Damoiseau's inclination only by somewhat less than a minute.

The remaining eclipses of IV in 1895 and the two following years do not show any extraordinary divergencies.

Now, as in 1908 the eclipses of the satellites will be nearly central, as may be gathered from the drawings in the Nautical Almanac accompanying the table of these phenomena, there is no need to fear that such great divergencies will occur for IV in that year.

Our result therefore is that the Nautical Almanac, which is based on the tables of Damoiseau (taking into account only a few necessary corrections), may be considered sufficient for preparing ourselves for the coming observations. The only exception would be for an early eclipse of IV after a period in which it is not eclipsed at all.

Utrecht, 23 November 1906.

RESULTS.

Mutual heliocentric conjunctions of the satellites in April and May 1908.

A.A. = Ann Arbor; Fl. = Flagstaff; H.K. = Hong Kong; La Pl. = La Plata; P. = Perth; Tac. = Tacubaja; To. = Tokio; We. = Wellington; Wi. = Windsor.

No.	Mean time at Greenwich	n = near f = far		$x = x'$	Eclipsed satellite y	Eclipsing satellite y'	$y - y'$	Visible at
		Eclipsed satellite	Eclipsing satellite					
1	1 April $4^h\ 8^m$	I_f	II_n	$+5^r70$	-0^r30	-0^r25^5	-0^r04^5	Kas., Taschk., Madras, HK., Perth
2	2 » 18 3	I_f	III_n	+3, 21	—0, 16	—0, 20	+0,04	Lick, Fl., Tac., AA., Harvard.
3	3 » 4 15	II_f	III_n	—2, 49	+0, 08	+0, 10	—0,02	Kas., Taschk., Madr., HK., Perth, To
4	3 » 9 51	II_f	I_n	+1, 50	—0, 10^5	—0, 09	—0,01^5	Grw., Pulk., Kas., Taschk., La Pl., Rio
5	3 » 11 10	IV_f	III_n	—6, 19^5	+0, 40	+0, 32	+0,08	Grw., Pulk., Kasan, La Pl., Rio.
6	3 » 16 26	IV_f	I_n	—4, 03	+0, 30	+0, 19	+0,11	Lick, Fl., Tac., AA., Harv., La Pl
7	4 » 16 52	IV_f	II_n	+6, 03	—0. 20	—0, 27	+0,07	Lick, Fl., Tac., AA., Harvard.
8	4 » 17 21	I_f	II_n	+5, 75	—0, 31	—0, 25	—0,06	Lick, Fl., Tac., AA., Harvard.
9	5 » 19 56	III_f	II_n	—9, 24	+0, 54	+0, 30	+0,24	Wi., We., Lick, Fl., Tac., AA.
10	6 » 20 12	III_f	I_n	+3, 61	—0, 18^5	—0, 21	+0,02^5	Wi., We., Lick, Fl., Tac., AA.
11	6 » 22 58	II_f	I_n	+1, 37	—0, 10	—0, 09	—0,01	Perth, Tokio, Wi., We.
12	8 » 6 31	$\text{I}_{e.e.}$	II_n	+5, 82	—0, 31	—0, 25	—0,06	Bresl., Pulk., Kas., Taschk., Madras
13	9 » 20 52	I_f	III_n	+3, 85^5	—0, 18	—0, 24	+0,06	Wi., We., Lick, Fl.
14	10 » 7 28	II_f	III_n	—2, 05^5	+0, 06	+0, 09^5	—0,03^5	Grw., Pulk., Kas., Taschk., Madras
15	10 » 12 4	II_f	I_n	+1, 24	—0, 09	—0, 08	—0,01	Grw., Pulk., Kas., Harv., La Pl., Rio
16	11 » 11 » 15 42 smallest distance	II	IV	II +7, 87 IV +7, 96	—0, 36	—0, 48	+0,12	Lick, Fl., Tac., AA., Harv., La Pl., Rio.
17	11 » 19 43	$\text{I}_{e.e.}$	II_n	+5, 88	—0, 31^5	—0, 26	—0,05^5	Wi., We., Lick, Fl., Tac., AA.
18	11 » 20 24	$\text{I}_{e.e.}$	IV_n	+5, 99	—0, 32	—0, 38	+0,06	Wi., We., Lick, Fl,
19	12 » 23 33	III_f	$\text{II}_{w.e.}$	—9, 41	+0, 54	+0, 45	+0,09	Perth, HK., Tokio, Wi., We.
20	13 » 3 57	III_f	IV_n	—7, 35	+0. 42	+0, 27	+0,15	Kasan, Taschk., Madr., HK.
21	13 » 23 22	III_f	I_n	+2, 64	—0, 16	—0, 19	+0,03	HK., Perth, Tokio, Wi., We.
22	14 » 1 11	II_f	I_n	+1, 11	—0, 09	—0, 06	—0,03	HK., Perth, Tokio, Wi.
23	15 » 8 57	$\text{I}_{e.e.}$	II_n	+5, 93	—0, 32	—0, 26	—0,06	Grw., Pulk., Kas., Taschk., Rio.
24	16 » 23 44	I_f	III_n	+4, 45^5	—0, 23	—0. 26	+0,03	HK., Pe., To., Wi., We.
25	17 » 10 41	II_f	III_n	—1, 61	+0, 03	+0, 08	—0,05	Grw., Pulk., Kasan, La Pl., Rio.
26	17 » 14 17	II_f	I_n	+0, 98	—0, 09	—0, 06	—0,03	Grw., Fl., Tac., AA., Harv., La Pl., Rio.
27	18 » 22 11	$\text{I}_{e.e.}$	II_n	+5, 97	—0, 32	—0, 26	—0,06	Perth, To., Wi., We.

Mean time at Greenwich	n = near f = far		$x=x'$	Eclipsed satellite y	Eclipsing satellite y'	$y-y'$	Visible at
	Eclipsed satellite	Eclipsing satellite					
19 April 5^h15^m	IV_f	$\mathrm{III}_{w.e.}$	$-\ 15^r28$	$+\ 0^r80$	$+\ 0^r85$	$-\ 0^r05$	Kasan, Taschk., Madras.
19 » 22 57	IV_f	II_n	— 8,69	+ 0,48	+ 0,43	+ 0,05	HK., Perth, Tokio, Wi., We.
20 » 3 14	III_f	II_n w.e.	— 9,54	+ 0,55	+ 0,45	+ 0,10	Taschk., Madras, HK., Perth, To.
21 » 1 45	III_f	I_n	+ 2,27	— 0,12	— 0,13	+ 0,01	Madras, HK., P., Tokio.
21 » 1 46	IV_f	I_n	+ 2,26	— 0,05	— 0,12	+ 0,07	Madras, HK., P., Tokio.
21 » 1 52	IV_f	III_f	+ 2,33	— 0,05	— 0,12	+ 0,07	Madras, HK., P., Tokio.
21 » 3 23	II_f	I_n	+ 0,845	—0,088	— 0,044	— 0,044	Taschk., Madr., HK., P., Tokio.
22 » 12 19	IV_f	II_f	+ 6,62	— 0,39	— 0,44	+ 0,05	Grw., Pulk., Harv., La Pl., Rio.
15 13	id. gr.	dist.	8,01 and 7.84	— 0.32	— 0,40	+ 0,08	Lick, Fl., Tac., A.A., Harv., La Pl.
17 56	»	»	+ 8,88	— 0,38	— 0,44	+ 0,06	We., Lick., Fl., Tac., A.A., Harv.
22 » 9 41	IV_f	$\mathrm{III}_{(o.e.)}$	+ 14,84	— 0,66	— 0,83	+ 0,17	Grw., Pulk., Kasan, La Pl., Rio.
22 » 11 27	$\mathrm{I}_{(e.e.)}$	II_n	+ 6,01	— 0,32	— 0,26	— 0,06	Grw., Pulk., (Kasan), La Pl., Rio.
24 » 2 41	I_f	III_n	+ 5,02	— 0,255	— 0,28	+ 0,025	Taschk., Madr., HK., P., To.
26 » 0 41	$\mathrm{I}_{e.e.}$	II_n	+ 6,03	— 0,33	— 0,25	— 0,08	HK., P., To., Wi.
27 » 7 5	III_f	II_f	— 9,62	+ 0,54	+ 0,45	+ 0,09	Bresl., Pulk., Kasan, Taschk.
28 » 4 28^5	I_f	III_n	+ 1,57	— 0,08	— 0,09	+ 0,01	Kasan, Taschk., Madr., HK.
28 » 5 36	II_f	I_n	+ 0,58	— 0,03	— 0,065	+ 0,035	Kasan, Taschk., Madras.
28 » 13 29	IV_f	III_n	+ 6,41	— 0,36	— 0,36	0,00	Grw., Tac., AA., Harv., La Pl., Rio.
* 28 » 16 18	II	III	II + 7,31 III + 7,80	— 0,38	— 0,49	+ 0,06	

$-x'$ diminishes gradually in absolute value, reaches its minimum 0,49 at the time assigned and then increases again. So there is no eclipse.

Mean time at Greenwich	Eclipsed satellite	Eclipsing satellite	$x=x'$	Eclipsed satellite y	Eclipsing satellite y'	$y-y'$	Visible at
29 » 3 45	I_f	IV_n	+ 0,27	— 0,02	— 0,08	+ 0,08	Taschk., Madr., HK.
29 » 13 57	$\mathrm{I}_{e.e.}$	II_n	+ 6,05	— 0,33	— 0,26	— 0,07	Tac., AA., Harv., La Pl., Rio.
1 May 17 5	II_f	III_n	— 0,74	— 0,01	— 0,62	+ 0,61	Lick, Fl., Tac., AA., Harv., La Pl.
1 » 18 43	II_f	I_n	+ 0,44	— 0,07	— 0,02	— 0,05	Lick, Fl., Tac., AA.
3 » 3 16	$\mathrm{I}_{e.e.}$	II_n	+ 6,06	— $0{,}32^5$	— 0,24	— $0{,}08^5$	Taschk., Madr., HK., P., Tokio.
4 » 11 7	III_f	$\mathrm{II}_{w.e.}$	— 9,61	+ 0,54	+ 0,45	+ 0,09	Grw., Pulkowa.
5 » 7 48	II_f	I_n	+ 0,31	— 0,07	— 0,02	— 0,05	Grw., Pulk., Kasan, Taschk.
5 » 8 17	III_f	I_n	— 0,10	— 0,09	— 0,01	— 0,08	Grw., Pulk., Kasan, (Taschk.).
5 » 14 2	III_f	II_f	+ 4,63	— 0,26	— 0,26	0,00	Tac., A.A., Harv., La Pl., Rio.
5 » 17 57	greatest	dist.	$+6\overset{''}{,}64+6\overset{''}{,}85$	— 0 38	— 0,36	+ 0,02	We., Lick, Fl., Tac., AA.
5 » 21 39	III_f	II_f	+ 8,43	— 0,42	— 0,49	+ 0,07	To., Wi., We., Lick.

No.	Mean time at Greenwich	$n =$ near $f =$ far Eclipsed satellite	 Eclipsing satellite	$x = x'$	Eclipsed satellite y	Eclipsing satellite y'	$y-y'$	Visible at
53	6 » $16^{h}38^{m}$	$\mathrm{I}_{e.e.}$	II_{n}	+ $6^{r}03$	— $0^{r}215$	— $0^{r}24$	+ $0^{r}02^{5}$	Lick., Fl., Tac., AA., Harvard.
54	7 » 6 27	IV_{n}	I_{n}	— 3,27	+ 0,20	+ 0,18	+ 0,02	Bresl. Pulk., Kasan, Taschk. Mad
55	7 Mei 6 37 5	IV_{v}	II_{n}	— 3,18	+ 0,19	+ 0,20	— 0,01	Bresl. Pulk., Kasan, Taschk., Madr
56	8 » 7 4	IV_{f}	III_{n}	+ 6,90	— 0,38	— 0,29	— 0,09	Bresl., Pulk., Kasan, Taschk., Mad
57	8 » 20 54	II_{f}	I_{n}	+ 0,18	— 0,06	— 0,00	— 0,06	Wi., Wellington.
58	8 » 23 25	I_{n}	III_{n}	— 2,04	+ 0,12	+ 0,13	— 0,01	Perth, Tokio, Windsor.
59	9 » 5 29	$\mathrm{I}_{w.e.}$	III_{n}	— 5,36	+ 0,32	+ 0,34	— 0,02	Kasan, Taschk., Madras.
60	10 » 6 0	I_{n}	II_{n}	+ 5,99	— 0,32	— 0,38	+ 0,06	Kasan, Taschk., Madras.
61	10 » 16 41	(e.e.) I_{n}	II_{n}	— 0,97	+ 0,05	+ 0,10	— 0,05	Lick., Fl., Tac., AA., Harvard.
62	11 » 0 13	I_{n}	II_{n}	— 5,80	+ 0,32	+ 0,32	0,00	HK., P., Tokio.
63	11 » 15 26	III_{f}	$\mathrm{II}_{w.e.}$	— 9,46	+ 0,25	+ 0,43	— 0,18	Lick., Fl., Tac., AA., Harvard.
64	12 » 9 54	III_{f}	I_{n}	+ 0,14	— 0,03	+ 0,01	— 0,04	Grw., Pulk., Kasan, La Pl., Rio.
65	12 » 10 0	II_{f}	I_{n}	+ 0,04	— 0,38	+ 0,12	— 0,50	Grw., Pulk., Kasan, La Pl., Rio.
66	12 » 10 41	III_{f}	II_{f}	+ 0,58	— 0,10	— 0,13	+ 0,03	Grw., Pulk., La Pl., Rio.
67	13 » 3 38	III_{f}	II_{f}	+ 9,32	— 0,55	— 0,45	— 0,10	Taschk., Madr., HK.
68	13 » 19 31	I_{n}	II_{n}	+ 5,89	— 0,33	— 0,25	— 0,08	We., Lick., Fl.
69	14 » 4 29	I_{n}	II_{n}	+ 0,10	— 0,05	+ 0,02	— 0,07	Taschk., Madras.
70	14 » 8 57	III_{n}	IV_{n}	+ 15,17	— 0,87	— 0,75	— 0,12	Grw., Pulk., Rio.
71	14 » 13 46	e.e. $\mathrm{I}_{(w.e.)}$	II_{n}	— 5,93	+ 0,32	+ 0,33	— 0,01	Tac., AA., Harv., La Pl., Rio.
72	15 » 9 48	I_{f}	IV_{n}	+ 5,59	— 0,32	— 0,29	— 0,03	Grw., Pulk., Kasan, La Pl., Rio.
73	15 » 22 59	II_{f}	IV_{f}	— 0,18	— 0,06	— 0,02	— 0,04	Perth, To., Wi.
74	15 » 23 7	II_{f}	I_{n}	— 0,09	— 0,06	+ 0,02	— 0,08	Perth, To., Wi.
75	16 » 11 59	I_{f}	IV_{n}	— 5,69	+ 0,30	+ 0,24	— 0,54	Grw., La Pl., Rio.
76	17 » 9 4	I_{n}	II_{n}	+ 5,75	— 0,31	— 0,23	— 0,08	Grw., Pulk., Kasan, La Pl., Rio.
77	17 » 11 22	III_{n}	IV_{n}	— 14,82	+ 0,80	+ 0,70	+ 0,10	Grw., Pulk., La Pl., Rio.
78	17 » 16 9	w. I_{n}	II_{n}	+ 1,22	— $0,08^{5}$	— 0,02	— $0,06^{5}$	Lick, Fl., Tac., AA., Harvard.
79	18 » 3 12	$\mathrm{I}_{(w.e.)}$	II_{n}	— 6,00	+ 0,32	+ 0,32	0,00	Taschk., Madras, HK.
80	18 » 20 36	III_{f}	II_{f}	— 8,935	+ 0,51	+ 0,41	+ 0,10	Wi., Wellington.
81	20 » 8 8	III_{f}	II_{f}	+ 9,57	— 0,56	— 0,45	— 0,11	Grw., Pulk., Kasan.

Physics. — *"Contribution to the knowledge of the ψ-surface of* VAN DER WAALS. XI. *A gas that sinks in a liquid."* By Prof. H. KAMERLINGH ONNES. Communication N°. 96 from the Physical Laboratory of Leiden.

If we have an ideal gas and an incompressible liquid without vapour tension, in which the gas does not dissolve, the gas will gather above the liquid under the action of gravity, if the pressure is sufficiently low, whereas the compressed gas will sink in the liquid if the pressure is made high enough.

I have observed a phenomenon approaching to this fictitious case in an experiment which roughly came to this, that helium gas was compressed more and more above liquid hydrogen till it sank in the liquid hydrogen. Roughly, for so simple a case as was premised is not to be realized. Every experiment in which a gas is compressed above a liquid, is practically an application of the theory of binary mixtures of VAN DER WAALS. In such an experiment the compressibility of the liquid phase and the solubility of gas and liquid inter se may not be neglected, as generally the pressure will even have to be increased considerably before the density of the gas-phase becomes comparable with that of the liquid phase.

If the theory of VAN DER WAALS is applied to suchlike experiments, the question lies at hand whether in the neighbourhood of the plaitpoint phenomena where gas and liquid approach each other so closely that of the ordinary gas and liquid state they have retained nothing but the name, perhaps on account of a higher proportion of the substance with greater molecular weight [1]) the phase, which must be called the gas phase, may become specifically heavier than the phase, which must be called the liquid phase. On closer investigation it appears however, to be due to relations between the physical properties and the chemical constitution (so also the molecular weight) of substances, that a liquid phase floating on a gas phase has not been observed even in this favourable region.

I was the more struck with an irregularity which I came across when experimenting with helium and hydrogen in a closed metal vessel, as I thought that I could explain it by the above mentioned not yet observed phenomenon, and so the conviction took hold of me, that at — 253° and at a pressure of 60 atmospheres the gaslike phase which chiefly consists of helium, sinks in the liquid phase which chiefly consists of hydrogen.

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[1]) The limiting case is that in the ψ-surface construed with the unity of weight the projection of the nodal chord on the xv-plane runs parallel to the line $x = 0$.

In order to ascertain myself of this I compressed by means of the mercury compressor described in Communication N°. 54 a mixture of about one part of helium and 6 parts of hydrogen in a glass tube, which had a capillary inflow tube at the top, and a capillary outlet tube at the bottom, and which was merged in liquid hydrogen. Up to 49 atmospheres the liquid hydrogen was seen to deposit from the gas mixture, bounded by a distinct hollow meniscus against the helium. At 49 atmospheres the helium, or properly speaking the gas phase consisting chiefly of helium, went down just as water through oil, and remained on the bottom as a large drop. With further compression to 60 atmospheres and decrease of pressure to 32 atmospheres the volume of the bubble appeared to follow the change of the pressure as that of a gas. At 32 atmospheres the bubble rose again. By changing the pressure the bubble was made to rise and descend at pleasure.

The closer investigation of these phenomena in connection with the isotherms of helium and the ψ-surfaces of H_2 and He is an extensive work, so that in anticipation of the results which most likely will be definitely drawn up only much later, I feel justified in confining myself to this sketchy communication.

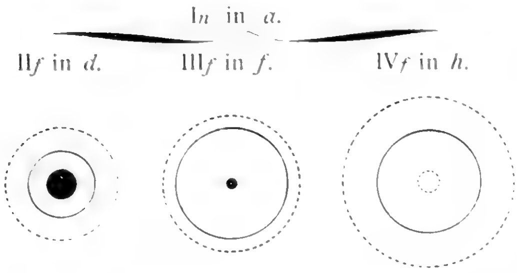
One remark may be added now. It appears that the b of helium must be small, from which follows again that a must have an exceedingly small value, because the critical temperature, if it exists, must lie very low. In this direction points also a single determination of the plaitpoint of a mixture of helium and hydrogen which I have already made. Whether a has really a positive value, whether it is zero, or whether (what is also conceivable) a is negative, will have to be decided by the determination of the isotherms of helium.

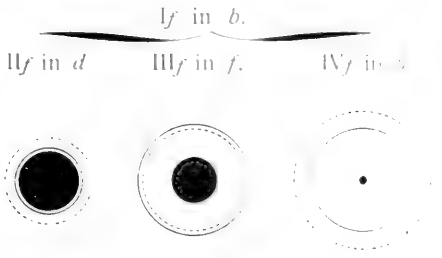
(December 21, 1906).

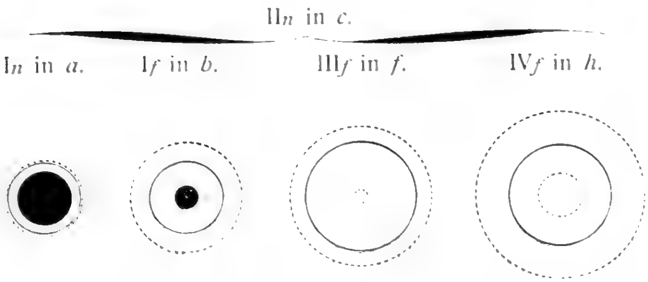
J. A. C. OUDEMANS. "Mutual occultations and eclipses of the satellites of Jupiter in 1908." Second part: eclipses.

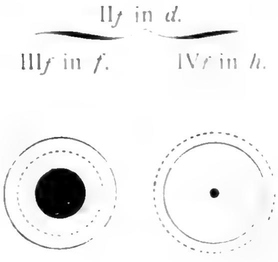
N. B. The continuous circles show the contour of the satellites, the dotted circles represent the penumbra.

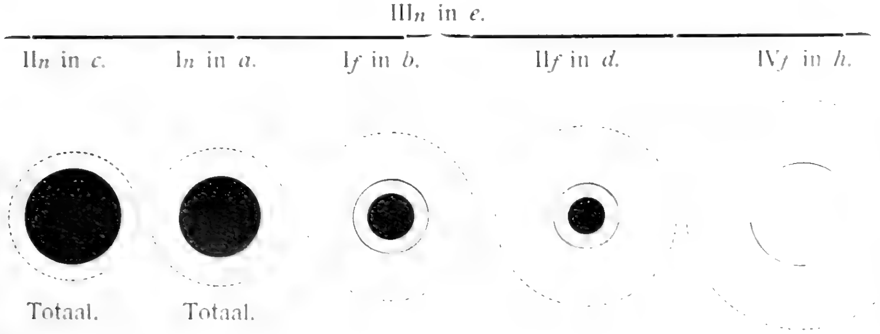
Scale 1 : 314 250 000. 12mm = 1" heliocentr.

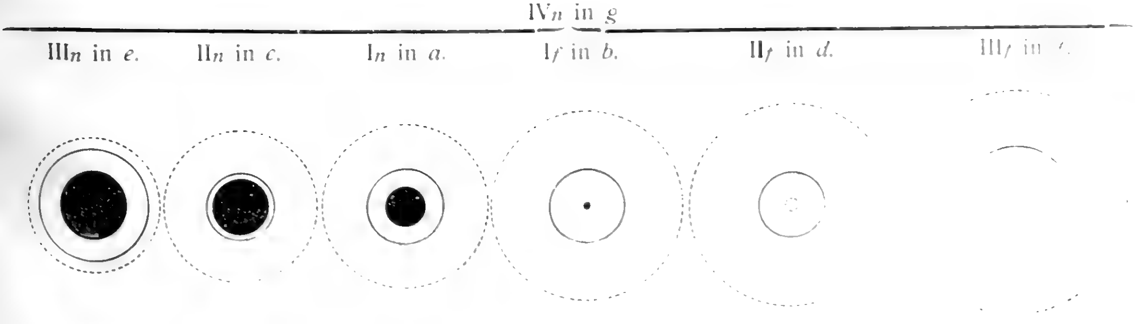












KONINKLIJKE AKADEMIE
VAN WETENSCHAPPEN
-:- TE AMSTERDAM -:-

PROCEEDINGS OF THE SECTION OF SCIENCES

VOLUME IX

(— 2ND PART —)

JOHANNES MÜLLER :—: AMSTERDAM
:═══════: JULY 1907 :═══════:

(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige
Afdeeling van 29 December 1906 tot 26 April 1907. Dl. XV.)

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday December 29, 1906.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 29 December 1906, Dl. XV).

CONTENTS.

Zoology. — *"On the fresh-water fish-fauna of New Guinea"*. By Prof. Max Weber.

(Communicated in the meeting of November 24, 1906).

In the year 1877 there appeared a "Quatrième mémoire sur la faune ichthyologique de la Nouvelle-Guinée", written by P. J. Bleeker and containing 341 species. These species are exclusively marine and brackish-water fishes and shew clearly, as might be expected, that the littoral fish-fauna of New Guinea belongs to the great Indo-Pacific fauna which extends from the East coast of Africa to the islands of the Western Pacific.

The same result is arrived at from the lists published by W. Macleay in 1876 and 1882, which treat of the fishes of the South coast of New Guinea and Torres Straits. But none of these lists accomplished what Bleeker desired, namely, to give some insight into the nature of the fresh-water fish-fauna of New Guinea. The information which Bleeker desired was partly supplied by certain communications, published by W. Macleay, E. P. Ramsay, J. Douglas Ogilby, A. Perugia and G. Boulenger, about fishes caught in the Strickland, Goldie and Paumomu rivers, and in a number of rivulets all situated in the south-eastern part of the island. The number of fishes mentioned amount to about 30, but so long as the fish-fauna of German and Dutch New Guinea remained unknown, it was impossible to give a complete idea of the ichthyological fauna of this big island.

This was the more to be regretted inasmuch as fresh-water fishes are of very great assistance in solving zoo-geographical problems. In using them for this purpose we should however keep well in mind the following points.

If in regions, at present separated by the sea, identical or closely allied fresh-water forms are found, to which the sea affords an insurmountable barrier, one may freely draw the conclusion that these regions were formerly either directly or indirectly connected. Among the fresh-water fishes there are however whole categories which cannot be used as factors in such an argument or only with great caution. These are the migratory fishes and those that can live also in brackish water and indeed even in sea-water.

The so-called law of E. von Martens states that from the Poles to the Equator the number of brackish water animals increases. This is also true for fishes and especially for those of the Indo-Australian Archipelago, and in a very remarkable degree for those of the islands east of Borneo and Java. The great Sunda Islands in consequence of their former connection with the continent of Asia possess a fish-fauna of which the most important elements, both as regards quality and quantity, had no chance of further distribution in an eastern direction. The rivers of the eastern islands of the Archipelago were therefore almost devoid of fishes, and offered a good place of abode for such forms as, though denizens of the sea or of brackish water, possessed sufficient capacity for accommodating themselves to a life in fresh-water. The competition of those Asiatic forms (Cyprinidae, Mastacembelidae, Ophiocephalidae, Labyrinthici etc.), originally better fitted for a fresh-water life, failing, everything was in favour of the immigrants from the sea. The river-fishes of Celebes favour this view, as also does all that we know about the fishes of Ternate, Ambon, Halmahera, etc.

We observe the same phenomenon in the fresh waters of Australia. These however contain also indigenous forms, partly very old, partly younger forms; the latter were obviously, at least in part, marine immigrants, which have accommodated themselves so entirely to a fresh-water life as to adopt the characters of fresh-water fishes.

The fauna of Australia enjoy at present a general and vivid interest — are there not even people who believe that the cradle of mankind stood there? A remarkable point of interest in the study of its fauna is the question how long Australia has been isolated from other parts of the globe. New Guinea plays a prominent rôle in answering this question.

It is therefore a welcome fact that the Dutch New Guinea Expedition of 1903 under the direction of Prof. A. WICHMANN has brought home, besides other treasures, a large collection of fishes from different lakes and many rivers and rivulets, giving us a good insight into the fresh-water fauna of the northern part of the island. It was of great help to me, while studying this collection, that I was able to make use of the fishes collected in the brackish water at the mouth of the Merauke river, by Dr. KOCH the medical man of the Royal Geographical Society's Expedition to South New Guinea. The results of this investigation will be published elsewhere, but some more general conclusions may be mentioned here.

When we reckon up all the fishes known up to the present date from the lakes, rivers, and rivulets of New Guinea, we find that their number amounts to more than 100 species, but only about 40 of these were found exclusively in fresh-water.

A careful examination shews further that the latter species, with a few exceptions, are either known from brackish or sea water at other places, or that their nearest relatives may be found in brackish or sea water. New Guinea shews clearly the fact that immigration from the sea or from brackish water has played and perhaps still plays a predominant part in the populating of its rivers.

Let us now return to the point at issue: namely, that the marine fish-fauna of New Guinea forms part of the great Indo-Pacific fish-fauna and particularly of that of the Indo-Australian Archipelago. Keeping this in mind one might be inclined to draw the conclusion that there is not much to be learned from the fauna of the rivers of New Guinea concerning the history of this island. Such a conclusion however would be erroneous, for it is clear that the very fishes which are characteristic of the fresh-water of New Guinea belong:

1. to genera which outside New Guinea are known only from Australia (Pseudomugil, Rhombatractus, Melanotaenia, Eumeda);

2. or to genera nearly related to exclusively Australian genera. Lambertia for instance is nearly related to Eumeda; Glossolepis to Rhombatractus and the three new species of Apogon are closely allied to Australian ones. Finally the species of Hemipimelodus from New Guinea form a special group, distinct from those of the neighbouring Indian Archipelago. Everything that gives to the fresh-water fish-fauna of New Guinea a character different from that of the Indian Archipelago is at the same time characteristic of Australia. Twelve of its species belonging to the genera Pseudomugil, Rhombatractus, Melanotaenia, Glossolepis, belong to the family or subfamily of the Melanotaenidae, only known from Australia. I do not hesitate therefore to maintain that the river-fishes of New Guinea belong to two groups:

1. A fluvio-marine group, which is Indo-Australian or, if one prefers, Indo-Pacific and which may also be met with, for instance, in Ambon or Celebes. To this category belongs also Rhiacichthys (Platyptera) novaeguineae Blgr. discovered by Pratt in mountain rivers of the Owen Stanley Range four thousand feet high. Boulenger speaks of the discovery of a fish of the genus Rhiacichthys "so admirably adapted to life in mountain torrents" as highly interesting. He tells us that the closely allied Rhiacichthys asper C. V. is known from Bantam, Celebes and Luzon. This is likely to create the impression that Rhiacichthys novaeguineae does not belong to this category, but is a species whose nearest relative is confined to rivers in regions occupied by the Asiatic fauna. Rhiacichthys asper however, differing but little from Rhiacichthys novaeguineae, was also found by Bleeker in Sumatra and, what is far more interesting, it occurs, according to Günther, also in Wanderer Bay on the island of Guadalcanar in the Solomon Islands — in "fresh-water". At all events it is thus found close to the sea. This

is also true for a specimen which I described from Ambon and still more so for a specimen that I caught near Balangnipa in the lower part of the Tangka, close to its mouth in the gulf of Boni. The water was here already brackish and ran slowly. Rhiacichtys has therefore a very wide distribution, it does not fear brackish water, and its presence in New Guinea loses therewith much of its importance.

2. The second group, the characteristic element, is Australian. This last group requires further explanation as to its origin. In the present state of things, now that New Guinea is separated from Australia by Torres Straits, these offer a barrier impassable to those fishes which I called characteristic. Some species of Rhombatractus and Melanotaenia may it is true, descend to the mouth of the river and be able to endure even slightly brackish water, but none of the 24 recorded species is known from the sea. The barrier can therefore not be bridged by the group of islands in the Torres Straits. They are too poorly supplied with fresh-water and far too strictly coral islands, even when we leave out of consideration the fact that they are separated from each other, from New Guinea and from Australia by broad tracts of sea with a high salt percentage and strong tidal currents. The simultaneous presence of these characteristic forms in New Guinea and in Australia cannot be explained otherwise than by the existence of a more solid and extensive connection in former ages. This connection must have been so far back in the past that, to take an instance, the representatives of the abovenamed Melanotaeniideae had time to separate themselves specifically. And this actually happened; for among the 12 species of Melanotaeniidae already known from New Guinea and among the 12 species described from tropical or sub-tropical Australia not one is common to the two regions, although the differences between some species are very small. On the other hand therefore it cannot have been so very long ago from a geological point of view that this connection between Australia and New Guinea existed. How long a time may have elapsed since that period is at present a matter of hypothesis. But if zoo-geographical and more particularly ichthyological experience may venture an opinion, I should seek the period of this connection not earlier than in the pliocene, and the breaking up of it in the pleistocene. Other zoological observations may perhaps be in favour of this supposition.

It will be a long time yet before the last word is spoken on this question. We may express the hope that the new expedition to Dutch Southern New Guinea under the guidance of Dr. H. A. Lorentz, which intends to investigate especially its big rivers, will bring us further light.

Chemistry. — *"On Lupeol"* [1]). By Dr. N. H. Cohen. (Communicated by Prof. P. v. Romburgh).

(Communicated in the meeting of November 24, 1906).

Notwithstanding the many and beautiful researches of several chemists, the structure of cholesterol, which is important also from a physiological point of view, is far from being known. Therefore, Prof. van Romburgh invited me to investigate a substance closely connected with the same, namely lupeol, a phytosterol. For the phytosterols may be included with the cholesterols in one common group "the cholesterollic substances". The original intention was to study the alstol found by Sack [2]) in "bresk" [3]). From the "bresk" investigated by me, alstol, alstonol and *iso*alstonol could not be isolated, although Sack claims to have found them in the same, but I obtained α- and β-amyrin and lupeol. It appeared afterwards that Sack's alstol is not a chemical individual.

Lupeol was first found by Likiernik [4]) in the skins of lupin seeds; afterwards Sack [5]) met with it in the bark of Roucheria Griffithiana, whilst van Romburgh and van der Linden [6]) demonstrated its presence as a cinnamate in the resin of Palaquium calophyllum. Finally, van Romburgh proved that Tschirch's [7]) crystal-albane simply consisted of lupeol cinnamate. The lupeol was prepared from "bresk" by extracting the same first with boiling alcohol. On cooling, a white mass was deposited which, without any further purification was saponified with alcoholic potassium hydroxide. The saponified product was then benzoylated with benzoyl chloride and pyridine and the reaction product treated repeatedly with acetone by heating just to boiling on the waterbath and then filtering off without delay.

Finally, a lupeol benzoate was left, which after repeated recrystallisation from acetone, consisted of fine, flat needles; m.p. 265°—266°, (corr. 273°—274°).

Found		Calculated for $C_{38}H_{54}O_2$
C	83.71—83.81	84.07
H	10.41—10.36	10.03

These, like all subsequent combustions, were made with lead chromate.

$$[\alpha]_D = + 60°,75 \text{ in chloroform.}$$

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[1]) For a more elaborate description see Dissertation N. H. Cohen. 1906, Utrecht.

[2]) Sack. Diss. 1901, Göttingen.

[3]) Bresk or djetulung is the dried milky juice of some varieties of Dyera.

[4]) Ztschr. f. physiol. Chem. **15**. 415 (1891).

[5]) Sack l. c.

[6]) Ber. **37**. 3440 (1904).

[7]) Arch. der Pharm. **241**. 653 (1903).

By saponification of lupeol benzoate with alcoholic potassium hydroxide and recrystallisation from alcohol or acetone, the lupeol was obtained in the form of fine, long needles m.p. 211°, (corr. 215°).

Found:					Calculated for $C_{31}H_{50}O$
C	84.62	84.65	84.40	84.50	84.85
H	11.78	11.93	11.82	12.02	11.49

$[\alpha]_D = + 27°,2$ in chloroform.

In the first place it seemed to me of importance to ascertain whether double bonds occur in lupeol. Therefore, a solution of lupeol in carbon disulphide was treated with a solution of bromine in the same solvent. Hydrogen bromide was evolved. By recrystallising the reaction product from methyl alcohol, needles containing 1 mol. of the latter are formed. The melting point of this substance, dried at 100°, was 184°, (corr. 185°).

Found:	I	II	III	IV	V	VI	VII	calc. for $C_{31}H_{49}OBr$.
C	72.14	72.30						71.90
H	10.26	10.07	Carius		Liebig			9.55
Br			14.48	14.50	15.40	15.07	14.67	15.45

$[\alpha]_D = + 3°,8$ in chloroform.

Most probably, a monosubstitution product had formed and I now tried to obtain an additive product of the benzoate. When dissolved in a mixture of glacial acetic acid and carbon disulphide and then treated with a solution of bromine in glacial acetic acid, it yielded, after spontaneous evaporation of the carbon disulphide, beautiful leaflets. On extracting this product with boiling acetone a less easily soluble substance was left, which proved to be a *monobromide*. After repeated recrystallisation from aethyl acetate, I obtained fine, thick crystals which when melting were decomposed. Placed in the bath at 240° it melted at 243°.

Found	I	II	III	IV	V	VI	VII	VIII	IX	X
C	72.62	72.90	72.58	72.46	72.59					
H	8.85	8.88	8.72	9.09	8.84	Carius			Liebig	
Br						13.14	13.04	12.97	13.40	13.01

Calculated $C_{38}H_{53}O_2Br$, $C = 73.38$, $H = 8.61$, $Br = 12.87$.

$[\alpha]_D = + 44°,9$ in chloroform.

The bromine atom is contained in the lupeol nucleus, because on saponification an alcohol containing bromine, and benzoicacid are formed.

The more readily soluble portion crystallises from acetone in beautiful leaflets. It is also a monobromide but could not with certainty be characterised as a chemical individual.

One of the means to trace the structure of a substance is the gradual destruction by oxidation.

The lupeol was, therefore, oxidised with the Kiliani mixture[1]. Lupeol dissolved in benzene was shaken with a weighed quantity of the oxidising liquid, 6 atoms of oxygen calculated for 1 mol. of lupeol. Titrations of the oxidising liquid with potassium iodide and sodium thiosulphate showed, that after six hours one atom of oxygen had been consumed and as the amount of chromic acid did not diminish any further, this one atom had been taken up quantitatively. The oxidation product, which crystallised from alcohol in beautiful, thick needles, melted at 169° (corr. 170°) and proved to be a *ketone*, to which I gave the name of *lupeon*.

Found							Calc. for $C_{31}H_{48}O$
	C		84.95	84.91	85.07	84.76	85.24
	H	11.64	11.81	11.62	11.61	11.59	11.09

$[\alpha]_D = + 63^\circ,1$ in chloroform.

Dr. Jaeger was kind enough to examine the crystalform of the lupeon. It belongs to the rhombo-bipyramidal class. A complete description will appear elsewhere.

With hydroxylamine an oxime of the lupeon was obtained, which is but little soluble in alcohol.

Recrystallised from ethyl acetate, it forms white, soft, light needles, which are decomposed when melting. Placed in the bath at 278°, they melt at 278°,5.

Found			Calc. for $C_{31}H_{48}NOH$
C	81.98		82.41
H	11.44	with lead chromate	10.94
N		3.08	3.11

$[\alpha]_D = + 20^\circ,5$ in chloroform.

Bromine dissolved in glacial acetic acid added to a solution of lupeon in the same solvent gave hydrogen bromide and a dibromide, which was deposited from the acid. Recrystallised from a mixture of benzene and glacial acetic acid it consisted of beautiful, hard needles, which were decomposed when melting. Placed in the bath at 253° the melting point was 254°.

Found	I	II	III	IV	V	VI	VII	VIII	IX	X
C	62.31	62.71	62.50	62.30						
H	8.13	8.26	8.05	8.06	Carius		Liebig			
Br					26.88	26.91	27.08	26.85	27.35	27.23

Calc. for $C_{31}H_{46}OBr_2$, C = 62.58, H = 7.80, Br = 26.90.

$[\alpha]_D = + 21^\circ,4$ in chloroform.

When dissolved in ether, lupeon gave with hydrogen cyanide under the influence of a trace of ammonia a cyanohydrin, which

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[1] Ber. **34**. 3564 (1901).

after some time deposited in the form of beautiful, thick needles. This substance is decomposed at a higher temperature and also on melting. Placed in the bath at 192°, it melts at 194°. By collecting the hydrogen cyanide liberated on heating in aqueous potassium hydroxide and then titrating with silver nitrate I determined the nitrogen content.

Found:	I	II	III	IV	V	VI	VII	calc. for $C_{32}H_{49}ON$
C	82.63	82.76						82.86
H	11.25	11.26						10.66
			copper oxide		lead chromate	titrated		
N			3.92	3.94	3.30	2.87	2.70	3.03

One mol. of cyanohydrin gave, with one mol. of ethyl alcohol and one mol. of hydrogen chloride, a substance, which, when placed in the bath at 230°, melted at 235°; as shown by a combustion, this was not, however, the expected ethyl ester of the corresponding acid. This substance has not been investigated further.

Lupeol benzoate treated in the same manner as lupeol with the KILIANI mixture was not affected. Lupeon dissolved in benzene and stirred with the mixture for four hours at 40° also remained unaltered.

By the action of chromic anhydride on lupeon at a higher temperature, acid products were formed, which could not be obtained in a crystalline state.

The neutral oxidation product of lupeol with potassium permanganate and sulphuric acid consisted of a mixture, which could be separated only with extreme difficulty. Excepting lupeon no well-defined substance could be isolated from it. As SENKOWSKI [1]) had obtained phthalic acid from cholic acid by oxidation with alkaline permanganate, I treated 23 grams of lupeol in the same manner, but it suffered complete destruction. This fact does, therefore, *not* favour the idea of a *benzene nucleus* in lupeol.

By the oxidation of an acetic acid solution of lupeol acetate with chromic acid, I obtained a product which, on analysis, gave figures which agree satisfactorily with the calculated values for $C_{33}H_{52}O_4$.

Placed in the bath at 285° it melted at 295° to a dark brown mass.

In alcoholic solution this substance did not turn blue litmus red, not even on diluting with water, but still it could be titrated very readily with alcoholic potassium hydroxide, phenolphtalein being used as an indicator. Assuming that one mol. consumes one mol. of KOH the titrations pointed to a molecular weight of 521 and 524, the formula $C_{33}H_{52}O_4$ representing 512,5.

Found:	C	77.59	77.23	76.87	77.24	calculat. for $C_{33}H_{52}O_4$ 77.28
	H	10.75	10.49	10.09	10.79	10.23

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[1]) Monatsh. f. Chem. **17.** 1 (1896).

On saponification with alcoholic potassium hydroxide a substance was obtained which crystallised from ether in needles. Placed in the bath at 260°, the melting point was 263—265°. In regard to litmus this substance behaves like the unsaponified product, but it may be again titrated with alcoholic potassium hydroxide and phenolphthalein. From these titrations the molecular weight was found to be 452 and 461 ; the formula C_{31} H_{50} O_3 represents 470,5.

Found: C 78.42 78.61 calculated for C_{31} H_{50} O_3 79.08
H 11.07 11.05 10.71

The potassium compound of this substance is soluble, with difficulty, in alcohol, and crystallises from this in needles.

On treating either the saponified or the unsaponified oxidation product the same compound was obtained, which seems to be a diacetylated substance. The results of the combustions, however, were not very concordant, but I have not been able to account for this.

Found: C 75.39 74.71 75.67 74.96 74.47 calcul. for C_{35} H_{54} O_5 75.75
H 10.12 10.16 10.51 10.24 9.81

By boiling with excess of alcoholic potassium hydroxide and titrating with alcoholic sulphuric acid the molecular weight was found to be 549, assuming that the molecule contains two acetyl groups. The formula C_{35} H_{54} O_5 represents 554.5.

It is desirable to investigate more closely these oxidation products, which are so important in the study of lupeol, before trying to explain their formation.

Lupeol is not reduced by metallic sodium and boiling amyl alcohol; whereas lupeon is reduced by sodium and ethyl alcohol to lupeol. Therefore, if lupeon should possess a double bond, this is sure not to be in $\alpha\beta$-position in regard to the carbonyl group.

Neither lupeol, nor lupeol acetate dissolved in boiling acetone are acted upon by potassium permanganate. This behaviour does not agree with the theory of a double bond, but the presence of the latter in lupeol and lupeon could be satisfactorily demonstrated by means of Hübl's iodine reagent. On the other hand the oxidation product C_{32} H_{52} O_4 no longer seemed to contain the double bond. On the strength of various combustions and bromine determinations, particularly of dibromolupeon, I consider C_{31} H_{50} O to be the most likely formula for lupeol. The formula C_{26} H_{42} O given by Likiernik 1) and Sack 2) is certainly not correct.

Utrecht, Org. Chem. Lab. University.

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1) Likiernik l. c.

2) Sack l. c.

Chemistry. — *"On α- and β-amyrin from bresk"* [1]. By Dr. N. H. Cohen. (Communicated by Prof. Van Romburgh).

(Communicated in the meeting of November 24, 1906).

Communications as to β-amyrin, which is present as acetate in "bresk" or "djelutung" have already been presented (These Proc. 1905, p. 544). Since then, I have prepared also β-amyrin cinnamate. This crystallises from acetone in small needles, which melt at 236,°5 (corr. 241°).

In addition to β-amyrin and lupeol another substance was obtained from "bresk", which proved to be identical with the α-amyrin found by Vesterberg.

This substance crystallises from alcohol in long, slender needles; m.p. 185° (corr. 186°). Vesterberg gives the melting point as 181—181°,5.

Found:	C	84.22	84.30	calculated for $C_{30}H_{50}O$	84.43
	H	11.91	12.02		11.82

These, like all subsequent combustions have been made with lead chromate.

$[\alpha]_D = +82°,6$ in chloroform; in benzene was found $[\alpha]_D = +88°,2.$ [2].

For the purpose of characterisation, different esters were prepared from α-amyrin.

α-Amyrin acetate was obtained by heating with acetic anhydride and sodium acetate. Recrystallised from alcohol it forms needle-shaped leaflets; m.p. 220—221°, (corr. 224—225°). Vesterberg gives the melting point as 221°.

Found:	C	81.85	82.27	81.79,	calculated for $C_{32}H_{52}O_2$	81.98
	H	11.34	11.40	11.33		11.19

$[\alpha]_D = + 75°,8$ in chloroform.

α-Amyrin benzoate was obtained with the aid of benzoyl chloride and pyridine. From acetone it crystallised in long, prismatic needles; m.p. 192°, (corr. 195°). According to Vesterberg it melts at 192°.

α-Amyrin cinnamate, which has not yet been described was obtained like the benzoate. When recrystallised repeatedly from acetone it forms small hard needles which melt at 176,5—177°, (corr. 178°).

Utrecht. Org. Chem. Lab. Univ.

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[1] For a more elaborate description see, Diss. N. H. Cohen. 1906, Utrecht.

[2] Vesterberg found in benzene $[\alpha]_D = + 91°,6$.

Chemistry. — "*On substances, which possess more than one stable liquid state, and on the phenomena observed in anisotropous liquids.*" By Dr. F. M. JAEGER. (Communicated by Prof. FRANCHIMONT).

§ 1. The compounds now investigated belong to the series of fatty cholesterol-esters, which were the subject of a recent communication [1]). They are intended to supplement the number of the synthetic esters, studied previously and include: *Cholesterol-Heptylate, Nonylate, Laurate, Myristate, Palmitate* and *Stearate.* The *Palmitic* ester, as is well known, is also important from a physiological point of view, as it occurs constantly in blood-serum accompanied by the *Oleate* m.p. (43° C.) [2]).

I have prepared these compounds by melting together equal parts by weight of pure cholesterol and fatty acid, and purifying by fractional crystallisation from mixtures of ether and alcohol, or ethyl acetate and ether. The details will be published later on in a more elaborate paper in the "Recueil". The substances were regarded as pure, when their characteristic temperature-limits and the typical transformations occurring therein, remained the same in every particular, even after another recrystallisation, whilst also the solid phase, when examined microscopically, did not appear to contain any heterogenous components.

Most of these esters were obtained in the form of very flexible, tabular crystals of great lustre and resembling fish-scales; some of them, such as the *heptylate* and the *laurate,* crystallise in long, hard needles.

The investigation showed, that most of these esters of the higher fatty acids possess *three stable liquid phases.* Whereas, in the first terms of the series one at least of these anisotropous phases was *labile* in regard to the isotropous fusion, all three are now *stable* under the existing circumstances, although sometimes definite, irreversible transitions may still occur. It is a remarkable fact, that the stearate again exhibits an analogy with the lower terms, as it appears that only labile liquid-anisotropous phases may occur, or else none at all. A relation and similarity between the initial and final terms

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[1]) F. M. JAEGER, These Proc. 1906; Rec. d. Trav. d. Chim. d. Pays-Bas, T. XXIV, p. 334—351.

[2]) K. HÜRTHLE, Z. f. physiol. Chem. **21**. 331. (1895); The blood serums of: man, horse, ox, sheep, hog and dog were investigated.

of the homologous series is plainly visible here. In what follows there will be described, firstly, the thermic, and then the microscopic behaviour of these substances.

§ 2. **The Thermometric Behaviour of these Substances.**

Cholesterol-Laurate exhibits the following phenomena: The isotropous fusion L of this substance has still, at 100° the consistency of glycerol, and gradually thickens on cooling. At 87°.8 C. ($= t_3$) there suddenly occurs a peculiar violet and green opalescence of the phase, which commencing at the surface, soon embraces the whole phase. The still transparent thin-jelly-like mass quite resembles a coagulating colloidal solution; the opalescence is analogous to that often noticed in the separation of two liquid layers.

As the cooling proceeds, the opalescence colours disappear and the mass gradually becomes less transparent and also more liquid. It is then even thinner than the isotropous fusion L. This doubly-refracting liquid A now solidifies at 82°.2 C. ($= t_1$) to a crystalline mass S, accompanied by a distinct heat effect.

If, however we start with the solid phase S and subject the same to fusion, the behaviour is apparently quite different. The substance softens and yields after some time a thick doubly-refracting mass, which will prove to be identical with the phase A. On heating further the viscosity decreases, and at about 86° it becomes very slight. There is, however, no sign of opalescence this time. The turbid mass may be heated to over 90°, without becoming clear and now and then A seems as if solid particles are floating in the liquid phase. At 90°.6 C. ($= t_5$) everything passes into the isotropous fused mass L. The microscopical investigation shows, that between A and L another stable, less powerfully refracting liquid phase B is now traversed, and that, owing to retardation occurring, the phase S may be kept for a few moments adjacent to L, when A and B have already disappeared.

This is therefore, a case where a substance may be heated a few degrees above its actual melting point without melting.

It should, however, be observed that the order of the temperatures is here quite irreconcilable with the phenomena considered possible up to the present, with homogenous substances; the temperature of 90°.6, at which these crystals disappear in contact with L finds no place in the p-t-diagram of Fig. 1. Such a position of the said temperatures might be possible, when the system could be regarded as containing two components, for instance, if there was question of *tautomeric* forms which are transformed into each other with finite velocities. I think it highly probable that in all these substances, "phenomena of retardation" play a great rôle; moreover the enormous undercooling which the phase *A* can undergo without transformation, proves this satisfactorily in the majority of these esters.

The different behaviour of the laurate on melting and on cooling the fused mass is so characteristic, that no doubt can be entertained as to the irreversibility of each series of transformations. Fuller details will be given below in the micro-physical investigation.

§ 3. *Cholesterol-Nonylate* forms at 90° an isotropous fused mass of the consistency of paraffin oil; on cooling to 89°5 a stable, greyish, doubly-refracting liquid *B* appears which, gradually thickening, passes into a second strongly doubly-refracting liquid phase *A*, — which transformation is accompanied with a brilliant display of colours. All three liquids are, however, quite stable within each specific temperature-traject. On melting, as well as on cooling the substance, they succeed each other in the proper order.

The viscous, strongly doubly-refracting, liquid phase *A* now becomes more viscous on cooling, and is finally transformed into a horny, transparent mass which exhibits no trace of crystallisation. Even after some hours, the often still very tenacious mass has not got crystallised. In the case of this substance it is therefore impossible to give the solidifying point or the exact temperature at which the heated mass begins to melt. The reason of this is, that the doubly refracting liquid *A* can be undercooled enormously and passes gradually into the solid condition without crystallising.

As the micro-physical research has shown, a spherolite-formation occurs afterwards suddenly in the mass, which ultimately leads to the complete crystallisation of the substance.

The velocity, with which such spherolites are formed appeared in some cases not to exceed 0.000035—0.000070 m.m. per second!

§ 4. *Cholesterol-Myristate*, at 80°, is still an isotropous, paraffin oil-like liquid. On cooling, it gradually becomes viscous; at about 82.°6 the glycerol-like phase then turns, with violet-blue opalescence, into a thick, strongly doubly-refracting mass *A* which, gradually assuming a thicker consistency, is finally converted into a horny mass, without any indication of a definite solidifying point. In this respect the substance is quite analogous to the previous one. On the other hand, on being melted, it behaves more like the laurate, in so far as it is converted into a double-refracting liquid *B*, before passing completely into *L*. The transition temperature cannot be determined sharply, but I estimate it at about 80°.

§ 5. *Cholesterol-Palmitate* at 80° is a clear, isotropous liquid as thick as simple syrup. On cooling, the isotropous phase is converted at 80° with green opalescence into a fairly clear, transparent, doubly-refracting jelly *A*, which rapidly assumes a thinner consistency, and becomes at the same time more turbid, and finally solidifies at 77.°2, with a perceptibte caloric effect, to a crystalline mass *S*. In this case also, a doubly-refracting phase *B* appears to be traversed when the mass is being melted, before the occurrence of the isotropous fusion *L*; I estimate the transition temperature at about 78°.

§ 6. With *Cholesterol-Stearate,* I did not succeed in demonstrating the occurrence of a doubly refracting liquid. The isotropous, thick-fluid fusion solidifies at 81° to well-formed crystals *S*.

§ 7. *Cholesterol-Heptylate* exhibits, in undercooled fusion only, one doubly-refracting liquid phase which is labile in regard to the solid phase *S*. The compound behaves, thermically, analogously to the caprylate. The temperature of solidification is at 110.°5, the transition-temperature of the labile doubly-refracting phase lies a little lower.

Of *Cholesterol-Arachate,* I could only obtain an impure product on which no further communications will be made. The ester could not be purified properly as it is not soluble to any extent in the ordinary solvents. The crude substance obtained does not seem to exhibit any anisotropous liquid phases.

§ 8. **Micro-physical behaviour of these substances.** If a little of the pure solid *cholesterol-laurate* is melted on an object glass to an isotropous, clear liquid *L*, and the same is allowed to cool very slowly, there is formed, usually, a very strongly doubly-refracting, liquid phase, gleaming with lucid interference colours. It consists of large, globular drops, which exhibit the black axial cross and, on alternate heating and cooling, readily amalgamate to a syrupy, highly coloured, but mainly yellowish-white liquid. This phase will be called *A* in future. On cooling, it gradually thickens, until no more movement of the mass is noticed, which continues to exhibit a granular structure. Around this mass an isotropous border liquid is found. At first I felt inclined to look upon this tenaceous, isotropous mass, which is visibly different from the fusion *L*, as a distinct phase differing from the fusion *A*. But on using a covering glass and pressing the same with a pair of pincers, or by stirring with a very thin platinum wire, I found that this border liquid is only "pseudo-isotropous" (LEHMANN) and is, in reality, not different from *A*; only, the optical axes of the liquid crystals are all directed perpendicularly to the glass-surface. The other cholesterol-esters also exhibit this phenomenon. On further cooling, this phase *A* crystallises like the pseudo-isotropous border to a similar mostly spherolitic crystalline mass *S*.

Between the spherolites one often sees currents of the pseudo-isotropous border liquid.

If now the entire mass is allowed to solidify to *S*, and then again is melted carefully, it is at once transformed into the liquid *A*, recognisable by its high interference colours and its slow currents. Then, there appears suddenly a new, greyish liquid *B*, consisting of smaller individuals with a less powerful double refraction, which after a short time is replaced suddenly by the isotropous fusion *L*. If *L* is now cooled again, it is *A* which appears at once and *not* the phase *B*.

Only a very feeble, greyish flash of light, lasting only for a moment, points to a rapid passing of the phase *B*; it cannot, however, be completely realised now. On further cooling, *S* is formed suddenly, sometimes in plate-like crystals. When once crystallisation has set in, *S* will not melt when the mass is heated, as might have been expected, but actually increase in size of the crystals occurs, and the velocity of crystallisation is now many times increased. It must be remarked that the growing flat needles of *S* drive before them, at their borders, the liquid phase *A* amid violent currents. If the heating is now continued a little longer, we may notice sometimes, that whilst the little plates of *S* remain partly in existence, *A* passes first into the grey phase *B*, which then is converted into the isotropous mass *L*. We then have adjacent to *L* the solid phase *S*, *which therefore, may be heated above its melting point*, before disappearing finally into the isotropous fusion *L*.

All this shows, that the *laurate* possesses *three stable liquid phases* and also that the isotropous fusion being coled, *B* is always passed over, but is realised when the solid phase is heated. All this is represented in the annexed *p-t*-diagram; the arrows, therefore, indicate the order of the phases traversed on melting and on cooling. The phase *A* in its quasi-immovable period may be kept a long time solid at the temperature of the room, and may be considerably undercooled before it passes into *S*. Notwithstanding its apparently solid appearance in that undercooled condition, *A* is still a tenaceous, thick liquid, as I could prove by stirring the mass with a thin platinum wire.

The point (t_3) agrees with the *opalescence* which occurs when

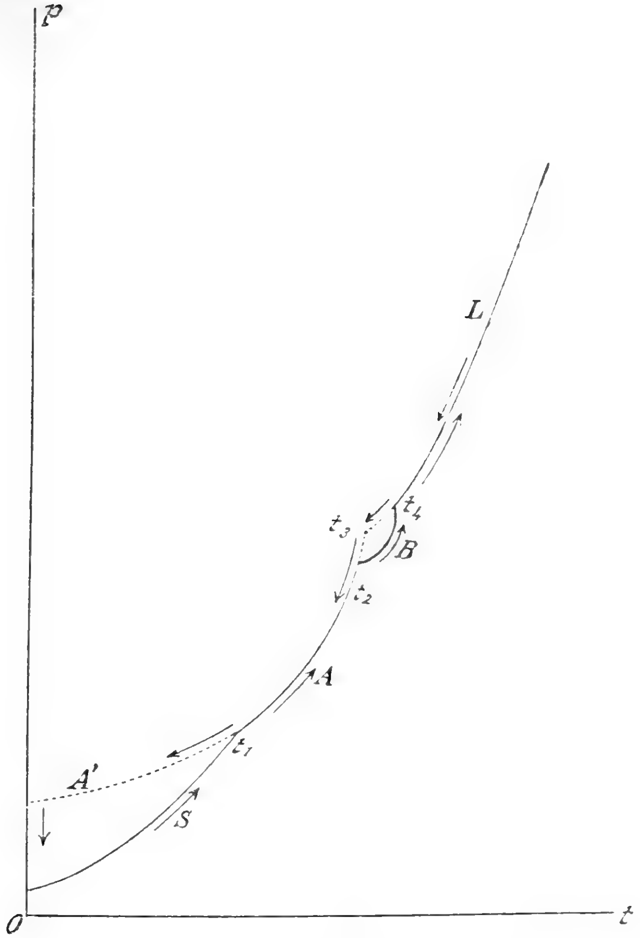

Fig. 1. Schematic p-t-diagram for Cholesterol-Laurate.

the isotropous fusion is cooled; this indicates, therefore, the moment *where the stable phase B is replaced by the as yet still less stable phase A*, which will soon afterwards be the more stable one: a fact which may be perhaps important in the future for the explanation of the analogous phenomena observed in the *separation of two liquid layers* and *the coagulation of a colloidal solution.*

Indeed, the transition at (t_3) presents quite the aspect of a gelatinising colloidal solution. The temperature of this transition point may be determined, but not sharply, at 87°.8. The temperature at which, when the solid substance melts, the liquid may be still kept turbid, owing probably to the presence of the meta-stable plate-like crystals of S, was determined at 90°.6: the solidifying temperature (t_1) lies at 82°.2.

That the border liquid, obtained by cooling the isotropous fusion L, differed from L itself, could be demonstrated in more way than one. By heating and cooling we may get so far that, apparently, nothing more of A is visible, but that we have only the border liquid, which on cooling, crystallises immediately to S. Occasionally, the doubly-refracting individuals of A turn up in the mass for a moment to disappear again immediately. However, that isotropous liquid thus obtained is nothing else but A itself, when owing to the temperature variations, all individuals have, like magnets, placed themselves parallel with their (optical) axes and the whole has, consequently, become pseudo-isotropous. This same phenomenon also occurs with the other esters, for instance very beautifully with the nonylate and the myristate. The difference between these pseudo-isotropous phases and the isotropous fused masses L of these substances, is shown by the fact that the pseudo-isomorphous mass of A, and also the doubly-refracting portion of the same has a very thick-fluid consistency; the isotropous fusion L of the laurate has a consistency more like that of glycerol.

As regards the solid phase and its transformation into the liquid condition, it cannot be proved in this case that there exists a continuous transformation between the last solid partic lesand the first anisotropous ones. From the velocity, with which the diverse phases usually make room for each other in the microscopic examination, one would feel inclined to believe just the opposite. The thermic observation of the transformation, which generally exhibit only insignificant caloric effects, would, however, make the observer feel more inclined to look upon the matter as an uninterrupted concatenation of more or less stable intermediate conditions, which I have observed previously with *cholesterol-cinnamylate.* A somewhat considerable heat effect occurs in some cases in the crystallisation of the solid phase only; in all other phases the exact transition temperature cannot be determined accurately by the thermic method.

§ 9. *Cholesterol-Nonylate* exhibits microscopically the following phenomena:

Starting from the crystallised substance, this was fused first on an object glass to an isotropous liquid L. On cooling a greyish doubly-refracting liquid phase B appears, which, at a lower temperature, makes room for a very tenaceous, strongly doubly-refracting, mostly yellowish-white phase, A. This phase A is often surrounded by an isotropous border; if pressure is applied to the covering glass or if the mass is stirred with a very thin platinum wire, this isotropous liquid appears to be identical with *A*, and to be pseudo-isotropous by homoeotropism only. The optical axes of the doubly-refracting modification *A* again place themselves perpendicularly on the surface of the covering glass. On continued cooling *A* becomes increasingly thicker: at last a movement in the mass can be seen only on stirring. After a longer time there are formed from numerous centres in this tenacious mass thin, radiated spherolites, whose velocity of growth is but very small. When a number of these spherolites have formed and the mass is then heated carefully, the spherolites do not melt, but actually *increase* owing to the greater crystallisation-velocity. Soon afterwards — however, they melt, on further heating, to the doubly-refracting phase *A*, *where the circumferences of the spherolites and the black axial crosses are preserved for some time;* so that the whole much resembles a liquid mozaic. Subsequently the phase *B* reappears and afterwards the isotropous fusion *L*. The whole series of phases is traversed in a *reversible* manner; the liquid phase *A*, however may be so much undercooled, that a proper melting or solidifying point of the substance cannot be given. In larger quantities of the substance, the crystallisation does not set in till after some hours, and the substance turns first to a horny mass, which always remains doubly-refracting to finally exhibit local, white spots, from which the spherolite-formation slowly spreads through the entire mass. One would feel inclined to call this transformation of liquid-anisotropous into crystallised substance a *continuous one*, if it were only possible to observe, even for a moment, the intermediate conditions in that transition. As the matter cannot be settled by direct experiment, the transition must be put down, provisionally as a *discontinuous one*.

In this case also, and the same applies to the other cholesterol-esters as well, the *spherolite-structure* of the solid phase is of great importance for this entire transformation of undercooled, anisotropous-liquid condition into the solid one. At the end of this communication I will allude briefly to a few cases from which the particular significance of the spherolite-structure in the transitions between anisotropous-liquid and anisotropous solid phases is shown also plainly in a different manner.

§ 10. *Cholesterol-Palmitate* behaves in quite an analogous manner: I observed one solid phase and three liquid conditions *A*, *B* and *L*: as in the case of the laurate, *B* is generally observed only on warming. The succession of the liquid and solid phases takes place, however comparatively rapidly, so that a real solidifying point may be observed, which has also been proved by the thermic research. The solid phase crystallises in broad flat needles, when fused and then solidified in conglomerated spherolites. On melting, the thick, doubly-refracting liquid A is mostly orientated in regard to the previous solid spherolites.

§ 11. *Cholesterol-Stearate* could not be obtained in a doubly-refracting liquid form: the isotropous fusion always crystallises immediately amid rapid, rotating movements, to small needles, which often consist of a conglomeration of rosettes. It is possible that labile anisotropous phases are formed, owing to strong undercooling or by addition of some admixture [1]).

§ 12. *Cholesterol-Myristiate* lends itself splendidly to the experiment. It behaves mainly in the same manner as the *laurate*; the phase B can only be observed on heating, but not on cooling the isotropous fusion L. Most brilliant is the formation of large, globular crystal-drops of the modification A, also the colour-zone which precedes the formation of A from L, on cooling. This phase A also exhibits the phenomenon of pseudo-isotropism in a particularly distinct form. On the other hand, an important difference between this compound and the laurate is the much smaller velocity with which, on cooling, the spherolites S are formed from A; in this respect the compound exhibits more similarity with the nonylate. Sometimes it may be observed readily how in the phase A, which consists of an enormous number of linked, globular crystal-drops, which all exhibit the black cross of the spherolite crystals, centrifugal current-lines are developed from a number of points in the mass, along which the crystal-drops range themselves. After the lapse of some time those doubly-refracting globules are seen to disappear, while the current-lines have now become rays of the spherolite. Here again, the question arises whether the transformation of the doubly-refracting liquid globules, which are orientated along the current-lines, into the true spherolite form, does not take place continuously, and whether we do not speak of a *sudden* transformation merely because we are not able to observe the stadia traversed in this transformation.

The liquid globules of the phase A themselves exhibit much similarity with a kind of liquid spherolites; a few times, I have even been able to observe such "liquid spherolites" of greater dimens-

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[1]) Prof. Lehmann informed me recently that the stearate possesses indeed two labile, anisotropous liquid phases.

ions, which rapidly solidified to solid spherolite crystals. In the case of this compound also, one feels convinced that there must exist a very intimate relation between the spherolite-formation of a substance and its power of forming anisotropous liquid phases: on the nature of this relation, I hope to make a communication later on.

It may, however, be observed, provisionably that in all transformations: liquid ⇄ solid, where serious "phenomena of retardation" may occur, the undercooling, or superfusion, for instance is generally abrogated amid a differentiation of the phase into spherolites. All the cholesterol-derivatives, mentioned in this paper, exhibit this spherolite-formation. In the case of *α-phytosterol-propionate*, I have been able to show, that a complex of a large number of doubly-refracting microscopic spherolites may imitate the optical peculiarities of the liquid phases in process of separation and of the colloidal opalescence. This might lead to the strengthening of the previous conception of the colloidal solidification as a separation-phenomenon of labile liquids.

§ 13. *Cholesterol-Heptylate* contains only *labile* liquid anisotropous phases. It exhibits great similarity with the caprylate described previously: I have only a few times been able to obtain one single thick-fluid phase *A* from the undercooled isotropous fusion *L*. The solid phase crystallises rapidly and in beautiful flat needles, which exhibit high interference colours. On warming, the substance readily migrates towards the colder parts of the object glass.

§ 14. In conclusion, I will communicate a few more points as regards some phenomena, which prove plainly the significance of the spherolite structure for with these questions.

Some time ago, I published a research on the fatty esters from *Phytosterol* from Calabar-fat and stated how they all are wont to crystallise in the spherolite-form from their cooled, isotropous fused mass, while anisotropous liquid phases are *not* observed therein, with the exception of the *normal valerate* which possesses a thick-fluid anisotropous modification, and exhibits the phenomenon of the changeable melting point, which again becomes normal on long keeping: a fact also observed in the case of a few fatty glycerol-esters. Since then, WINDAUS has proved that the phytosterol, extracted from Calabar fat is a mixture of two isomorphous phytosterols, which cannot be separated by crystallisation. Being engaged in preparing the pure fatty esters from the principal of those two phytosterols, namely the *α*-compound (m.p. 136°), I discovered that the fused *propionate* of *α-phytosterol* (m.p. 108°), when cooled rapidly in cold water, exhibited the most brilliant interference-colours, which is also the case with the cholesterol esters (acetate for instance), which possess *labile* anisotropous liquid phases. The thought naturally at once occurred, to attribute these phenomena to the appearance of liquid crystals in the now *pure* α-phytosterol-ester. A similar behaviour was also shown by perfectly pure *α-phytosterol-acetate*, but with a much less display of colours. It was, however, a remarkable fact, that *α-phytosterol-propionate* even after complete solidification *still retained those colours for an indefinite length of time*, particularly at those sides of the testtube, where the layer of the substance was thinner and had cooled rapidly.

The microscopic investigation now showed that these two substances exhibit extremely rapidly disappearing anisotropous liquid phases or, more probably, *none at all*[1]); but that *the said colour-phenomenon is caused by a very peculiar spherolite-structure.*

In what follows, I have given the description of the solidifying phenomena of the *α-propionate*, and also a figure representing the typical structure of the fused and then cooled compound, such as is present at the coloured sides of the tube.

Fig. 2.

If a little of the solid substance is fused on a slide to an isotropous liquid the following will be noticed on cooling. The mass solidifies completely to spherolites, namely to a conglomeration of circular, concentrically grouped figures, which appear connected with a series of girdles. When three spherolites meet, they are joined by means of straight lines which inclose angles of about 120°.

The mass is slightly doubly-refracting and of a greyish colour; the rings and girdles are light greyish on a darker back-ground. Each spherolite exhibits besides a concentric structure, the black cross, but generally very faint. The whole resembles a drawing of polished malachite from the Oeral, or of some polished agates.

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[1]) Whereas the *phytosterol*-esters from Calabar fat which, of course, contain a definite amount of the β-homologue, exhibit *no* liquid crystals, the pure α-esters commencing with the butyrate [or perhaps the propionate] did show this phenomenon. This discovery is a powerful argument against the remarks often made in regard to the *cholesterol*-esters, that the remarkable phenomena described are attributable to an admixture of homologous cholesterols. Foreign admixtures prevent as a rule these phenomena altogether: in any case they are rather spoiled than improved.

The walls of the test-tube or the object-glass, which exhibit the said colour-phenomena, have that same structure, but with this difference, that the globular, concentrically deposited spherolites have much smaller dimensions and lie much closer together. Each little spherolite has also a cross; this however, is not dark, but coloured with yellow and violet arms. The spherolite is also coloured in the alternate circle-quadrants.

This ensemble of small, coloured spherolites is the cause of the said brilliant colour-phenomena; they are quite analogous to those which are wont to appear in the case of liquid crystals and remain in existence for an indefinite period. Each of them exhibits one or generally two luminous points in the centre; they exhibit a strong circular polarisation and are left-handed. The whole appears between crossed nicols as a splendid variegated mozaic of coloured cellular parts. The size of each individual is 0.5—1 micron.

The acetate also exhibits something similar, but the spherolites are built more radial and the whole is not at all so distinct.

I hope to contribute more particulars as to these remarkable phytosterol-compounds shortly. I have mentioned them here merely to show the importance of this structure-form for the optical phenomena, observed in the anisotropous phases.

Zaandam, 14 November 1906.

Chemistry. — "*On irreversible phase-transitions in substances which may exhibit more than one liquid condition.*" By Dr. F. M. Jaeger. (Communicated by Prof. Franchimont).

(Communicated in the meeting of November 24, 1906).

§ 1. The fatty esters of *a-Phytosterol* from *Calabar*-fat, which the Phytosterol mostly occurring in the vegetable kingdom, and which has also been isolated from rye and wheat under the name of "sitosterol", exhibit very remarkable properties in more than one respect.

In my previous communication, I alluded briefly to the colour phenomena and the spherolite-structure in the *propionate* and the *acetate*. In the latter I could not observe anisotropous liquid phases: in the former a doubly-refracting phase is discernible just before melting, but it lasts too short a time to allow the accurate measurement of the temperature-traject.

With the following four terms of the series, however, these phenomena are more distinct, and occur under conditions so favourable as could hardly be realised up to the present in the other known substances. They also exhibit enormous phenomena of retardation in their diverse transitions and often a typical irreversibility thereof, of which I will now communicate some particulars.

§ 2. **Thermometrical behaviour of the fatty α-phytosterol-esters.**

A. α-Phytosterol-n.-Butyrate, on very slowly raising the temperature, melts at 89°.5 to a turbid, doubly-refracting liquid *A*, which at first is very viscous but rapidly becomes thinner and is converted, at 90°.6, into a clear isotropous fusion *L* of the consistency of glycerol.

On cooling the same carefully, the thermometer falls gradually while the isotropous liquid thickens more and more but remains quite clear. At 80° the whole mass crystallises all at once to small crystals *S* with so great a caloric effect that the thermometer goes up to 85°. There is no question now of anisotropous liquid phases at all. These two experiments may be repeated at will but always with the same result. As to the nature of the turbid phase, compare "micro-physical behaviour".

If the isotropous fusion is suddenly cooled in cold water, a bluish-grey coloration appears and a soft, doubly-refracting mass is obtained, which does not become crystalline until after a very long time.

B. α-Phytosterol-Isobutyrate, when treated in the same manner, melts at 101°.4 to a glycerol-like, turbid, doubly-refracting liquid *A*, which gradually assumes the consistency of paraffin-oil and is converted at about 103°.2, apparently continuously, into a clear fusion *L*.

If this is cooled, it certainly becomes gradually thicker but it still remains quite clear and isotropous.

At 80°.4 it becomes turbid and doubly-refracting; this phase is identical with *A*, and it has the consistency of glycerol; at 73° it has become as thick as butter, and at 66° the thermometer can be moved only with difficulty, whilst it may now be drawn into sticky, doubly-refracting threads. At 65° the thermometer suddenly goes up to 68°.8 and the mass crystallises in long, delicate needles *S*.

On rapid cooling of the fused mass, this is converted into a turbid, greasy looking, doubly-refracting mass, which crystallises but very slowly; no colour-phenomena occur.

C. α-Phytosterol-n.-Valerate melts, when in the crystallised condition, at an *uncertain* temperature. At about 48°, the substance commences to soften visibly, at 54° its consistency is that of thick butter, at 80° it is somewhat thinner, at 85° it is actually liquid, but still turbid and doubly-refracting. *All these transformations proceed quite* *continuously*. At about 97.°5 the liquid is clear and isotropous; it has then the thickness of paraffin-oil.

If, however, the isotropous fused mass is cooled, the isotropous paraffin-oil-like liquid remains clear to about 87.°3, when a turbid doubly-refracting phase is formed. This, on further cooling, gradually becomes more viscous; at 80° it is as thick as butter, at 66° it can hardly be stirred, and may be drawn into threads. It may be cooled to the temperature of the room without solidifying. It remains in this condition for hours, but after 24 hours it has again become crystalline. The substance, therefore, has no determinable melting or solidifying point.

D. α-Phytosterol-Isovalerate behaves quite analogously to the *n*-valerate. Neither a definite melting point, nor a solidifying point can be observed. The mass softens at about 45°, is anisotropous thick-fluid at 65°, and becomes clear and isotropous at 81°.

On cooling to 78.°1, a beginning of turbidity is noticed, the liquid gradually becomes thicker and is converted at an uncertain temperature into a tenacious sticky, doubly-refracting mass, which after 24 hours has again solidified to a crystalline mass.

§ 3. The thermometrical behaviour of these remarkable substances is represented in the annexed schematic *p-t*-diagram, for the case of the *n-butyrate* and *isobutyrate*. The typical irreversibility of these phenomena is thus seen at once. Moreover in the case of the two valerates, the whole behaviour can be described only as a real, *gradual* transformation, solid $\rightleftarrows$ liquid with an intermediate realisation of an indefinite number of optically-anisotropous liquids.

§ 4. **The micro-physical behaviour of the fatty α-phytosterol esters.** Perhaps, there are no substances known, which exhibit under the microscope the characteristic phenomena of anisotropous liquids in so beautiful and singular a manner as these esters; in this respect the isobutyrate and the valerate excel in particular. In the normal butyrate, the traject, where the liquid crystals are capable of existence is rather too small. For this reason, although the behaviour of the four substances differs in details, I will describe more particularly the behaviour of the *n*-valerate and as to the others, I will state occasionally in what respect they differ from the valerate. In consequence of the totally different circumstances which the microscopic method involves, nothing more is seen of the thermically observed peculiar irreversibility and even progression of the transformations. For the study of the nature of the diverse phase-transformations, the

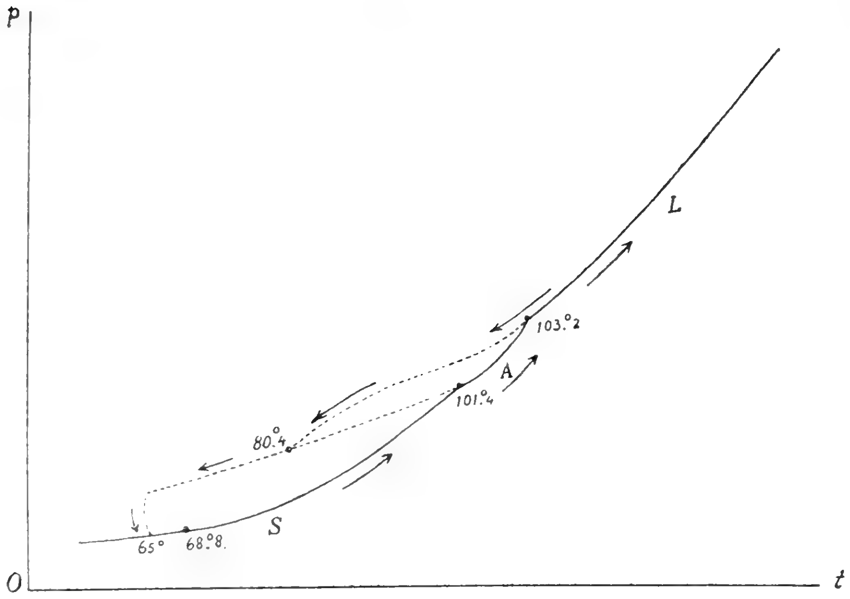

Fig. 1. Schematic p-t-diagram for α-Phytosteryl-Isobutyrate.

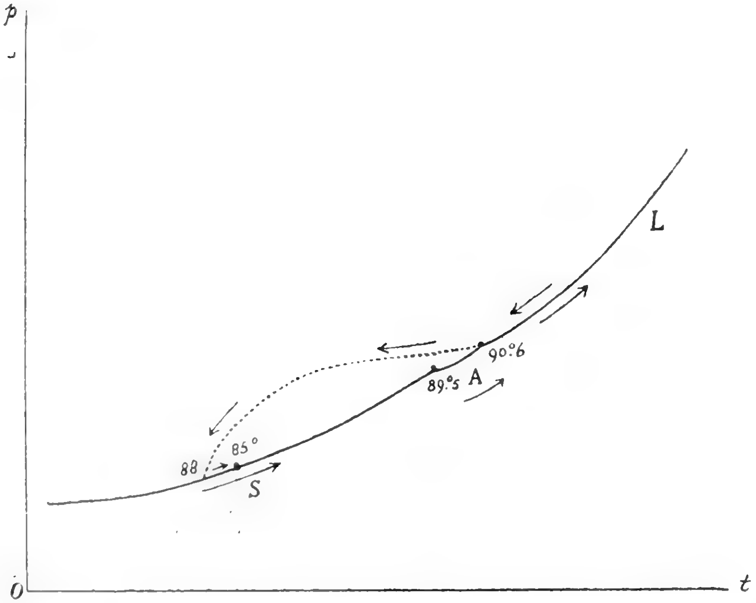

Fig. 2. Schematic p-t-diagram for α-Phytosteryl-n-Butyrate.

thermometric method is certainly preferable to the microscopic one, because in the latter, the delicate changes in temperature cannot be controlled so surely as in the first method. For this reason, the phase-transformations, when observed microscopically, convey the impression of being more *sudden* than in the thermic observation.

Still, the microscope completes the task of the thermometer in a manner not to be undervalued, at it gives an insight into the structure of the diverse phases and allows one to demonstrate their difference or their identity.

§ 5. If a little of the beautifully crystallised *n-valerate* is carefully melted on an object glass, the substance, at a definite temperature changes, apparently suddenly, into an aggregate of an enormous number of globular, very large and strongly doubly-refracting liquid-drops, which all exhibit the black cross of the spherolites [1]) but can flow really all the same. This condition may be rendered permanent for a long time at will. But they may also amalgamate afterwards to larger, plate-like, highly coloured liquid individuals, somewhat resembling sharply limited crystals. These are frequently multiplets of liquid drops; the demarcations between the separate individuals vary constantly by changes in temperature.

The isotropous border of the mass is very striking. By pressure or by moving the covering glass, also by the sliding currents which we can induce herein by changes in temperature, it may be readily shown that this isotropous border, owing to a parallel orientation of the liquid individuals, is only pseudo-isotropous and really identical with the rest of the phase. Sometimes one may succeed even in communicating this pseudo-isotropous aspect to the entire mass [2]) by

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[1]) We can, however, often observe a slanting projection of the optical symmetry axis, which gives the same impression as if we look perpendicularly to one of the optical axes of a biaxial crystal, or on a monoxial crystal cut obliquely to the optical axis. We observe at the same time coloured rings which exhibit an elliptic form. It is very remarkable that, when the phase has become very viscous on cooling, these ellipsoidal drops, provided with rings and slanting but mutually parallel-directed axes may be kept for a long time in an apparently immobile condition in the midst of the pseudo-isotropous or double-refracting liquid. They place themselves mutually like little ellipsoidal magnets.

However, I could observe, that these drops are often not quite ellipsoidal, but that they are sharply broken a little at the one side, just there, where the optical axis is slanting. By turning the object-table, the axial point turns in the same direction as the table, while the black line or cross is preserved. (Added in the English translation Januari 1907).

[2]) The anisotropous-liquid phase has, in the case of the two valerates, an extraordinary tendency to place itself in this pseudo-isotropous condition. We can observe this, because the border of the drop often moves inward with widening of the isotropous-looking line. It is also remarkable to see how the flowing crystals when meeting an air bubble arrange themselves close together, normally on the border thereof.

often repeated warming followed by rapid cooling. This substance is about the best known example of this phenomenon.

§ 6. If now we go on heating very cautiously, the larger flowing crystals and also the smaller drops situated between them are seen to move about rapidly; the larger individuals, which consist mostly of twins or quadruplets, are split up into a multitude of globular drops and these, together with the smaller ones, disappear at a definite temperature entirely in the isotropous liquid, which is now isotropous in *reality*. The globules of the liquid rotate to the right and the left under distortion of the mass, as may be observed from the spiral-shaped transformation of the black cross. Sometimes, before the mass becomes isotropous we may notice a temporary aggrandisement of the plate-like flowing crystals at the expense of the smaller interjacent globules; a result of the momentarily increased crystallisation-velocity due to heating.

§ 7. On cooling the isotropous fusion this is first differentiated into an infinite number of the double-refracting liquid globulus, which here and there amalgamate to the more plate-like flowing crystals. On further cooling, these latter individuals remain in existence notwithstanding the undercooling, while the little globules in the meanwhile unite to the same kind of plate-like individuals. This aggregate, brilliant in higher interference colours becomes in course of time thicker and thicker in consistency while the aggregation, owing to an apparent splitting, becomes more and more finely granulated. But even after the lapse of some hours, the phase remains anisotropous-liquid as may be easily proved by shifting the mass and by the pseudo-isotropous border, which commences to exhibit delicate, double refracting current-lines. In the end when the pseudo-isotropous liquid has passed like the remainder into the same, almost completely immobile aggregation of doubly-refracting individuals, it is, gradually, transformed after a very long time into an aggregate of plates and spherolite-like masses, which possess a strong double refraction.

§ 8. If, after the lapse of some hours, the partially or completely solidified mass is melted cautiously, we sometimes succeed, in the case of the two *valerates*, in keeping the crystals of the phase S (therefore the *solid* crystals) for a few minutes near the isotropous fusion L at a temperature above the highest transition point. This phenomenon is, therefore, again quite homologous to that first observed by me with *cholesterol-laurate* and which might be described as a *heating of a solid substance S above its melting point without fusion taking place.* For the present, at least according to existing ideas, this behaviour can only be explained by assuming the presence of a two-component-system with tautomeric transformations subject to a strong retardation.

When the isotropous fusion L which has scarcely cooled to a few doubly-refracting drops is melted cautiously, we may observe sometimes that where a moment before the strongly luminous, yellowish-white globules were visible, there are now present greyish globules showing the black cross, which gradually decrease in size and also darken, to disappear finally as (isotropous ?) little globules in the isotropous fusion [1]). This phenomenon, in connection with those of crystallised ferric chloride to be described later, and with similar phenomena observed with the cholesterol esters appears to me to have great significance for the theory of the formation of liquid crystals.

§ 9. Finally, there is something to be observed as to the separation of *α-Phytosterol-valerate* from organic solvents. The substance may be obtained from ethyl acetate + a little alcohol in beautiful, hard, well-formed little crystals. If, however, the saturated *cold* solution in ethyl acetate is mixed with much acetone (in which the substance is but sparingly soluble) the liquid suddenly becomes a milky-white emulsion which deposits the compound *not* as a fine powder, but in the form of a *doubly-refracting, very thick and very sticky liquid.*

I have repeated this precipitation in a hollow object glass under the microscope. The emulsion consists of a very great number of doubly-refracting, globular liquid-globules, which are either moving about rapidly in the liquid, or, when united to larger masses, are quite identical with the ordinary anisotropous phase A, when this is cooled to the temperature of the room. These little globules all exhibit the cross of the spherolites, and the doubly-refracting liquids. They soon become solid and then form small needles and spherolitic aggregations. It may be easily proved by stirring that the globules deposited first are liquid; moreover, the doubly-refracting masses often communicate with each other by means of very narrow, doubly-refracting currents, while they often exhibit the phenomena of pseudo-isotropism.

Therefore, we have evidently obtained here the liquid-anisotropous

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[1]) Before that happens, we may sometimes see here the globules becoming enlarged to multiplets by amalgamation there larger ones being changed into smaller ones, sometimes here one disappearing in the liquid while very close by new individuals appear.

phase A from a solution by rapid precipitation at the temperature of the room, and that in isolated drops! A few other phytosterol esters exhibit analogous phenomena which I will describe later on in a more elaborate communication on these substances.

§ 10. A very remarkable fact in the *n-valerate*, the *iso-valerate* and the *isobutyrate*, is the differentiation of the isotropous fusion into a large number of globular, doubly-refracting liquid drops of considerable dimensions, which like the circles of fat on soup float alongside and over each other and often unite to multiplets, whose separate parts are still recognisable. Wreathed aggregations of the liquid globules are also observed occasionally. In most cases the separate liquid globules exhibit the black cross and the four luminous quadrants grouped centrically. They are, however, also seen to roll about frequently, so that the projection of the optical symmetry axis now takes place excentrically. Owing to the enormous size of the individuals and the low temperature-limits, these esters lend themselves to the study of these phenomena certainly VORLÄNDER'S *p*-azoxybenzoic-ethylester.

If the temperature of the mass, when totally differentiated into liquid globules — and the *isobutyrate* is particularly adapted for this differentiation — is slightly raised, the liquid globules are often seen to disappear suddenly just after they have enlarged their limits as it were by an expansion. It is like a soap-bubble bursting by over blowing.

§ 11. Finally, I wish to observe that the thermical transitions just described and particularly those of the two *valerates*, can only be interpreted by assuming a quite continuous progressive change. For all these gradual transformations. either on melting or on solidifying. a measurable time is required and nowhere is to be found any indication of a sudden leap. An exception is, however, afforded by the sudden crystallisation of the two *butyrates*.

§ 12. As regards the differentiation of the fusion L into an aggregate of anisotropous liquid globules, I will now make a communication as to an experiment upon the crystallising of *ferric chloride hexahydrate*, which substance exhibits something similar, and which, like most undercooled fusions and like many compounds which exhibit liquid crystals, crystallises in typical spherolites.

If we melt the compound $Fe_2Cl_6 + 12\,H_2O$ cautiously in a little tube, taking care that no water escapes, and a drop of this brownish-red fusion is put on an object glass, it may be left for hours at the temperature of the room without a trace of crystallisation being noticed. The liquid is now greatly undercooled and exists in a state of metastable equilibrium. For all that, it has the same chemical composition as the solid phase from which it was formed.

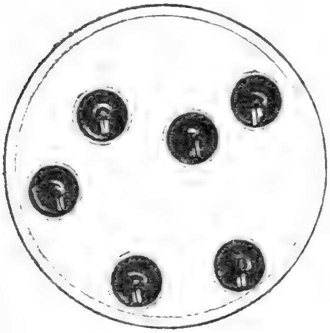

Fig. 3*a*.

On prolonged exposure, *small liquid globules* appear locally in the fairly viscous mass, probably owing to local cooling, or by a spontaneous evaporation of water at those points. These liquid globules are quite isotropous and are surrounded by a delicate aureole having an index of refraction different from that of the rest of the liquid (fig. 3*a*). The observation shows that, optically, they are, practically, no denser than the liquid, and from the fact that they afterwards become, *in their entirety*, a spherolite of the hexahydrate, we must conclude that their chemical composition does not differ from that of the fused mass.

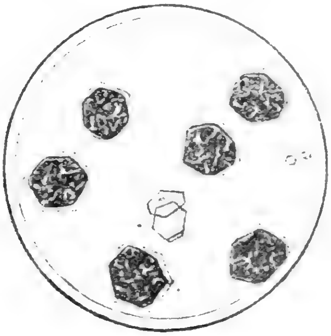

Fig. 3*b*.

These globules of liquid are converted gradually into doubly-refracting masses whose section is that of a regular hexangle with rounded off angles; individual crystals are not yet visible in the doubly-refracting mass and the luminous zone around still appears to exist (fig. 3*b*).

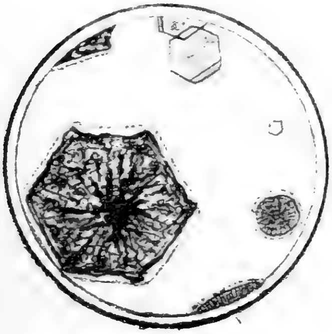

Fig. 3*c*.

Here and there, hexangular, sharply limited, very small plate-shaped crystals are also seen to form in the liquid without previous formation of liquid globules [1]). In the end, the doubly-refracting hexangular mass gets gradually limited by more irregular sides, while a greater differentiation of the mass into light and dark portions points to a crystallisation process commencing and progressing slowly.

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[1]) These may, however, be formed perhaps owing to the presence of traces of sal ammoniac.

Finally, we can observe a *spherolite* of the hexahydrate with a radial structure which now grows centrifugally to the large well-known semi-spheroidal spherolites of ferric chloride (fig. 3*c*).

§ 13. This experiment proves that the abrogation of the metastable condition, or at all events of a liquid condition which is possible under the influence of *phenomena* of retardation may happen owing to the formation of *spherolites which are preceded by the differentiation of the fusion into an aggregate of liquid globules.* True, the latter are here isotropous in contrast with the phytosterol esters just described, but the anisotropism of the latter liquids may be caused also by factors which are of secondary importance for the apparently existing connection between: metastability of liquid conditions, their abrogation by spherolite formation and the possible appearance of liquid globules as an intermediate phenomenon. I will just call attention to the fact that if we set aside a solution to crystallise with addition of a substance which retards the crystallisation, this will commence with the separation of originally isotropous liquid globules, so-called globulites, which BEHRENDS and VOGELSANG commenced to study long time ago.

All this leads to the presumption that the formation of the anisotropous liquid phases as aggregates of doubly-refracting liquid globules may have its origin in a kind of *phenomena* of retardation, the nature of which is still unknown to us at the present. Before long, I hope to revert again to this question.

Zaandam, 21 Nov. 1906.

Physics. — "*Some additional remarks on the quantity H and* MAXWELL'S *distribution of velocities.*" By Dr. O. POSTMA. (Communicated by Prof. H. A. LORENTZ).

§ 1. In these proceedings of Jan. 27th 1906 occur some remarks by me under the title of: "Some remarks on the quantity *H* in BOLTZMANN'S Vorlesungen über Gastheorie".

My intention is now to add something to these remarks, more particularly in connection with GIBBS' book on Statistical Mechanics [1]), and a paper by Dr. C. H. Wind: "Zur Gastheorie" [2]).

In my above-mentioned paper I specially criticised the proofs given

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[1]) J. WILLARD GIBBS "Elementary Principles in Statistical Mechanics", New-York, 1902.

[2]) Wien. Sitzungsber. Bd. 106, p. 21, Jan. 1897.

by BOLTZMANN and JEANS that MAXWELL's distribution of velocities in a gas should give the most probable state, and demonstrated that they wrongly assume an equality of the probabilities a priori that the point of velocity of an arbitrary molecule would fall into an arbitrary element of the space.

The question, however, may be raised whether it would not be possible to interpret the analysis given by BOLTZMANN and JEANS in a somewhat different way, so that avoiding the incorrect fundamental assumption, the result could all the same be retained. And then this proves really to be the case. When the most probable distribution of velocities is sought from the ensemble of equally possible combinations of velocities with equal total energy, we make only use of the fact that the different combinations of velocities *are* equally possible, how they have *got* to be so is after all of no consequence. Or else, it had not been necessary to occupy ourselves with the separate velocities of the molecules and make an assumption as to them.

This way of looking upon the matter is of exactly the same nature as that constantly followed by GIBBS in his above-mentioned work. GIBBS treats in his book all the time instead of a definite system, an ensemble of systems of the same nature and determined mostly by the same number of general coordinates and momenta $(p_1 \ldots p_n, q_1 \ldots q_n)$, which he follows in their general course. Such an ensemble will best illustrate the behaviour of a system (e.g. a gas-mass), of which only a few data are known and of which the others can assume all kinds of values. He calls such an ensemble *micro-canonical* when all systems, belonging to it, have an energy lying between E and $E+dE$ and for the rest the systems are uniformly distributed over all possibilities of phase or uniformly distributed over the whole *extension-in-phase* the energy of which lies between E and $E+dE$. When the energy of a gas-mass is given (naturally only up to a certain degree of accuracy) we should have reason according to GIBBS to study the microcanonical ensemble determined by this energy, and to consider the gas-mass as taken at random from such an ensemble. The extension-in-phase considered is thought to be determined by $\int dp_1 \ldots dq_n$; but in the case of a gas-mass with simple equal molecules this is proportional to

$$\int dx_1\, dy_1\, dz_1 \ldots dx_n\, dy_n\, dz_n,\, d\dot{x}_1\, d\dot{y}_1\, d\dot{z}_1 \ldots d\dot{x}_n\, d\dot{y}_n\, d\dot{z}_n,$$

so that we may say that every combination of velocities and configuration is of equally frequent occurrence in the ensemble.

It is now easy to see that when the energy is purely kinetic the same cases occur in such an ensemble, *with regard to the distribution of velocities,* as are considered as equally possible cases by BOLTZMANN and JEANS. The difference in the way of treatment of GIBBS on one side, and that of BOLTZMANN and JEANS on the other consists besides in the fact that the one occupies himself with separate velocities and the other not, in this that GIBBS treats the configuration and the distribution of velocities at the same time (both belong to the idea phase), whereas JEANS treats the latter separately, and BOLTZMANN does not occupy himself with the configuration in this connection.

Every phase of BOLTZMANN (combination of velocities) corresponds with as many phases of GIBBS (combination of velocities and configuration) as the molecules can be placed in different ways with that special combination of velocities. This number being the same for every combination of velocities according to the independence of the distribution of velocities and configuration following from the fundamental assumption, it will be of no consequence, comparing the different combinations of velocities inter se, whether we also take the configuration of the molecules into account or not. So when seeking the most probable distribution of velocities (that, with which the most combinations of velocities coincide), we must arrive at the same result whether we follow GIBBS or BOLTZMANN.

It is obvious that the phases of the microcanonical ensemble meant here are what GIBBS calls the specific phases. GIBBS distinguishes namely between specific and generic phases: in the former we consider as different cases those where we find at the same place and with the same velocity, other, even though quite equal molecules, in the latter we do not. In other words: in the former we consider also the individual molecules, in the second only the number of the molecules. So we may now say that in such a microcanonical ensemble the most probable distribution of velocities and that which will also occur in the great majority of cases (compare JEANS' analysis discussed in the first paper) will be that of MAXWELL. When therefore an arbitrary mass of gas in stationary state may be considered as taken at random out of such a microcanonic ensemble, MAXWELL's distribution of velocities or one closely resembling it will most probably occur in it. In this way a derivation of the law has been obtained to which the original objection no longer applies, though, of course, the assumption of the microcanonical ensemble remains somewhat arbitrary ¹).

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¹) With the more general assumption of a *canonical* ensemble MAXWELL's law is derived by LORENTZ: "Abhandlungen über Theoretische Physik", Lpzg. 1906 I, p. 295.

Finally the question might be raised, when we want to consider the separate velocities, whether it is possible to arrive at the equally possible combinations under discussion on another supposition a priori about the chances of every value for the velocity than the one indicated by BOLTZMANN and JEANS. The supposition must of course be such, that the chance is independent of the direction of the velocity, so that the chance of a velocity c, at which the point of velocity falls into a certain element of volume $d\xi d\eta d\zeta$, may be represented by $f(c) d\xi d\eta d\zeta$. When we moreover assume that the probabilities for the different molecules are independent of each other, the probability of a certain combination of velocities is proportional to $f(c_1) f(c_2) \dots f(c_n)$, and this must remain the same when the kinetic energy L, or because the molecules are assumed to be equal, Σc^2 remains the same. For every change of c_k and c_l into c'_k and c'_l, so that $c^2_k + c^2_l = c'^2_k + c'^2_l$, must $f(c_k) \cdot f(c_l) = f(c'_k) \cdot f(c'_l)$. This is an equation which frequently occurs in the theory of gases, from which follows $f(c) = ae^{bc^2}$. As a special case follows from this: $f(c) = a$, i. e. the assumption of BOLTZMANN and JEANS, that the probability a priori would be equal for every value of the velocity.

§ 2. In the second place I wish to make some remarks in connection with the proof that BOLTZMANN gives in his "Gastheory", that for an "ungeordnetes" gas with simple suppositions on the nature of the molecules in the stationary state MAXWELL's distribution of velocities is found. Dr. C. H. WIND shows in his above-mentioned paper that in this BOLTZMANN makes a mistake in the calculation of the number of collisions of opposite kind. BOLTZMANN, namely, assumes, that when molecules whose points of velocity lie in an element of volume $d\omega$, collide with others whose points of velocity lie in $d\omega_1$, so that after the collision the former points lie in $d\omega'$ and the latter in $d\omega_1'$, now the elements of volume $d\omega$ and $d\omega'$, $d\omega_1$ and $d\omega_1'$ would be equal, so that now $d\omega' d\omega'_1 = d\omega\, d\omega_1$. He further assumes that when molecules collide whose points of velocity lie in $d\omega'$ and $d\omega_1'$, they will be found in $d\omega$ and $d\omega_1$ after the collision. These last collisions he calls collisions of opposite kind. WIND now shows that this assumption is untrue; $d\omega$ is not $= d\omega'$, $d\omega_1$ not $= d\omega'_1$, nor even $d\omega d\omega_1 = d\omega' d\omega_1'$, except when the masses of the two colliding molecules are equal[1]).

Further the points of velocity of colliding molecules which lay in $d\omega'$ and $d\omega_1'$, do not always get to $d\omega$ and $d\omega_1$ after collision,

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[1]) I point out here that even then it is not universally true, but only when the elements of volume $d\omega$ and $d\omega_1$ have the shape of rectangular prisms or cylindres whose side or axis has the direction of the normal of collision.

so that another definition is necessary for collisions of opposite kind, viz. such for which the points of velocity get in $d\omega$ and $d\omega_1$ after the collision. WIND proves further that the number of collisions of opposite kind is all the same represented by the expression which BOLTZMANN had found for it.

It is then easy to change (what WIND does not do) the proof given by BOLTZMANN in § 5 of his "Gastheory", that Maxwell's distribution of velocities is the only one possible, in such a way that it is perfectly correct. But the error in question makes itself felt all through BOLTZMANN's book. Already with the proof of the *H*-theorem given in more analytical form in a footnote to § 5 we have some difficulty in getting rid of this error.

We meet the same thing when the molecules are treated as centres of force, and when they are treated as compound molecules. At the appearance of the second volume of his work, BOLTZMANN had taken notice of WIND's views, but the inaccurate definition for collisions of opposite kind has been retained [1]).

In connection with this error, made by BOLTZMANN in a geometrical treatment of the phenomena of collision, is another error of more analytical nature, so that also JEANS, who treats the matter more analytically, gives a derivation which in my opinion is not altogether correct. Though preferring the geometrical method, BOLTZMANN repeatedly refers to the other [2]). The method would then consist in this, that the components of the velocities after the collision $\xi'\eta'\zeta'\xi'_1\eta'_1\zeta'_1$ are expressed by $f(\xi\eta\zeta\xi_1\eta_1\zeta_1)$ and then by means of JACOBI's functional determinant $d\xi'd\eta'd\zeta'd\xi'_1d\eta'_1d\zeta'_1$ is expressed in $d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1$. We find then that here this determinant is $=1$ and so

$$d\xi'd\eta'd\zeta'd\xi'_1d\eta'_1d\zeta'_1 = d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1 \text{ or } d\omega' d\omega'_1 = d\omega d\omega_1 .$$

The number of collisions of opposite kind $= f'F'_1 d\omega' d\omega'_1 \sigma^2 g \cos \vartheta d\lambda dt$ according to BOLTZMANN, and so also $= f'F'_1 d\omega d\omega_1 \sigma^2 g \cos \vartheta d\lambda dt$. In this the mistake is made, however, that $d\xi'd\eta'd\zeta'd\xi'_1d\eta'_1d\zeta'_1$ the volume in the space of 6 dimensions that would correspond with the volume $d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1$ before the collision, is thought as bounded by planes such as $\xi' = c$, which is not the case. JEANS too equates the products of the differentials, in which according to him, $d\xi' \ldots d\zeta'_1$ being arbitrary, the $d\xi \ldots d\zeta$ must be chosen in such a way, that the values of $\xi' \ldots \zeta'_1$ calculated by the aid of the functions $\xi' = f(\xi \ldots \zeta_1)$ etc. fall within the limits fixed by $d\xi'$ etc [3]). This, however, is impossible.

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[1] Cf. § 78, 2nd paragraph.

[2] Cf. among others volume I, p. 25 and 27.

[3] Cf. "The dynamical Theory of Gases" p. 18.

In my opinion the correct principle that the calculation of the extension occupied by the combinations of the points of velocity after the collision when that before the collision is known and vice versa, would come to the same thing as a transition to other variables in an integration, has not been applied in exactly the correct way. The property in question says that in an integral with transition from the variables $\xi'\eta'\zeta'\xi'_1\eta'_1\zeta'_1$ to $\xi\eta\zeta\xi_1\eta_1\zeta_1$ the product of the differentials $d\xi' d\eta' d\zeta' d\xi'_1 d\eta'_1 d\zeta'_1$ may be replaced by $\frac{d(\xi'\eta'\zeta'\xi'_1\eta'_1\zeta'_1)}{d(\xi\eta\zeta\xi_1\eta_1\zeta_1)}$ $d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1$, if we integrate every time with respect to the corresponding regions, *but these expressions are not equal for all that.* The first expression may be said to represent the elementary volume in the space of 6 dimensions, bounded with regard to $\xi' \ldots \zeta'_1$, the second the elementary volume bounded with regard to $\xi \ldots \zeta_1$ [1]).

We have a simple example when in the space of three dimensions we replace $\int p\,dx\,dy\,dz$, which e.g. represents the weight of a body, by $\int p r^2 \sin\vartheta\, dr\, d\vartheta\, d\varphi$, which represents the same thing, without $dx\, dy\, dz$ having to be equal to $r^2 \sin\vartheta\, dr\, d\vartheta\, d\varphi$.

So we have here:

$$\int d\xi'\, d\eta'\, d\zeta'\, d\xi'_1\, d\eta'_1\, d\zeta'_1 = \int \left| \frac{d\,(\xi' - \zeta'_1)}{d\,(\xi - \zeta_1)} \right| d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta_1,$$

which two expresssions represent the "extension" in the space of 6 dimensions after the collision. That before the collision is $\int d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta_1$, so that, when the determinant $= 1$, the extension remains unchanged by the collision. This proves really to be the case, as JEANS shows. We may, however also consider this property as a special case of the theorem of LIOUVILLE, and derive it from this [2]). This theorem says, that with an ensemble of identical, mutually independent, mechanic systems, to which HAMILTON's equations of motion apply, $\int dp_1 \ldots dq_n = \int dP_1 \ldots dQ_n$, when $p_1 \ldots q_n$ represent the coordinates and momenta of the systems at an arbitrary point of time, $P_1 \ldots Q_n$ those at the beginning. GIBBS calls this law: the principle of conservation of extension-in-phase, which extension we must now think extended over a space of $2n$ dimensions. When now the two colliding molecules are considered as a system which does not experience any influence of other systems, and it is assumed that during the

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[1]) Cf. LORENTZ, l. c. Abhandlung VII.

[2]) As BOLTZMANN cursorily remarks: volume II p. 225.

collisions forces act which only depend on the place of the particles and not on the velocities, we may apply the formula $\int dp'_1 \ldots dq'_n = \int dp_1 \ldots dq_n$ to an ensemble of such pairs of molecules, the former representing the extension-in-phase after, the latter that before the collision. In the case discussed by BOLTZMANN the masses of these molecules are m and m_1 so that we get:

$$\int dx'\, dy'\, dz'\, m^3\, d\xi'\, d\eta'\, d\zeta'\, dx'_1\, dy'_1\, dz'_1\, m_1^{\,3}\, d\xi'_1\, d\eta'_1\, d\zeta'_1 =$$

$$= \int dx\, dy\, dz\, m^3\, d\xi\, d\eta\, d\zeta\, dx'\, dy'\, dz'\, m_1^{\,3}\, d\xi'\, d\eta'\, d\zeta'.$$

As we may consider the coordinates during the collision as invariable, it follows from this that:

$$\int d\xi'\, d\eta'\, d\zeta'\, d\xi'_1\, d\eta'_1\, d\zeta'_1 = \int d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta.$$

§ 3. However as has been referred to above, we may, without assuming anything about the mechanism of the collision, prove the property by means of the formulae for the final velocities with elastic collision, making use of the functional determinant. Another method is followed by WIND in his above-mentioned paper (the second proof) and by BOLTZMANN (vol. II p. 225 and 226); this method differs in so far from the preceding one, that the changing of the variables takes place by parts (by means of the components of velocity of the centre of gravity), which simplifies the calculation [1]). A third more geometrical method is given by WIND in his first proof. This last method seems best adapted to me to convey an idea of the significance of the principle of conservation of extension-in-phase in this special case. I shall, however, make free to apply a modification which seems an abridgment to me, by also making use of the functional determinant. So it might now also be called a somewhat modified first method.

In the first place I will call attention to the fact that with these phenomena of collision it is necessary to compare infinitely small volumes; if we, therefore, want to use the formula:

$$\int d\xi'\, d\eta'\, d\zeta'\, d\xi'_1\, d\eta'_1\, d\zeta'_1 = \int \left| \frac{d\,(\xi' \ldots \zeta'_1)}{d\,(\xi \ldots \zeta)} \right| d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta_1$$

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[1]) It seems to me that in this proof BOLTZMANN does not abide by what he himself has observed before (§ 27 and § 28, vol. II), viz. that the equality of the differential products means that they may be substituted for each other in integrals. The beginning of § 77 and the assumption of $du\, dv\, dw$, and $dU\, dV\, dW$, as reciprocal elements of volume, is, in my opinion, inconsistent with this

we must take infinitesimals of the $2^{\text{nl.}}$ order. We can, however, also proceed in a somewhat different way. For how is the above formula derived? By making use of the fact, that with a volume $d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta_1$ in the region of the $\xi \ldots \zeta_1$ corresponds a volume

$$\left|\frac{d(\xi' \ldots \zeta'_1)}{d(\xi \ldots \zeta_1)}\right| d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta_1$$

in the region of the $\xi' \ldots \zeta'_1$, or also that the first mentioned extension, occupied by the representing points in the space of 6 dimensions before the collision, will give rise to the second extension after the collision. We can, therefore very well compare these expressions inter se, without integration, if only the second expression is not interchanged with $d\xi'\, d\eta'\, d\zeta'\, d\xi'_1\, d\eta'_1\, d\zeta'_1$, i. e. the volume element obtained by dividing the extension after the collision in another way.

We now suppose the points of velocity before the collision to be situated in two cylindres, the axes of which are parallel to the normal of collision. The bases of the cylindres are $dOdO_1$ and the heights $d\sigma$ and $d\sigma_1$. The extension occupied by the combinations of the points of velocity is evidently equal to the product of the contents of the cylindres : $dOdO_1\, d\sigma d\sigma_1$. In case of collision the components of the velocities perpendicular to the normal remain unchanged, so the points of velocity are shifted in the cylindres in the direction of the axis, so that σ becomes σ', and σ_1 becomes σ'_1. Between these quantities exist the relations : $\sigma' = \dfrac{m\sigma + m_1(2\sigma_1 - \sigma)}{m + m_1}$ and $\sigma'_1 = \dfrac{m_1\sigma_1 + m(2\sigma - \sigma_1)}{m + m_1}$, when m and m_1 denote the masses of the colliding molecules (i.e. the same relations as between the normal initial and final velocities with elastic collision.

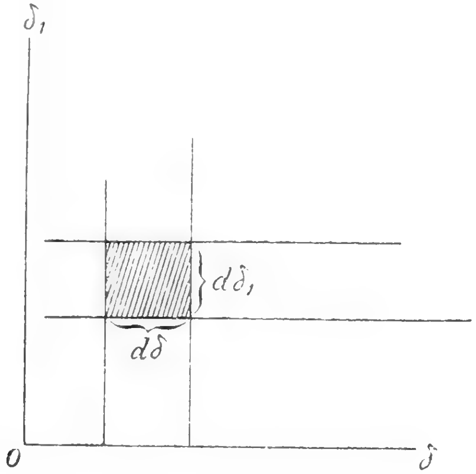
If we now wish to calculate the extension after impact we may make use of the fact that dO and dO_1 have not changed, so that we need only examine what happens to $d\sigma d\sigma_1$ or what extension in the region of the $\sigma'\sigma'_1$ corresponds to the extension $d\sigma d\sigma_1$ in the region of the $\sigma\sigma_1$.

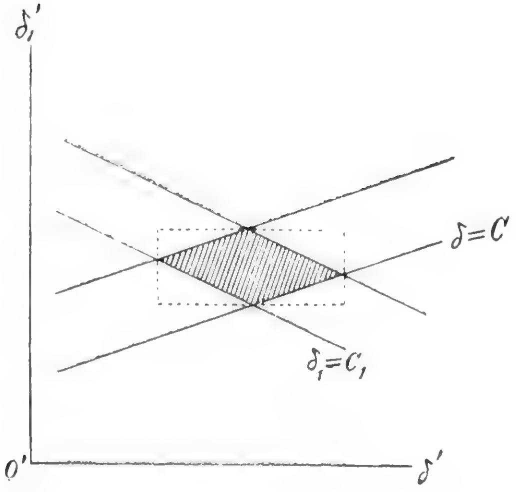
According to the above this is: $\left|\dfrac{d(\sigma'\sigma'_1)}{d(\sigma\sigma_1)}\right| d\sigma d\sigma_1$, and as it follows from the formulae for σ' and σ'_1 that the absolute value of the determinant $= 1$, the extensions before and after impact are equal.

The extension after the collision is, however, not equal to the product of the cylindres in which the points of velocity will be found after the collision. This will be easily seen with the aid of the geometrical representation given by WIND. The extension before impact may be thought as the product of the extension in the space of four dimensions $dOdO_1$ and the extension $d\delta d\delta_1$, which we may imagine as a rectangle in the region of the $\delta\delta_1$, when we project them as two mutually normal coordinates in a plane.

Every point in the rectangle represents therefore a number of combinations of velocities with equal δ and δ_1. The sides of the rectangle with equations $\delta = c$ and $\delta_1 = c_1$, correspond in the region of the $\delta'\delta'_1$ with the right lines $m\delta' + m_1(2\delta'_1 - \delta) = (m + m_1)c$ and $m_1\delta'_1 + m(2\delta' - \delta'_1) = (m + m_1)c_1$, so that from the combinations represented by points within the rectangle after the impact others follow represented by points within an oblique parallelogram.

The formula $\frac{d(\delta'\delta'_1)}{d(\delta\delta_1)} = 1$ expresses that the two figures have the same area. Now the extension after impact is equal to this paralel-





logram $\times\, dOdO_1$ or the product of the two cylindres in which points of velocity were found before impact. The product of the cylindres, in which points of velocity are found after impact is equal to the product of $dOdO_1$ and the area of the rectangle with sides parallel to the axes $O'\delta'$ and $O'\delta'_1$ described round the parallellogram under investigation. In this rectangle lie a number of points which have no corresponding points in the first rectangle. Only when $m = m_1$ rectangle and paralellogram coincide.

Collisions of opposite kind, now, are such for which the combinations of velocity before impact are represented by points of the paralellogram in the plane $\delta' O \delta'_1$ and after impact by points of the rectangle in the plane $\delta O \delta_1$.

Physics. — "*Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XII. *On the gas phase sinking in the liquid phase for binary mixtures.*" By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Communication N°. 96^b from the Physical Laboratory at Leiden.

§ 1. *Introduction.* In what follows we have examined the equilibrium of the gas phase with the liquid phase for binary systems, with which the sinking of the gas phase in the liquid phase may occur.

It lies to hand to treat this problem by the aid of ψ (free energy)-surfaces for the unity of mass of the mixture (VAN DER WAALS, Continuität II p. 27) for different temperatures construed on the coordinates v (volume of the unity of mass of the mixture) and x (quantity of mass of the second component contained in the unity of mass of the mixture).

As VAN DER WAALS (loc. cit.) has already observed, the laws referring to the stability and the coexistence of the phases are the same for these ψ-surfaces as for the more generally used ψ-surfaces for the molecular quantity: in particular also the coexisting phases are indicated by the points of contact of the ψ-surface with a plane which rolls with double contact over the plait in the ψ-surface. In what follows we have chiefly to consider the projections of the connodal curve and of the connodal tangent-chords on the xv-plane.

More particular cases as the occurrence of minimum or maximum critical temperature or minimum or maximum pressure of coexistence we shall leave out of account; we shall further confine ourselves to the case that retrograde condensation of the first kind occurs. Moreover we shall restrict ourselves to temperatures, at which the appearance of the longitudinal plait does not cause any irregularity[1]). The component with the higher critical temperature (T_k) is chosen as first component; its critical temperature is, accordingly, denoted by T_{k_1}. The special case that $T_{k_2} = 0$, is that of a *gas without cohesion* with molecules having a certain extension. The investigation of the ψ-surfaces becomes simpler for this case. For the present it seems probable to us that helium still possesses some degree of cohesion. We will, however, in a following communication compare the case of a gas without cohesion with what the observations yield concerning mixtures with H_e.

§ 2. *Barotropic pressure and barotropic concentration.* We shall call v and x of the gas phase v_g and x_g, of the liquid phase v_l and x_l. At a temperature T a little below T_{k_1}, we shall always have $v_g > v_l$. For then the plait extends only little on the ψ-surface (see fig. 1), the plaitpoint is near the top of the connodal curve, which is turned to $x = 1$, and all the projections of the connodal tangent-chords deviate little in direction from the v-axis, the angle with the v-axis, $\theta_p = \text{arc tg} \frac{x_g - x_l}{v_g - v_l}$, increases regularly if we go from $x = 0$ along the connodal curve to the plaitpoint, but it has but a small value, when $T_k - T$ is small. Only when we take for T a value a certain amount lower than T_{k_1}, the plait extends sufficiently on the ψ-surface to allow that $v_g = v_l$ and $\theta = \frac{\pi}{2}$.

If at a suitable temperature T we have substances as mentioned at the beginning, as e. g. helium and hydrogen at the boiling-point of hydrogen, we shall find the projection of a connodal tangent-chord denoting the equilibrium considered in the xv projection of the gas-liquid-plait on the ψ-surface for T; to reach it we shall have to ascend from $x = 0$ along the connodal curve up to a certain value of the pressure of coexistence p, before θ, which itself is zero for $x = 0$, can become $\frac{\pi}{2}$. A pressure of coexistence $p = p_b$, under which $v_g = v_l$ at the temperature T, we call *a barotropic pressure for that temperature*, the corresponding concentrations of liquid and gas phase *the barotropic concentration of the liquid and of the gas phase at that pressure and that temperature.* For when $v_g - v_l$ with increasing pressure of coexistence p passes through zero at $p = p_b$, we find in equilibria with pressures of coexistence above and below the value p_b the phases to have changed positions under the influence of gravity.

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[1]) This will be treated in a following communication.

In order to examine how a barotropic tangent-chord first makes its appearance on the plait on decrease of T, we point out that with extension of the plait from T_{k_1} at first $\frac{d\theta}{dx}$ remains positive all over the liquid branch of the connodal curve, so that at first we have to look for the greatest value of θ at the plaitpoint, where we shall denote its value by θ_{pl}.

When, however, on decrease of T the plait extends over the ψ-surface, this need not continue to be the case, and we may find $\frac{d\theta}{dx}$ alternately positive and negative. This is immediately seen when we notice that this must always be the case when the plait extends all over the ψ-surface.

If with decrease of T the maximum value of θ more and more increases, and T has fallen so low, that the maximum of θ somewhere in the plait has just ascended to $\frac{\pi}{2}$, then at this T the condition for the barotropic equilibrium $v_g = v_e$ will be satisfied just for the corresponding tangent-chord, and only for this tangent-chord. The *higher barotropic limiting temperature* is then reached. On further decrease of temperature the barotropic tangent-chord will then split into two parallel barotropic tangent-chords, the *higher* and the *lower* tangent-chord, which at first continue to diverge with further falling temperature, so that the higher barotropic tangent-chord may even vanish from the plait through a *barotropic plaitpoint,* and then, at a lower temperature, make its appearance again through a barotropic plaitpoint[1]).

At still lower temperature it follows from the broadening of the plait in the direction of the v-axis, which at sufficiently low temperature renders the occurrence of a barotropic tangent-chord impossible, that the maximum of θ falls again, and the barotropic tangent-chords draw again nearer to each other. At $\theta_{max} = \frac{\pi}{2}$ the tangent-chords coincide again, and the *lower barotropic limiting temperature* is reached. At lower temperatures $v_g = v_l$ is no longer to be realized, and v_g is always $> v_l$.

Figs. 2, 3 and 4 represent different cases schematically. In the spacial diagram of the ψ-surfaces for different temperatures the barotropic tangent-chords supplemented with the portions of the con-

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[1]) The latter supposes that T_{k_1}/T_{k_2} is not very great; in accepting the contrary we would come in conflict with the supposition that the longitudinal plait does not become of influence Moreover we preliminarily leave out of account the case that both barotropic tangent-chords follow one another in disappearing or appearing through a barotropic plaitpoint. [Added in the translation].

nodal curves between the lower and the higher tangent-chords form together a closed surface, which bounds the *barotropic region.*

If on the other hand $\theta_{max} = \theta_{pl}$ remains, till it has reached or exceeded the value $\frac{\pi}{2}$, and if not a second maximum value for $\theta > \frac{\pi}{2}$ occurs on the plait, a barotropic plaitpoint will occur at the higher barotropic limiting temperature, whereas at lower temperature a *single* barotropic tangent-chord on the plait indicates the equilibrium with $v_g = v_l$. With decreasing temperature this barotropic tangent-chord will at first move along the plait starting from the plaitpoint, but at lower temperatures it will return, and finally (the occurrence of a longitudinal plait being left out of consideration) it will disappear from the plait through a barotropic plaitpoint at the lower barotropic limiting temperature. In this case the barotropic region is bounded on the side towards which the plait extends by barotropic tangent-chords, on the other side by the portions of the connodal curve which are cut off.

It follows from the above that — when the occurrence of barotropic tangent-chords on the ψ-surfaces for a definite pair of substances is attended by the occurrence of barotropic plaitpoints — if $T_b > T_{bpls}$ (*higher baratropic plaitpoint temperature*) or $T_b < T_{bpli}$ *lower barotropic plaitpoint temperature* there always exists at the same time a higher and a lower barotropic tangent-chord; if $T_{bpls} > T_b > T_{bpli}$ there exists only one barotropic tangent-chord.

The nature of the barotropic phenomenon for He and H_2 may serve for arriving at an estimation of the critical temperature of He. According to the investigation of one of us (K. See Comm. N°. 96 c.) it is probable that the appearance of *a single* barotropic tangent-chord for He—H_2 at the temperature of boiling hydrogen would point to $T_{kHe} <$ about 2°, whereas on the other hand when T_{kHe} is higher, a higher and a lower barotropic tangent-chord is to be expected. Further that, as was already observed in Comm. No. 96 a. (Nov. '06) a barotropic tangent-chord can only appear in the gas-liquid-plait when very unusual relations are satisfied between the properties of the mixed substances, which for the present will most likely only be observed for He and H_2.

Whether it is possible that more than one barotropic region occurs, and whether one or more barotropic tangent-chords can move from the plaitpoint past the critical point of contact, is still to be examined. Also whether it is possible that the lower barotropic limiting temperature descends lower than T_{k_2}, so that fig. 5 might be realised. With regard to these questions too it is only of practical importance to know in how far the properties of He and H_2 create that possibility.

§ 3. *Barotropic phenomena at the compression of a mixture of definite concentration.* What will take place in this case is easy to be derived from the foregoing survey of the different equilibria which are possible at a same temperature. For the further discussion we have to trace the *isomignic* line, the line of equal concentration ($x =$ const.) for this mixture, and to examine the section with the connodal curve, the successive chords, and finally again with the connodal curve.

In the description of the barotropic phenomena we shall confine ourselves to the more complicated case, that at the T considered both a higher and a lower barotropic tangent-chord occur, after which it will be easy to survey the phenomena when only one barotropic tangent-chord appears.

To distinguish the different cases we must divide the liquid branch of the connodal curve at T into an *infra-* ($x = 0$ to $x = x_{lbiT}$, *lower barotropic concentration of the liquid phase at* T), *inter-* (x_{lbiT} to x_{lbsT}) and *supra-* ($x = x_{lbsT}$ to $x = x_{pl}$)*-barotropic* part, and the gasbranch into the three corresponding pieces falling within and on either side of the region between the two barotropic tangent-chords (the lower b_{iT} and the higher b_{sT}) at that temperature.

Whether the phenomena of retrograde condensation attend those of the barotropic change of phase or not depends on this: whether both barotropic concentrations of the gas phases fall below the plait-point concentration or not.

Let us restrict ourselves in this description to the case that this complication does not present itself or let us only consider mixtures for which $x < x_{pl}$. On compression the first liquid accumulates in the lower part of the tube for $x < x_{gbiT}$ and for $x_R > x > x_{gbsT}$, and in the higher part for $x_{gbsT} > x > x_{gbiT}$. On further compression, when $x_{gbiT} > x_{lbsT}$, change of phase will take place *once* for mixtures of the concentration x, so that $x_{gbsT} > x > x_{gbiT}$ or $x_{lbsT} > x > x_{lbiT}$; it will take place *twice* for mixtures of the concentration x, so that $x_{gbiT} > x > x_{lbsT}$. So the last remains of the gasphase will vanish above for $x < x_{lbiT}$ and for $x_{pl} > x > x_{lbsT}$, and below for $x_{lbsT} > x > x_{lbiT}$. If it is possible that over a certain range of temperature the barotropic tangent-chords get so far apart that $x_{lbsT} > x_{gbiT}$, change of phase will again take place *once* for these temperatures for mixtures of the concentration x, so that $x_{gbsT} > x > x_{lbsT}$ or $x_{gbiT} > x > x_{lbiT}$.

This description will, of course, only be applicable to He and H_2 when the suppositions mentioned prove to be satisfied.

§ 4. *Disturbances by capillary action.* As is always tacitly assumed in the application of the ψ-surface when the reverse is not expressly stated, the curvature of the surfaces of separation of the phases is put zero in the foregoing discussion. If the curvature may not be neglected, e. g. at the compression of a mixture in a narrow tube, then, when the barotropic pressure is exceeded, the phase which has thus become heavier, will only sink through the lighter phase under it, when the equilibrium has become labile taking the capillary energy of the surface of separation into account. For this it is required that θ_p has become larger than $\frac{\pi}{2}$ to an amount of $\Delta\theta_{cap}$, which will depend on the capillary energy of the surface of separation and the diameter of the tube in which the experiment is made. Thus capillarity causes a retardation of the appearance of the barotropic phenomenon: both with increase and with decrease of pressure the barotropic tangent-chord must be exceeded by increase or decrease of pressure to a certain amount, before the two phases interchange positions. In this way the difference of pressure mentioned in Comm. N°. 96a, (Nov. 1906, p. 460) between the sinking of the gas phase chiefly consisting of helium and its rising again at expansion (49 and 32 atms.) is e. g. to be explained by the aid of the following suppositions which are admissible for a first estimation.

1. that at — 253° and 32, resp. 49 atms. He is in corresponding state with H_2 at 150° and 160, resp. 245 atm., in agreement with the assumptions $M_{He} v_{kHe} = \frac{1}{4} M_H v_{kH}$ according to the ratio of the molecular refractive powers, $T_{kHe} = 1^\circ.5$ (according to OLSZEWSKI $< 1^\circ.7$); if the gas phase consisted only of He (molec. weight 4), the density at the temperature and pressures mentioned would be 0.062, resp. 0.081, and if moreover the liquid phase had the same density with the two pressures, $\Delta\theta_{cap}$ would have to correspond to a difference of density of $\pm$ 0.01; owing to the fact that the two last mentioned suppositions are not satisfied, the difference of density will be smaller;

2. that the capillary energy of the surface of separation between the phases coexisting at the above temperature and pressures is not many times smaller (or greater) than that of liquid hydrogen at that temperature in equilibrium with its saturated vapour, and that the latter may be derived from that of nitrogen [1]) by the aid of the principle of corresponding states. The gas bubble will then in a tube like that in which the experiment described in Comm. N°. 96*a* was made (int. diam. 8 mm.) only sink through the liquid or rise again, when

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[1]) BALY and DONNAN, Trans. Chem. Soc. 81 (1902) p. 907.

Prof. H. KAMERLINGH ONNES and **Dr. W. H. KEESOM.** "Contribution to the knowledge of the ψ-surface of van der Waals.
XII. On the gasphase sinking in the liquid phase for binary mixtures."

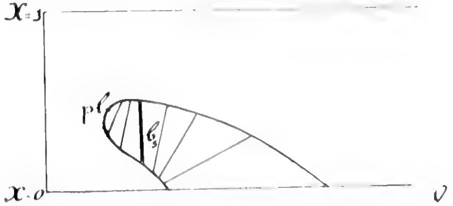

Fig. 2.

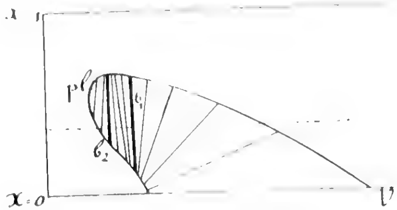

Fig. 3.

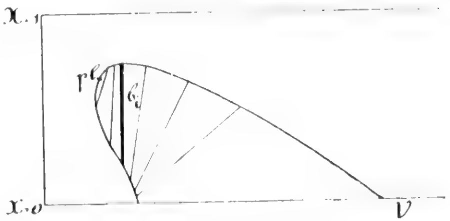

Fig. 4.

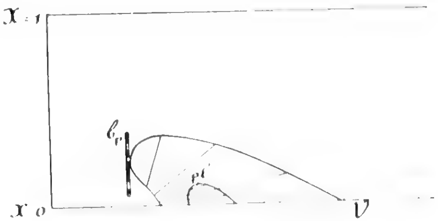

Fig. 1.

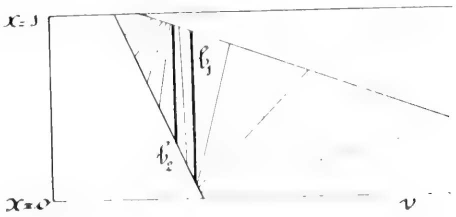

Fig. 5.

the difference of the radii of curvature of the tops of the bounding menisci exceeds that between 3 and 5 mm.

At those temperatures for which $\theta_{max} < \frac{\pi}{2} + \Delta\, \theta_{cap}$, the phenomenon of the phase which is uppermost at low pressure, sinking and rising again does not make its appearance in consequence of gravity alone. If this condition is satisfied for mixtures of a definite pair of substances for every temperature between the lower and the higher barotropic limiting temperature, the phenomenon could only be realised for these mixtures by the aid of a suitable stirrer.

§ 5. *Remarks on further experiments with helium and hydrogen.*

a. In the experiments mentioned in Comm. N°. 96^a the gas phase proved to remain below on compression to the highest pressure which the apparatus will allow. When we repeat these experiments at a higher temperature (which may e. g. be obtained by boiling the hydrogen of the bath under higher pressure[1])) it is to be expected that the barotropic pressure will first rise, as in the beginning starting from — 253° the gas phase will continue to expand more strongly than the liquid phase. At higher temperature the liquid phase begins to expand more strongly than the gas phase, but the mutual solubility plays already such an important rôle then that a definite expectation cannot be expressed, unless this, that on account of the retreating of the plait and the impossibility of the barotropic tangent-chord to reach the side of the hydrogen, the higher barotropic limiting temperature may be pretty soon reached. Also in connection with the estimation, which may be made from this concerning T_{kHe}, it will be of importance to investigate whether with a suitable concentration and at a suitable higher temperature we may observe *the liquid phase sinking after it had first risen.* That the phenomena at higher temperature, if the glass tube used should prove strong enough to bear the pressure, should be prevented by capillary action, is not probable, as capillarity together with the differences of density decreases at higher temperature; moreover in spite of capillarity the phenomena might be realised by the aid of a suitable stirrer.

b. With decrease of temperature the limit is soon reached at which we meet with the solid phase. The question rises whether then the phenomenon: the *solid phase,* (*the solid hydrogen*) *floating on the gas phase* (*chiefly the as yet still gaslike helium*), might not be realised.

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[1]) Or by using the vapour from boiling hydrogen in a separate vessel [added in the translation].

Physics. — *"Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XIII. *On the conditions for the sinking and again rising of the gas phase in the liquid phase for binary mixtures,"* by Dr. W. H. KEESOM. Communication N°. 96*c* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

§ 1. *Introduction.* As has been observed in Communication N°. 96*b* (See the preceding paper) (cf. Comm. N°. 96*a*, Nov. '06, p. 459, note 1) it lies to hand, to take as point of issue the ψ-surface for the unity of mass of the mixture considered, in the investigation according to VAN DER WAALS' theory of binary mixtures, of the sinking and subsequent rising of the gas phase in the liquid phase, i.e. the barotropic phenomenon. Two coexisting phases of equal density are joined on this ψ-surface by a tangent-chord whose projection on the x, v-plane[1]) is parallel to the x-axis. It has already been observed in Comm. N°. 96*b*, that with decrease of temperature starting from the critical temperature of the first (least volatile) component such a barotropic tangent-chord may make its appearance in two ways:

a. by the angle of inclination of the tangent to the plait in the plaitpoint, θ_{pl}, reaching the value of $\frac{\pi}{2}$ at a certain temperature T_{bpl} and by its exceeding this value at lower temperature.

b. by θ showing a maximum and a minimum on the plait at a certain temperature, and by this maximum reaching or exceeding the value of $\frac{\pi}{2}$. Also in this latter case one of the two barotropic tangents-chords which then appear, might reach the plaitpoint at lower temperature, and thus become $\theta_{pl} = \frac{\pi}{2}$.

In both cases in which $\theta_{pl} = \frac{\pi}{2}$ at a certain temperature it should be expected apart from complications as e. g. a longitudinal plait etc. (cf. Comm. N°. 96*b*, p. 502), the description of which will be given later on, that θ_{pl} becomes again $= \frac{\pi}{2}$ for mixtures of the same substances at a lower temperature.

In the first part of this paper the conditions are discussed on which a plaitpoint with $\theta_{pl} = \frac{\pi}{2}$, barotropic plaitpoint, occurs on the ψ-sur-

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[1]) Cf. for the meaning of x and v Comm. N°. 96*b*.

face, whereas in the second part the conditions are treated for the appearance of a barotropic tangent-chord on the plait.

A. On the conditions for the occurrence of a barotropic-plaitpoint.

§ 2. In a barotropic plaitpoint the isobar, which in a plaitpoint always touches the plait, must run parallel to the x-axis. This gives the condition:

$$\left(\frac{\partial^2\psi}{\partial x\partial v}\right)=0 \quad \ldots\ldots\ldots\ldots \quad (1a)$$

Moreover a section $v=v_{pl}$ of the ψ-surface with the limiting position of the tangent-chord must then have a contact of the 3rd order. This furnishes:

$$\left(\frac{\partial^2\psi}{\partial x^2}\right)=0 \quad , \quad \left(\frac{\partial^3\psi}{\partial x^3}\right)=0 \quad \ldots\ldots \quad (1\ b \text{ and } c)$$

The two conditions ($1\ b$) and ($1\ c$) follow also by applying ($1\ a$) to the general relations for the plaitpoint of Comm. N°. 75 (Dec. 1901) p. 294.

The same may be obtained from the property of the barotropic points on the connodal curve that there $\left(\frac{\partial\psi}{\partial x}\right)$ along the connodal shows a maximum or minimum [1], so that the substitution-curve $\left(\frac{\partial\psi}{\partial x}\right)=$ const. (see for the substitution curves on the ψ-surface for the molecular quantity Comm. N°. 59[1]), touches the connodal line in these points.

§ 3. For a first investigation we shall use VAN DER WAALS' equation of state:

$$p=\frac{R_xT}{v-b_x}-\frac{a_x}{v^2} \quad \ldots\ldots\ldots\ldots \quad (2)$$

with an a_x and b_x not depending on v and T for a definite x. In this:

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[1] This property for coexistence with $v_2=v_1$ is analogous to the property that $\left(\frac{\partial\psi}{\partial v}\right)=-p$ along the connodal line is a minimum or a maximum for coexisting phases with $x_2=x_1$. In the same way the mean value of $\left(\frac{\partial\psi}{\partial x}\right)$ along an isometric line $v=v_b$, which joins two barotropic phases on the ψ-surface, is equal to the value of $\left(\frac{\partial\psi}{\partial x}\right)$ for these phases.

$$R_x = R_1\,(1-x) + R_2 x \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

if $R_1 = R/M_1$, $R_2 = R/M_2$, R representing the molecular gas-constant, M_1 and M_2 representing the molecular weights; we put for this first investigation $a_{12} = \sqrt{a_{11}\,a_{22}}$, so that

$$a_x = \{\sqrt{a_{11}}\,.\,(1-x) + \sqrt{a_{22}}\,.\,x\}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

and when we put for the molecular volumes $2b_{12M} = b_{11M} + b_{22M}$, the relation for b_x given by VAN DER WAALS Contin. II p. 27, reduces to:

$$b_x = b_{11}\,(1-x) + b_{22}\,x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3c)$$

We get then (VAN DER WAALS Contin. II p. 28):

$$\psi = -\,R_x T\, ln\,(v-b_x) - \frac{a_x}{v} + T\,\{R_1\,(1-x)\, ln\,(1-x) + R_2\, x\, ln\, x\} \quad . \quad (4)$$

§ 4. Taking equations (3) into consideration, and putting

$$\frac{b_{22}-b_{11}}{v-b} = u, \quad x = \frac{1+z}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

we get by the conditions (1):

$$R_2\,.\,\frac{1+z}{2}\left\{u + \frac{2}{1+z}\right\} + R_1\,\frac{1-z}{2}\left\{u - \frac{2}{1-z}\right\} = \frac{v-b}{Tv^2}\,\frac{da}{dx} \quad . \quad . \quad . \quad . \quad (6a)$$

$$R_2\,.\,\frac{1+z}{2}\left\{u + \frac{2}{1+z}\right\}^2 + R_1\,\frac{1-z}{2}\left\{u - \frac{2}{1-z}\right\}^2 = \frac{1}{Tv}\,\frac{d^2a}{dx^2} \quad . \quad . \quad . \quad . \quad (6b)$$

$$R_2\,.\,\frac{1+z}{2}\left\{u+\frac{2}{1+z}\right\}^2\left\{u-\frac{1}{1+z}\right\} + R_1\,\frac{1-z}{2}\left\{u-\frac{2}{1-z}\right\}^2\left\{u+\frac{1}{1-z}\right\}=0 \quad (6c)$$

These equations are sufficient to calculate the data for a barotropic plaitpoint x_{bpl}, v_{bpl}, T_{bpl} for a definite pair of substances. Eliminating T from (6a) and (6b), we get, taking (6c) into consideration and putting:

$$(\sqrt{a_{22}} + \sqrt{a_{11}})\;(\sqrt{a_{22}} - \sqrt{a_{11}}) = \mu \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

$$\tfrac{1}{2}\,(v-b)\left\{u + \frac{2}{1+z}\right\}\left\{u - \frac{2}{1-z}\right\}(\mu+z) + v\left\{u + \frac{4z}{1-z^2}\right\} = 0, \quad (8)$$

while elimination of v from this equation and (5), putting:

$$(b_{22}+b_{11})\,/\,(b_{22}-b_{11}) = \boldsymbol{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7b)$$

yields:

$$\tfrac{1}{2}\left\{u + \frac{2}{1+z}\right\}\left\{u - \frac{2}{1-z}\right\}(\mu+z) + \left\{u + \frac{4z}{1-z^2}\right\}\{\tfrac{1}{2}\,(\boldsymbol{v}+z)\,u+1\} = 0 \;. \quad (9)$$

From this equation with (6c): z_{bpl} may be found for given R_2/R_1, μ and $\boldsymbol{v}$, after which x_{bpl}, v_{bpl} and T_{bpl}, as well as p_{bpl} follow easily.

§ 5. That a barotropic plaitpoint exists on the liquid-gas-plait with the assumed suppositions (2), (3b), (3c) and with suitable values of the constants, appears as follows: for $z=0.5$, $R_2/R_1={}^1/_2$, $b_{22}/b_{11}={}^1/_8$, (6c) yields: $u=-1.957$, after which (9) yields: $\mu=-1.176$, so that $a_{22}/a_{11}=0.00653$. Thus we find for a mixture of two substances with $M_2=2\,M_1$, $v_{k_2}={}^1/_8\,v_{k_1}$ (so that the ratio of the molecular critical volumes is ${}^1/_4$), $T_{k_2}=0.052\,T_{k_1}$, a barotropic plaitpoint for $v_{bpl}=0.26\,v_{k_1}$, $T_{bpl}=0.80\,T_{k_1}$, $p_{bpl}=4.8\,p_{k_1}$.

(To be continued).

ERRATUM.

In the Proceedings of the meeting of September 29, 1906.

p. 209, line 15 from the bottom: for § 10 read § 9.
p. 210, Table I, line 5 and 4 from the bottom, for: 5 July read 6 July.
,, 3 from the bottom, for 3 March '05 read 3 March '06.

(January 24, 1907).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday January 26, 1907.

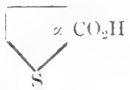
(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 26 Janunri 1907, Dl. XV).

CONTENTS.

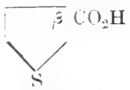
Chemistry. — *"α- and β-thiophenic acid."* By Prof. A. F. Holleman and Dr. G. L. Voerman.

(Communicated in the meeting of December 29, 1907).

A very remarkable research on these acids was published in 1886 by V. Meyer, who discovered the same. In the main it amounts to this, that in addition to the theoretically possible monocarboxylic acids of thiophen



Mp. 126°.2



Mp. 138°.4

a third isomer was obtained, called *a*-thiophenic acid m.p. 117.5—118°, which, however, in its derivatives such as the amide, the phenylurea derivative of the amide, the amidoxime and the thienone $(C_4H_3S)_2CO$, so completely resembled the corresponding derivatives of the *α*-acid that they would have been declared identical, were it not that from the *a*-derivates the *a*-acid m.p. 118° was regenerated, whilst the *α*-derivates yielded the *α*-acid m.p. 126°. V. Meyer expresses himself as follows: "Die Vergleichung der *a*- und *α*-Säure ergab immer von "Neuem das merkwürdige Resultat, dass die beiden Säuren wirklich "in ihren Eigenschaften durchaus verschieden sind, und dass die Ver-"schiedenheiten sich als constante, durch keinerlei Reinigung oder "Umwandlungen zu entfernende Eigenschaften erwiesen; dass aber "alle Derivate der beiden Säuren in ihren physikalischen Eigenschaften "absolut zusammenfallen und für identisch (im gewöhnlichen Sinne) "erklärt werden müssten, wenn sie nicht die Eigenschaft besässen, "dass jedes aus der *α*-Säure dargestellte Derivat bei der Rückführung "auch wieder *α*-Säure, jedes *a*-Derivat dagegen *a*-Säure lieferte."

As the *a*-acid had also been obtained by oxidation of tar-thiotolene which is a mixture of *α*- and *β*-thiotolene [2—3 methylthiophen], V. Meyer suspected that this *a*-acid might be after all a mixture of *α*- and *β*-acid, and he really succeeded, by oxidation of a mixture of the two thiotolenes in definite proportion, or by slow crystallisation of a mixture of *α*- and *β*-acid from cold water, in obtaining an acid which agreed in every respect with the *a*-acid. This was no doubt an important step forward, but the behaviour of such a mixture and also of the derivatives obtained therefrom still remained a very remarkable one.

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[1] A. **236**, 200; also V. Meyer, die Thiophengruppe p. 188—207.

Notwithstanding all this, nobody, since this elaborate research of V. Meyer, has been engaged during the last 20 years in the study of these acids, although it might have been expected from the development of the phase-rule that the latter might possibly give us a closer insight into the phenomena described above.

The probable cause of all this is that these acids are not readily accessible, and that those engaged in researches connected with the phase-rule have not ventured to prepare the same. When Dr. Voerman, at my request, undertook the closer study of these acids we had, first of all, to find a better process for the preparation of these substances.

In the case of the α-acid we have indeed succeeded in a very satisfactory manner. We have also worked out another and improved method for the preparation of the β-acid; but it is still unsatisfactory owing to the small yield. Therefore, we have been obliged to restrict ourselves, provisionally, to the study of the acids themselves; the derivatives will be taken in hand when more material has been obtained.

Preparation of α-thiophenic acid. By V. Meyer and his pupils, this acid was best obtained by oxidation of propiothienon $C_4H_3S.COC_2H_5$, because the oxidation of the much more readily accessible acetothienon $C_4H_3S.COCH_3$ yielded a mixture of α-thiophenic acid and thienylglyoxylic acid, which it was rather troublesome to separate. We have succeeded in converting acetothienon almost quantitatively into α-thiophenic acid, being guided by the following considerations. If we oxidise a methyl ketone, experience has taught that the methyl group very readily changes to carboxyl thus forming a glyoxylic acid: $R.CO.CH_3 \rightarrow R.CO.CO_2H$. If, however, we attempt to go further and obtain the corresponding carboxylic acid: $R.CO.CO_2H \rightarrow R.CO_2H$ a difficulty is experienced and the oxidising mixture then also attacks the group R so that the yield of the carboxylic acid becomes generally unsatisfactory. Now some time ago, I found a method for converting acids $R.CO.CO_2H$ quantitatively into $R.CO_2H$; this is rendered possible by the application of hydrogen peroxide which causes a ready resolution according to the scheme:

$$\begin{array}{c}\mathrm{R.CO.\,CO_2H}\\ \mathrm{HO}\,\vdots\,\mathrm{OH}\end{array} = \mathrm{R.COOH} + \mathrm{CO_2} + \mathrm{H_2O}$$

This method has led to the desired result in this case. The oxidation of acetothienon is, therefore, done in two stages, first the formation of thienylglyoxylic acid which is subsequently oxidised to -thiophenic acid. The practical application of these processes was as follows:

Acetothienon was prepared from thiophen according to the method of FRIEDEL and CRAFTS, and a very good yield was obtained. The thiophen was prepared by ourselves by distillation of sodium succinate with P_2S_3. 11.5 grams of ketone and 12 grams of sodium hydroxide were introduced into a litre of water, and to this was added slowly, at the ordinary temperature, a solution of 42 grams of potassium permanganate dissolved in a litre of water. After each addition the pink colour was allowed to change to green before addition of a fresh portion.

After all the permanganate had been added the liquid was allowed to remain overnight; the solution was heated gently on the waterbath until the green colour had disappeared, then filtered off from the manganese dioxide, and concentrated to 250 cc. Without isolation of the thienylglyoxylic acid, beforehand the liquid, after being *nearly* neutralised with hydrochloric acid, is mixed with 9 grams of 30 % hydrogen peroxide previously diluted with its own volume of water. The whole is set aside for a few hours, and afterwards heated for a few moments on a waterbath. On acidification the liquid the greater part of the α-thiophenic acid formed is precipitated in a pure condition; a further small quantity may be recovered from the mother-liquor by extraction with ether. By recrystallisation from water and distillation in vacuo, the acid may be obtained pure and quite free from thienylglyoxylic acid. The yield amounts to about 9 grams.

The solution of α-thiophenic acid saturated at 24°.9 contains 0.75 %.

Preparation of β-thiophenic acid. V. MEYER has effected this by oxidising with potassium permanganate in very dilute, cold solution. The yield of β-acid was however very poor, in fact only about 5—8 % of the thiotolene employed. After trying various modifications of this direct oxidation process without arriving at a better result we decided to follow an indirect way by first chlorinating the side chain, then preparing the aldehyde from the thienalchloride and finally oxidising the former to the acid:

$$C_4H_3S \, . \, CH_3 \rightarrow C_4H_3S \, . \, CHCl_2 \rightarrow C_4H_3S \, . \, CHO \rightarrow C_4H_3S \, . \, COOH.$$

Bearing in mind VAN DER LAAN's research[1]) on the bromination of toluene where it was shown that in presence of PCl_5 the substitution in the side chain is accelerated, this substance was added in the chlorination of β-thiotolene. The above mentioned processes all proceeded very smoothly, but unfortunately an acid rich in chlorine was finally obtained as, apparently, the chlorination had also extended to the nucleus. This certainly could be freed from chlorine by treatment with sodium-amalgam but a large proportion of the β-thiophenic acid was lost thereby so that the yield did, finally, not exceed 10 % of the thiotolene employed.

We add a few particulars as to the *modus operandi* followed.

β-thiotolene was prepared by ourselves by distilling sodium pyrotartrate with phosphorus trisulphide. The chlorination took place in direct sunlight in the presence of 10 % of PCl_5. The reaction product is boiled in a reflux apparatus with water and calcium carbonate. The aldehyde is distilled in steam and purified over the

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[1]) These Proc. Oct. 1905).

bisulphite compound. From 10 grams of thiotolene about 5 grams of the aldehyde are obtained. Of this, 3 grams are oxidised with 500 cc. of water containing 3.2 grams of potassium permanganate and 1.3 gram of 80 $^0/_0$ potassium hydroxide; after standing over night the liquid is filtered from the manganese dioxide, concentrated and acidified when about 3 grams of thiophenic acid are precipitated. The dechlorination of this product with sodium amalgam in dilute aqueous solution takes 15—20 days during which a large portion of the acid gets lost.

As regards the solubility of β-thiophenic acid at 25° it was found that the saturated solution contains 0.43 $^0/_0$ of acid.

Melting point line of mixtures of the two acids. According to the present views of the phase rule it was natural to suppose that the impossibility of separating these acids by crystallisation is due to the fact that they yield mixed crystals. In fact by determining the melting point line, Dr. VOERMAN has succeeded in demonstrating with certainty that they give an interrupted mixing series. The initial solidifying points may be observed very sharply but the final solidifying points can only be determined within 0°.5.

A list of the initial and final solidifying points is appended; and in the annexed curve these figures are represented graphically.

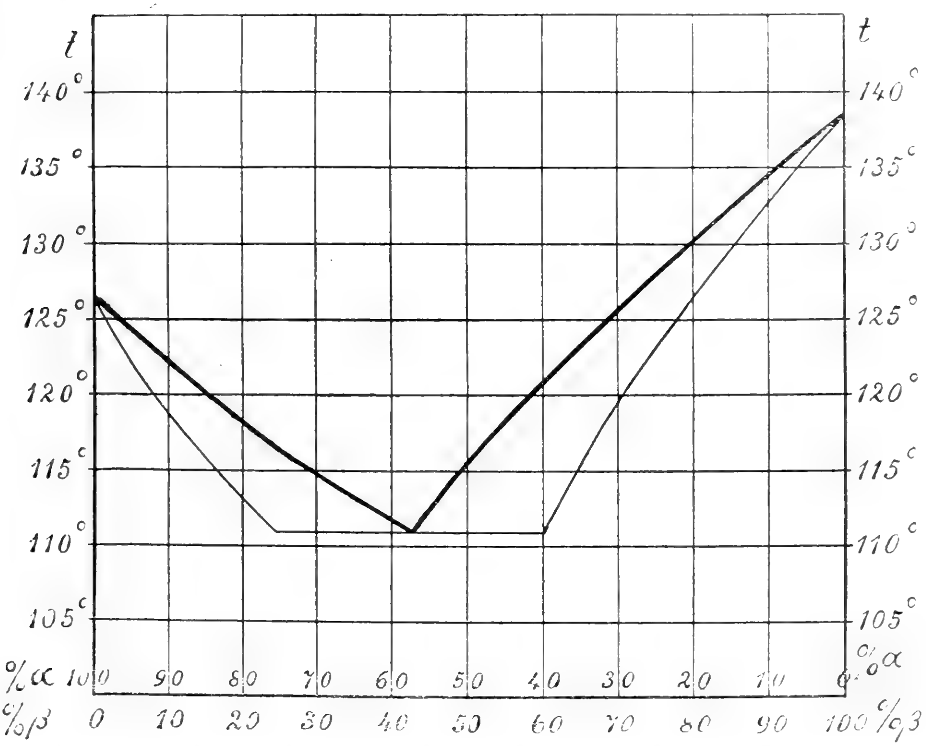

Fig. 1.

SOLIDIFYING POINTS OF α AND β-THIOPHENIC ACID AND THEIR MIXTURES.

$^0/_0$ α	$^0/_0$ β	1st solidifying point	2nd solidifying point
100	0	126°.2	
99.01	0.99	125.4	123°.9—124°.4
98.25	1.75	125.1	
96.56	3.44	124.6	123.1—123.6
94.3	5.7	124.1	121.0
93.60	6.40	123.4	
90.60	9.40	122.2	
88.20	11.80	121.3	± 118
85.82	14.28	120.3	± 116.6
85.0	15.0	120.1	
79.45	20.55	117.7	113.5—114
77.45	22.55	117.2	112 —112.6
75.3	24.7	116.3	110.8—111.2
74.60	25.40	116.0	± 110.6
69.45	30.55	114.3	110 —111
66.20	33.80	113.3	110.5—110.8
63.35	36.65	112.5	110.8
59.70	40.30	111.5	110.5
58.0	42.0	111.0	110.7
55.0	45.0	112.6	110.8
50.85	49.15	115.0	110.7
42.50	57.50	119.6	id.
38.9	61.1	121.2	111.2
33.60	66.40	124.0	116.5—117.5
23.80	76.20	128.2	123—124 (±123.5)
14.0	86.0	132.6	129.5—129.8
5.4	94.6	136.3	134 —134.3
0	100	138.4	

It appears that the series of mixed crystals is interrupted on one side at $25^0/_0$ β-acid, and on the other side at $61^0/_0$; and that there is a eutectic point at $42.5^0/_0$ β-acid at a temperature of 111°.

The crystallographical investigation of these acids and their mixtures kindly carried out by Dr. Jaeger leads to exactly the same result. Dr. Jaeger reports as follows:

Of the two isomeric compounds β-*Thiophenic acid* crystallises the most readily in sharply defined, small crystalline plates.

Whether obtained by crystallisation from solvents or by fusion and subsequent cooling, the compound exhibits the microscopical appearance of the subjoined figure. The crystals are monoclino-prismatic, and combinations of the form: { 001 }, very predominant, { 110 } and { 100 }; the angle of inclination β deviates considerably from 90°, so that the smaller individuals often exhibit rhomboidal form owing to simultaneous development of { 110 } and { 001 }. Often the plates are so thin that only a single parallelogrammatic circumference can be observed with a very slight stunting of the sharp angle which was determined at 42°—43°, by { 100 }.

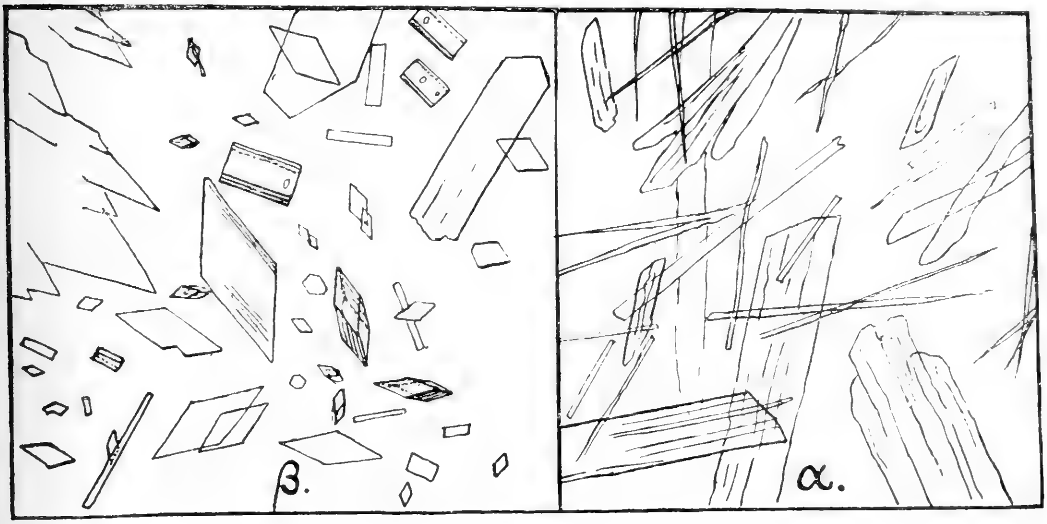

Fig. 2. Microscopcial aspect of α- and β-Thiophenic acid.

In addition, small rectangular plates occur which, as the investigation shows, are formed with { 100 } as predominant form, and therefore show prolongation along the *b*-axis. Although representing apparently a second form they are, however, quite identical with the parallelogrammatic phase.

The optical axial plane is parallel { 010 } and falls along the longest diagonal of the parallelograms or perpendicular to the longitudinal direction of the needle-shaped individuals. In convergent light one hyperbole with rings is visible at the border of the field of vision.

Very feeble inclined dispersion with $\varrho > v$; double refraction negative. The longitudinal axis of the parallelograms and the shortest dimension (breadth) of the more needle-shaped individuals are the directions of a smaller optical elasticity.

α-Thiophenic acid crystallises from solvents or from the fused mass in long more or less broad needle-shaped individuals, which usually exhibit only a rudimentary limitation and cannot therefore be properly determined morphologically. Although the optical properties seem to point to a monoclinic symmetry one might also feel inclined to conclude to a triclinic symmetry on account of the form limitations occurring here and there. The extinction of the needles is, however apparently orientated perpendicularly to their longitudinal direction. The smaller optical elasticity axis coincides with the longitudinal direction of the needles. The optical axial plane is orientated perpendicularly to the longitude of the needles; in convergent light a single very characteristically coloured hyperbole is visible at about $^2/_8$ of the diameter of the fields of vision.

Enormously strong dispersion with $\varrho < v$; the sign of the double refraction around the correlated bissectrix is positive.

The two isomers are, therefore, readily distinguished microscopically by the following properties:

β-Thiophenic acid	*α-Thiophenic acid*
Parallellogrammic limitation, or short rods of rectangular form.	Long, very slender needles, mostly with rudimentary limitation.
Very high interference colours.	Grey, or unconspicuous colours.
One optical axis with elliptical rings, very weak dispersion $\varrho < v$.	One coloured hyperbole; very strong dispersion: $\varrho < v$.
Negative double refraction.	Positive double refraction.
Monoclinic symmetry; angle of the parallelograms 42°—43°.	Triclinic or monoclinic symmetry.
Optical axial plane for the parallelograms // to the longest diagonal for the needles perpendicular to the longitudinal direction.	The optical axial plane is perpendicular to the longitudinal direction of the needles. The latter coincides with the shortest elasticity-axis of the crystals.
The largest elasticity-axis is parallel to the longitudinal direction of the needles or to the shortest diagonal of the parallelograms.	

On account of the evaporation of the two substances when melting, one is obliged always to use a covering glass under the crystallisation-microscope.

On mixing the two isomers I have noticed the following on melting and subsequently cooling the mixtures.

a. Mixture containing 61,6 $^0/_0$ of β-acid yields exclusively *mixed crystals* of the β-form; formation of *minute traces* of α-crystals is not improbable.

b. Mixture containing 42 $^0/_0$ of β-acid yields chiefly *mixed crystals* of the α-form; at the edges of the fused mass, however, are found also *very small*, slightly coloured parallelograms of the β-form. Negative mixed crystals in the α-form (see *d*) were not noticed; only positive ones with $\varrho < v$.

c. Mixture containing 35,5$^0/_0$ of β-acid behaves on solidification like *b*.

d. Mixture containing 22,5 $^0/_0$ of β-acid, only yields mixed crystals of the α-form both positive and negative doubly-refracting but with $\varrho < v$ like the α-acid itself.

e. Mixture containing 86 $^0/_0$ of α-acid only gives mixed crystals of the α-type with strong dispersion $\varrho < v$ and a positive double refraction.

Dr. Jaeger comes to the following conclusion:

"There exists here an isodimorphous mixing series with hiatus. This extends from a β-acid concentration $> 22,5^0/_0$ to mixtures containing 61—62 $^0/_0$ of the β-compound. The mixed crystals of the α-type become on addition of the negative β-compound less strongly positive optically and in the immediate vicinity of the hiatus even negative; they, however still retain the strong dispersion with $\varrho < v$, which is so characteristic for the pure α-compound.

On the other hand, the mixed crystals of the β-type have at all concentrations of 62—100 $^0/_0$ a negative double refraction and a very feeble inclined dispersion."

V. Meyer states in his treatise that in the oxidation of mixtures of the two thiotolenes, he has obtained various other mixtures of α- and β-thiophenic acid, and that these showed no sign of separation into their components when subjected to fractional crystallisation.

Dr. Voerman, however, cannot confirm this observation. When he recrystallised a mixture of 85.3$^0/_0$ α-acid and 14.7$^0/_0$ of β-acid (solidifying point 120°.3) from hot water, the solidifying point increased to 121 .6 which corresponds with a mixture of 89$^0/_0$ α- and 11$^0/_0$ of β-acid. As, however, V. Meyer does not state the temperature at which he carried out his fractional crystallisations, it is possible that this was not the same as in VOERMAN's experiment and this might account for the difference.

Dr. VOERMAN has finally been engaged in the determination of the conductivity power of the two acids and their mixtures in the hope of obtaining indications of a combination of the two acids when in solution. The observations are as follows:

CONDUCTIVITY POWER OF α-THIOPHENIC ACID AT 25°.

v	μ	α	100 k	
25	32.44	0.085	0.0314	
50	45.37	0.118	0.0319	
100	62.49	0.163	0.0319	
200	85.06	0.222	0.0318	$\mu_\infty = 382.7$
400	113.87	0.298	0.0315	
800	149.41	0.390	0.0312	
[1600	189.34	0.495	0.0303]	
			Average 0.0316	

In this table, v represents the volume in which 1 mol. is dissolved, μ the molecular conductivity power, α the degree of dissociation, 100 k the dissociation constant according to OSTWALD × 100.

The conductivity power has been determined, previously, by OSTWALD (Ph. Ch. **3**, 384) who found for 100 k 0,0302, and by BADER, (Ph. Ch. **6**, 313) who found for 100 k 0,0329.

CONDUCTIVITY POWER OF β-THIOPHENIC ACID AT 25°.

v		α	100 k	
50	23.20	0.061	0.00783	
100	32.32	0.084	0.00779	
200	44.90	0.117	0.007795	$\mu_\infty = 382.7$
400	62.06	0.162	0.00784	
800	84.66	0.221	0.00785	
[1600	114.17	0.298	0.00793]	
			Average 0.00783	

CONDUCTIVITY POWER OF MIXTURES OF $\alpha + \beta$-THIOPHENIC ACID AT 25°.

11% } thiophenic acid
89% α }

v	μ	α	100 k
50	43.26	0.113	0.0288
100	59.49	0.155	0.0286
200	80.94	0.211	0.0284
400	108.05	0.282	0.0278
800	141.29	0.369	0.0270
1600	180.75	0.572	0.0264

33.33% β } thiophenic acid
66.66% }

v	μ	α	100 k
33.333	31.79	0.083	0.0226
66.666	44.28	0.116	0.0227
133.333	60.86	0.159	0.0226
266.666	82.33	0.215	0.0221
533.333	109.83	0.287	0.0217
1066.666	143.38	0.375	0.0210

50% β } thiophenic acid
50% α }

v	μ	α	100 k
50	35.12	0.092	0.0185
100	48.52	0.127	0.0184
200	66.01	0.172	0.0180
400	88.58	0.231	0.0174
800	117.15	0.306	0.0170
1600	151.7	0.396	0.0163

70.4% β } thiophenic acid
29.6% α }

v	μ	α	100 k
100	43.04	0.112	0.0143
200	58.63	0.153	0.0139
400	79.06	0.207	0.0135
800	105.02	0.274	0.0130
1600	138.20	0.361	0.0128

The conductivity of the pure β-acid has been determined previously by Lovén (Ph. Ch. **19**, 458) who found:

$$100\,k = 0{,}0078.$$

which agrees well with the value found by myself.

The influence of the position of the sulphur atom in regard to the carboxyl group is very marked.

From these observations it appears that the acids in aequeous solutions exert but very little influence on their mutual conductivity power, as the conductivity power of the mixtures agrees fairly well with the calculated result. A condensation of their molecules in such a solution cannot therefore be supposed to take place.

Physics. — "*A remark on the theory of the ψ-surface for binary mixtures.*" By Prof. J. D. van der Waals.

(Communicated in the meeting of December 29, 1906).

Kamerlingh Onnes' startling experiment, in which a gas was obtained that sinks in a liquid, has drawn the attention more closely to the direction of the tangent in the plaitpoint of a binary mixture. Leaving the further particulars required for the realisation of such a mixture to the investigations of Kamerlingh Onnes and his collaborators, I will make a remark of general significance, in close connection with this experiment.

In my Théorie moléculaire and more fully in Cont. II I have examined the condition, on which the tangent in the plaitpoint runs parallel to the v-axis, or in other words $\left(\frac{dv}{dx}\right)=\infty$. The problems related to this may be reduced to 3. All three refer to the intersection of the two curves $\left(\frac{dp}{dv}\right)_{xT}=0$ and $\left(\frac{dp}{dx}\right)_{vT}=0$.

As first problem I should like to regard the principal one, namely that where $\frac{\partial^2\psi}{\partial v^2}=0$ and $\frac{\partial^2\psi}{\partial x\,\partial v}=0$. The point considered lies, therefore, on the spinodal curve, and at the same time the curve $\frac{\partial^2\psi}{\partial v^2}=0$ has for constant value of x two equal values for v and so also $\frac{\partial^3\psi}{\partial v^3}=0$. Then the point considered is the critical point of the mixture taken as homogeneous. The value of T is that of T_k for such a mixture and the value of x is then found, when the approximate equation of state with b constant is applied, from:

$$\frac{\frac{1}{a}\frac{da}{dx}}{\frac{1}{b}\frac{db}{dx}}=\frac{2}{3},$$

which value $^2/_3$ becomes $= {}^6/_7$, when the independence of b of the volume is relinquished.

In this case the line $\frac{\partial^2\psi}{\partial x\,\partial v}$ cuts the line $\frac{\partial^2\psi}{\partial v^2}=0$ still in two points. One point is that above mentioned, the second lies at smaller x and larger v. So nearer the component with the smallest value of b.

With increase of temperature the two points of intersection draw nearer to each other, and as second problem we may put: to examine the circumstances under which the two points of intersection of these curves coincide. The three equations from which this circumstance is determined, are then: $\frac{\partial^2\psi}{\partial v^2}=0$, $\frac{\partial^2\psi}{\partial x\,\partial v}=0$ and a third which expresses that these curves touch, viz.:

$$\left(\frac{\partial^3\psi}{\partial v^2\,\partial x}\right)^2=\frac{\partial^3\psi}{\partial x^2\,\partial v}\,\frac{\partial^3\psi}{\partial v^3}$$

or

$$\left(\frac{\partial^2 p}{\partial x\,\partial v}\right)^2=\frac{\partial^2 p}{\partial x^2}\,\frac{\partial^2 p}{\partial v^2}$$

Above the temperature at which these circumstances are fulfilled, $\frac{\partial^2\psi}{\partial v^2}=0$ and $\frac{\partial^2\psi}{\partial x\partial v}=0$ do not intersect any longer, and the complication in the course of the isobars, viz. that there is one that intersects itself, has disappeared.

The third problem is more or less isolated, but yet I should like to treat it in this connection: viz. that for which the line $\frac{\partial^2\psi}{\partial v^2}=0$ has a double point, and so at the same time $\frac{\partial^3\psi}{\partial v^3}=0$ and $\frac{\partial^3\psi}{\partial x\partial v^2}=0$. If there is a minimum T_k for mixtures taken us homogeneous, such a point is really a double point. If there should be a maximum T_k, it is an isolated point. We find then again $v=v_k$, $T=T_k$ and the value of x is that for which T_k has a minimum or maximum value. Let us call the three values of x obtained for those three problems x_1, x_2 and x_3, then:

$$x_2<x_1<x_3$$
$$T_2>T_1>T_3\,.$$

Now there are three more problems, and to this I will call attention in this note, which may be considered as the analogues to the three above-mentioned ones.

If in the above problems we substitute the quantity x for v and vice versa, so that $\frac{\partial^2\psi}{\partial v^2}$ changes into $\frac{\partial^2\psi}{\partial x^2}$, and $\frac{\partial^2\psi}{\partial x\partial v}$ remains unchanged then the intersection of the curves $\frac{\partial^2\psi}{\partial x^2}=0$ and $\frac{\partial^2\psi}{\partial x\partial v}=0$ will give rise to three problems, which are of as much importance for the theory of the binary mixtures as the three above-mentioned problems, which relate to the intersection of $\frac{\partial^2\psi}{\partial v^2}=0$ and $\frac{\partial^2\psi}{\partial x\partial v}=0$.

In the first place the points at which the two curves $\frac{\partial^2\psi}{\partial x^2}=0$ and $\frac{\partial^2\psi}{\partial x\partial v}=0$ intersect will belong to the spinodal curve, as appears from $\frac{\partial^2\psi}{\partial x^2}\frac{\partial^2\psi}{\partial v^2}=\left(\frac{\partial^2\psi}{\partial x\partial v}\right)^2$.

In the second place these points of intersection will have the same significance for the course of the curves $\left(\frac{\partial\psi}{\partial x}\right)_v=q=$ constant, as the points of intersection $\frac{\partial^2\psi}{\partial v^2}=0$ and $\frac{\partial^2\psi}{\partial x\partial v}=0$ have for the course of the curves $\left(\frac{\partial\psi}{\partial v}\right)_x=-p=$ constant. The first point of intersection will be a double-point for the q lines, whereas the other point of intersection will present itself as an isolated point, the centre of detached closed portions of the q lines.

In the third place there will be a limiting temperature for the existence of the locus $\frac{\partial^2\psi}{\partial x^2}=0$. With increasing value of T this curve contracts to an isolated point, just as is the case with $\frac{\partial^2\psi}{\partial v^2}=0$ with maximum T_k, or as the curve $\frac{\partial^2\psi}{\partial v^2}=0$ has a double point with minimum T_k.

In the fourth place there is a temperature at which the curves $\frac{\partial^2\psi}{\partial x^2}=0$ and $\frac{\partial^2\psi}{\partial x\partial v}=0$ only touch, and the two points of intersection have, accordingly, coincided.

And finally, and this is the most important case, there is a temperature at which the intersection of these curves takes place in such a way that at one of the points of intersection a tangent may be drawn to $\frac{\partial^2\psi}{\partial x^2}=0$, for which $\frac{dv}{dx}=0$.

To determine these circumstances we have the three equations $\frac{\partial^2\psi}{\partial x^2}=0$, $\frac{\partial^2\psi}{\partial x\partial v}=0$ and $\frac{\partial^3\psi}{\partial x^3}=0$ and this problem proves to be the analogue of that mentioned above, for which $\frac{\partial^2\psi}{\partial v^2}=0$, $\frac{\partial^2\psi}{\partial x dv}=0$ and $\frac{\partial^3\psi}{\partial v^3}=0$. If there $\frac{dv}{dx}$ was $=\infty$, now $\frac{dx}{dv}=\infty$ or $\frac{dv}{dx}=0$.

So if the 3 equations $\frac{\partial^2\psi}{\partial x^2}=0$, $\frac{\partial^2\psi}{\partial x\partial v}=0$ and $\frac{\partial^3\psi}{\partial x^3}=0$ admit of a solution, the circumstances may be realised in which at the plaitpoint a tangent may be drawn // x-axis. Neglecting the variability of b with v we find for the three equations:

$$\frac{\partial^2\psi}{\partial x^2}=\frac{MRT}{x(1-x}+\frac{MRT\left(\frac{db}{dx}\right)^2}{(v-b)^2}-\frac{\frac{d^2a}{dx^2}}{v}=0 \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{\partial^3\psi}{\partial x^3}=-\frac{MRT(1-2x)}{x^2(1-x)^2}+2\frac{MRT\left(\frac{db}{dx}\right)^3}{(v-b)^3}=0 \quad . \quad . \quad (2)$$

$$\frac{\partial^2\psi}{\partial x\partial v}=\frac{MRT\frac{db}{dx}}{(v-b)^2}-\frac{\frac{da}{dx}}{v^2}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we put $a=A+2Bx+Cx^2$ and $b=b_1+x\beta=b_1+x(b_2-b_1)$ we get the equation:

$$\sqrt[3]{\frac{2x^2}{1-3x+2x^2}}=\tfrac{1}{2}\frac{C_2}{B+Cx}\left\{1\pm\sqrt{\left[1+\frac{4(B+Cx)(Cb_1-\beta B)}{C^2x\beta(1-x)}\right]}\right\}$$

If $B=a_{12}-a_1$ should be small in comparison with $a_1+a_2-2a_{12})x=Cx$, we get x equal to $^1/_3$ by approximation, at least if $\frac{b_1}{\beta}$ is also small.

Then real values are found both for x and for T and v; only this value of T can lie below the melting point in many cases, and consequently it cannot be observed.

However, I shall not enter into a further discussion. I will only point out, that for suitable values of T the curve $\frac{\partial^2\psi}{\partial x^2}=0$ represents a closed curve, which contracts with increasing value of T, and may contract into a point.

In the problem, for which $\frac{dv}{dx}=\infty$ at the plaitpoint, this case is the transition for the cases where $\frac{dv}{dx}$ is positive or negative. In the same way in the problem for which $\frac{dv}{dx}=0$ in the plaitpoint, this is a transition case between $\frac{dv}{dx}$ positive or negative. So the cases may also exist for which on the side of the small volumes, the quantity $\frac{dv}{dx}$ in the plaitpoint may have reversed sign.

When we examine the shape of the curves $\frac{\partial^2\psi}{\partial x\partial v}=0$ and $\frac{\partial^2\psi}{\partial x^2}=0$, it appears that it is required for the realisation of the case, that when $\frac{db}{dx}$ is positive, also $\frac{da}{dx}$ and $\frac{d^2a}{dx^2}$ are positive, and that the calculated temperature must lie above T_k of the first component when we want to apply the result to the coexistence of gas and liquid phases.

At the top we have the limiting case of two coexisting phases. If the tangent is // x-axis, the molecular volume is equal and the density will be proportional to $m_1(1-x)+m_2x$.

Put

$$d=\frac{m_1(1-x)+m_2x}{v} \text{ and } d'=\frac{m_1(1-x')+m_2x'}{v} \text{ and } d'-d=\frac{(m_2-m_1)(x'-x)}{v}.$$

When (m_2-m_1) and $(x'-x)$ have the same sign, $d'-d$ is positive. As $x'-x$ is negative when the first component has the smallest size of molecule, m_2-m_1 must also be negative, which is satisfied for helium and hydrogen.

We can, in general, represent the limiting density of a substance by $\frac{m}{b}$, and then the law would hold: When the most volatile substance has the greatest limiting density, the gas phase can be specifically heavier than the liquid phase. For Helium the limiting density is probably equal to that of the heavy metals. From the supposition that it is formed by splitting off from heavy metals this follows already with a certain degree of probability.

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[1] On further investigation it has appeared to me that a point that satisfies the equations $\frac{\partial^2\psi}{\partial x^2}=0$, $\frac{\partial^2\psi}{\partial x\partial v}=0$, and $\frac{\partial^3\psi}{\partial x^3}=0$, possesses the analytical character of a plaitpoint, but at least in many cases, does not behave practically as such. I hope to show this before long. (Added in the English translation).

Mathematics. — *"The rule of Neper in the four dimensional space."* By Dr. W. A. Wythoff). (Communicated by Prof. P. H. Schoute.

(Communicated in the meeting of December 29, 1906).

1. The wellknown "rule of Neper" can in principle be formulated as follows:

If we regard as elements of a spherical triangle $A_1 A_2 A_3$, rectangular in A_2, the two oblique angles A_1 and A_3 the hypothenuse a_2 and the complements of the two other sides $\frac{1}{2}\pi - a_1$ and $\frac{1}{2}\pi - a_3$ [1]) we can apply to each formula generally holding for the rectangular spherical triangle the cyclic transformation

$$(A_3, \quad \tfrac{1}{2}\pi - a_3, \quad a_2, \quad \tfrac{1}{2}\pi - a_1, \quad A_1)$$

without its ceasing to hold.

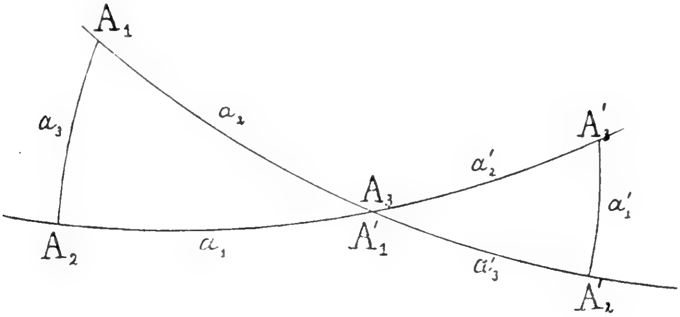

Fig. 1.

We prove this rule by prolonging the sides $A_1 A_3$ and $A_2 A_3$ which (Fig. 1) for convenience'sake we shall imagine as $< \frac{1}{2}\pi$, through the vertex $A_3 = A'_1$ with segments $A'_1 A'_2$ and $A'_1 A'_3$ so that $A_1 A'_2 = A_2 A'_3 = \frac{1}{2}\pi$. The spherical triangle $A'_1 A'_2 A'_3$ then proves to be again rectangular, namely in A'_2, whilst furthermore between the elements of both spherical triangles the following relations prove to exist:

$$A'_3 = \tfrac{1}{2}\pi - a_3 \quad ; \quad \tfrac{1}{2}\pi - a'_3 = a_2 \quad ; \quad a'_2 = \tfrac{1}{2}\pi - a_1 \; ;$$
$$\tfrac{1}{2}\pi - a'_1 = A_1 \quad ; \quad A'_1 = A_3 .$$

From this is evident that the above mentioned cyclic transformation can be applied to the elements of each rectangular spherical triangle without their ceasing to be the elements of a possible rectangular

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[1]) These are the complements of what Neper himself calls the "quinque circulares partes" of the rectangular spherical triangle. See N. L. W. A. Gravelaar, John Napier's werken, Verh. K. A. v. W., First section, vol. VI, N^0., 6, page 40.

spherical triangle, from which further the rule of NEPER immediately follows.

The train of thoughts followed here will be found back entirely in the following.

2. A hyperspherical tetrahedron I shall call *doublerectangular,* if two opposite edges stand each normal to one of the faces.

Let us suppose the letters A_1, A_2, A_3 and A_4 at the vertices of the tetahedron in such a manner that $A_1 A_2$ is perpendicular to the face $A_2 A_3 A_4$ and $A_3 A_4$ perpendicular to the face $A_1 A_2 A_3$.

To make the tetrahedron doublerectangular it is necessary and sufficient for the angles of position on the edges $A_1 A_3$, $A_2 A_4$ and $A_2 A_3$ to be right: ¹)

$$\alpha_{24} = \alpha_{13} = \alpha_{14} = \tfrac{1}{2}\pi\,;$$

from which then ensues:

$$\begin{aligned} &A_{23} = A_{24} = A_{32} = A_{31} = \tfrac{1}{2}\pi\,, \\ &A_{21} = \alpha_{34}\,, \\ &A_{34} = \alpha_{12}\,. \end{aligned}$$

If we do not count the rectangular elements and if we count those which are equal only once the doublerectangular hyperspherical tetrahedron has 15 elements, namely a_{12}, a_{13}, a_{14}, a_{23}, a_{24}, a_{34}, α_{12}, α_{23}, α_{34}, A_{12}, A_{13}, A_{14}, A_{41}, A_{42}, A_{43}.

3. We now form, starting from a doublerectangular hyperspherical tetrahedron $A_1 A_2 A_3 A_4$ of which we think the edges all $< \frac{1}{2}\pi$, a second hyperspherical tetrahedron (Fig. 2) by prolonging the edges meeting in $A_4 = A'_1$ through this vertex, namely the edge $A_1 A_4$ with a segment $A'_1 A'_2$, the edge $A_2 A_4$ with $A'_1 A'_3$ and the edge $A_3 A_4$ with $A'_1 A'_4$, so that $A_1 A'_2 = A_2 A'_3 = A_3 A'_4 = \frac{1}{2}\pi$.

By very simple geometrical considerations we find that the tetrahedron $A'_1 A'_2 A'_3 A'_4$ is again doublerectangular, that namely $A'_1 A'_2$ is perpendicular to $A'_2 A'_3 A'_4$ and $A'_3 A'_4$ perpendicular to $A'_1 A'_2 A'_3$; furthermore it is evident that the following relations exist between

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[1] The signs used here I have derived from Prof. Dr. P. H. SCHOUTE, Mehrdimensionale Geometrie, 1st vol., page 267, Sammlung SCHUBERT XXXV, Leipzig, G. J. GÖSCHEN, 1902.

So I understand

by a_{12} the edge $A_1 A_2$;

by α_{12} the angle of position formed by the faces lying opposite the vertices A_1 and A_2, i. e. the angle of position on the edge $A_3 A_4$;

by A_{12} the facial angle having A_1 as vertex and lying in the face opposite A_2, i. e. the angle $A_3 A_1 A_4$.

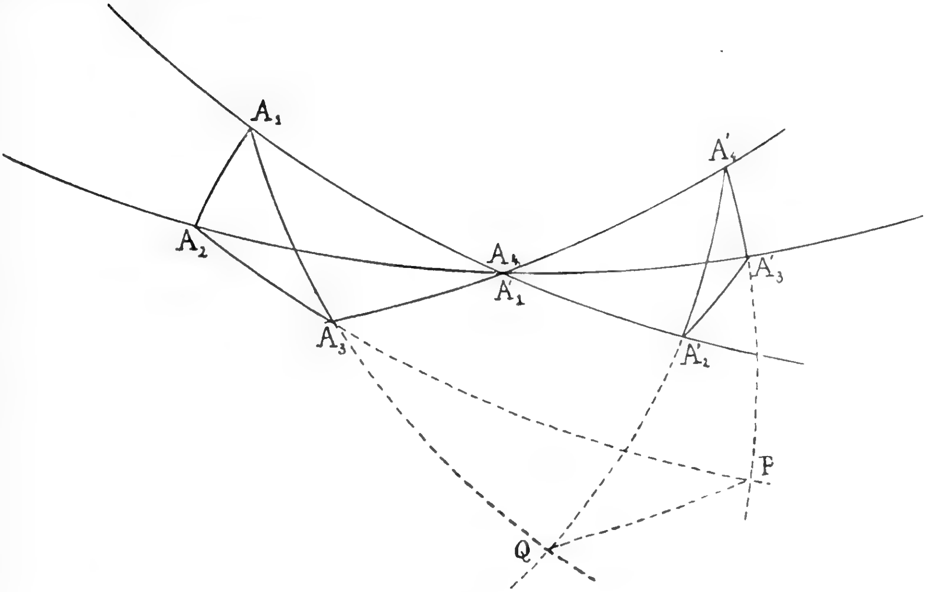

Fig. 2.

the elements of the two tetrahedra

$$\tfrac{1}{2}\pi - a'_{12} = a_{14} ,$$
$$a'_{14} = \tfrac{1}{2}\pi - a_{34} ,$$
$$\tfrac{1}{2}\pi - a'_{34} = a_{34} ,$$
$$a'_{34} = a_{23} ,$$
$$a'_{23} = a_{12} ,$$
$$a'_{12} = \tfrac{1}{2}\pi - a_{12} ;$$

$A'_{14} = A_{43}$, i. e. $(\tfrac{1}{2}\pi - A'_{14}) + A_{43} = \tfrac{1}{2}\pi$,

$A'_{43} + a_{13} = \tfrac{1}{2}\pi$,

$a'_{13} + a_{24} = \tfrac{1}{2}\pi$,

$a'_{24} + A_{12} = \tfrac{1}{2}\pi$,

$A'_{12} = A_{41}$, i. e. $A'_{12} + (\tfrac{1}{2}\pi - A_{41}) = \tfrac{1}{2}\pi$,

$A'_{41} + A_{14} = \tfrac{1}{2}\pi$ 1), i. e. $(\tfrac{1}{2}\pi - A'_{41}) + (\tfrac{1}{2}\pi - A_{14}) = \tfrac{1}{2}\pi$;

$$A'_{42} = \tfrac{1}{2}\pi - a_{23} ,$$
$$\tfrac{1}{2}\pi - a'_{23} = A_{13} ,$$
$$A'_{13} = A_{42} .$$

4. So if we regard instead of a_{12}, a_{34}, A_{14}, A_{41} and a_{23} their complements as elements of the tetrahedron, then the elements of the

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1) In giving the proof of this we must remember that $A'_4 A'_3$ and $A_2 A_3$ lie on a sphere and therefore cut each other in a point P, just as $A'_4 A'_2$ and $A_1 A_3$ cut each other in a point Q.

doublerectangular hyperspherical tetrahedron can be arranged in three cycles, two of 6 and one of 3 elements, namely

1. $(\frac{1}{2}\pi - a_{12}\,,\; a_{14}\,,\; \frac{1}{2}\pi - a_{34}\,,\; a_{34}\,,\; a_{23}\,,\; a_{12})$,
2. $(\frac{1}{2}\pi - A_{14}\,,\; A_{43}\,,\; a_{13}\,,\; a_{24}\,,\; A_{12}\,,\; \frac{1}{2}\pi - A_{41})$,
3. $(A_{42}\,,\; \frac{1}{2}\pi - a_{23}\,,\; A_{13})$,

so that it is possible to allow the elements of each cycle to undergo all simultaneously a cyclic transformation, if only afterwards those of the second cycle are replaced by their complements,[1]) without these elements ceasing to be the elements of a possible doublerectangular hyperspherical tetrahedron.

These same simultaneous transformations may thus be applied to each formula holding in general for elements of the doublerectangular hyperspherical tetrahedron.

5. If we again apply the construction described in § 1 to the newly formed spherical triangle, etc. we find a closed range of five spherical triangles of which the hypothenusae form a spherical pentagon.

The sides of these five spherical triangles are parts of five great circles on the sphere, namely the circles part of which is formed by the three sides of the original spherical triangle and the two polar circles of the vertices of its oblique angles. These five great circles form, however, another second similar range of five spherical triangles, namely that of the opposite triangles of the former range.

6. We can likewise deduce in a manner indicated in § 3 out of a doublerectangular hyperspherical tetrahedron a range of such tetrahedra of which the faces all belong to six spheres, namely the spheres part of which is formed by the faces of the original tetrahedron and the polar spheres of the points A_1 and A_4.

Let us call B_1 the polar sphere of A_1, B_2 that of A_4, B_3 the sphere $A_1 A_2 A_3$, B_4 the sphere $A_4 A_1 A_2$, B_5 the sphere $A_3 A_4 A_1$ and B_6 the sphere $A_2 A_3 A_4$.

Each of these spheres divides the hypersphere into two halves of which I shall designate the one to which the original tetrahedron

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[1]) If we write the second cycle

$$(\tfrac{1}{2}\pi - A_{14}\,,\; \tfrac{1}{2}\pi - A_{43}\,,\; a_{13}\,,\; \tfrac{1}{2}\pi - a_{24}\,,\; A_{12},\; A_{41})$$

or

$$(A_{14}\,,\; A_{43}\,,\; \tfrac{1}{2}\pi - a_{13}\,,\; a_{24}\,,\; \tfrac{1}{2}\pi - A_{12}\,,\; \tfrac{1}{2}\pi - A_{41}),$$

then no replacement of the elements by their complements is necessary, but the cycle has lost its symmetry with respect to the tetrahedron.

belongs by +, the other by —. The following list then indicates on which side of each of the six spheres the successive tetrahedra I, II, etc. are situated and by which they are limited. For the non-limiting spheres the sign has been placed in brackets.

	B_1	B_2	B_3	B_4	B_5	B_6
I	(+)	(+)	+	+	+	+
II	+	(+)	(+)	—	—	—
III	—	+	(+)	(—)	+	+
IV	+	—	+	(—)	(+)	—
V	—	+	—	—	(+)	(—)
VI	(—)	—	+	+	+	(—)
VII	(—)	(—)	—	—	—	—
VIII	—	(—)	(—)	+	+	+
IX	+	—	(—)	(+)	—	—
X	—	+	—	(+)	(—)	+
XI	+	—	+	+	(—)	(+)
XII	(+)	+	—	—	—	(+)
I	(+)	(+)	+	+	+	+

It is clear that the tetrahedra I and VII are opposite to each other, likewise II and VIII, III and IX, etc., whilst the tetrahedron I again follows tetrahedron XII.

Thus the whole range consists of 12 tetrahedra which are two by two opposite to each other, in contrast to what we found in the three-dimensional space, where *two* ranges of spherical triangles are formed of which one contains the triangles opposite to those of the other.

7. Between the volumes of each pair of tetrahedra belonging to the range exists a simple relation.

If we call V_I the volume of the first tetrahedron then the relation:

$$dV_I = \tfrac{1}{2}\, a_{12}\, da_{34} + \tfrac{1}{2}\, a_{14}\, da_{23} + \tfrac{1}{2}\, a_{34}\, da_{12}$$

holds for each variation of the tetrahedron remaining doublerectangular (thus a_{13}, a_{24} and a_{14} not changing).

Likewise

$$dV_{II} = \tfrac{1}{2}\left(\tfrac{1}{2}\pi - a_{14}\right) da_{23} + \tfrac{1}{2}\left(\tfrac{1}{2}\pi - a_{34}\right) da_{12} - \tfrac{1}{2}\left(\tfrac{1}{2}\pi - a_{34}\right) da_{12}\,.$$

So therefore

$$V_I + I_{II} = \tfrac{1}{4}\pi\alpha_{23} + \tfrac{1}{4}\pi\alpha_{12} - \tfrac{1}{2}\alpha_{12}(\tfrac{1}{2}\pi - \alpha_{34}) + \text{ constant.}$$

The constant is found by putting α_{12} equal to $\alpha_{23} = \alpha_{34} = \alpha_{12} = \frac{1}{2}\pi$, in which case V_I takes up the sixteenth part of the whole hypersphere, i. e. $\frac{1}{8}\pi^2$, whilst V_{II} becomes $= 0$.

The constant then proves to be $-\frac{1}{8}\pi^2$, hence

$$V_I + V_{II} = -\tfrac{1}{8}\pi^2 + \tfrac{1}{4}\pi\alpha_{12} + \tfrac{1}{4}\pi\alpha_{23} - \tfrac{1}{2}\alpha_{12}(\tfrac{1}{2}\pi - \alpha_{34}).$$

Likewise we find.

$$V_{II} + V_{III} = -\tfrac{1}{8}\pi^2 + \tfrac{1}{4}\pi(\tfrac{1}{2}\pi - \alpha_{12}) + \tfrac{1}{4}\pi\alpha_{12} - \tfrac{1}{2}(\tfrac{1}{2}\pi - \alpha_{14})(\tfrac{1}{2}\pi - \alpha_{23}),$$

$$V_{III} + V_{IV} = -\tfrac{1}{8}\pi^2 + \tfrac{1}{4}\pi\alpha_{14} + \tfrac{1}{4}\pi(\tfrac{1}{2}\pi - \alpha_{12}) - \tfrac{1}{2}\alpha_{34}(\tfrac{1}{2}\pi - \alpha_{12}), \text{ etc.}$$

Every time the sum of the volumes of two successive tetrahedra can be expressed by means of four successive elements of the first cycle mentioned in § 4. We deduce easily from this:

$$V_I - V_{III} = \tfrac{1}{2}\alpha_{12}\alpha_{34} - \tfrac{1}{2}\alpha_{14}(\tfrac{1}{2}\pi - \alpha_{23}),$$

whilst in like manner we can find $V_{II} - V_{IV}$, $V_{III} - V_V$, etc. Further we find

$$V_I + V_{IV} = \tfrac{1}{2}\alpha_{14}\alpha_{23} - \tfrac{1}{2}\alpha_{34}(\tfrac{1}{2}\pi - \alpha_{12}) - \tfrac{1}{2}\alpha_{12}(\tfrac{1}{2}\pi - \alpha_{34})$$

and in like manner $V_{II} + V_V$, etc.

If we remember that the tetrahedra I and VII are alike with respect to their elements and volumes, II and VIII also, etc. and that with respect to the volumes we have to deal with only a closed range of six terms we see that of each arbitrary pair always either the sum or the difference of the volumes can be expressed in a simple manner.

Mathematics. — *“The locus of the cusps of a threefold infinite linear system of plane cubics with six basepoints.”* By Prof. P. H. Schoute.

In the generally known representation of a cubic surface S^3 on a plane α to the plane sections of S^3 correspond the cubics through six points in α; here to the parabolic curve s^{12} of S^3 answers the locus C^{12} of the cusps of the linear system of those cubics. The principal aim of this short study is to deduce from wellknown properties of s^{12} properties of c^{12} and reversely.

1. If a plane rotates around a right line l of S^3 the points of intersection of that line l with the completing conic describe on l an involution, the double points of which are called the asymptotic points of l. According to the condition of reality of these asymptotic

points the 27 right lines of S^3, supposed to be real, are to be divided into two groups, into a group of 12 lines with imaginary asymptotic points, the lines

$$\left|\begin{array}{cccccc} a_1 & a_2 & a_3 & a_4 & a_5 & a_6 \\ b_1 & b_2 & b_3 & b_4 & b_5 & b_6 \end{array}\right.$$

of a doublesix and into a group of 15 lines $c_{12}, c_{13}, \ldots, c_{56}$ with real asymptotic points. If to the six basepoints A'_i of the linear system of the cubics the six lines a_i correspond — and this case we shall in the following continually have in view — then to the six lines b_i correspond the six conics $b_i^{\prime 2}$ through all the basepoints except A'_i and to the fifteen lines c_{ik} correspond the connecting lines $c'_{ik} = (A'_i, A'_k)$, whilst to the systems of conics (a_i^2) in planes through a_i, (b_i^2) in planes through b_i, (c_{ik}^2) in planes through c_{ik} correspond successively the pencils of the curves of the linear system with A'_i as doublepoint, the lines (b'_i) through A'_i and the conics $(c_{ik}^{\prime 2})$ through the four basepoints differing from A_i and A_k. The situation of the six points A'_i is then such that each of the fifteen lines c'_{ik} is touched in real points by two conics of the pencils $(c_{ik}^{\prime 2})$, whilst on the other hand the points of contact of the tangents out of the points A'_i to the conics $b_i^{\prime 2}$ are imaginary so that each point A'_i lies within the conic $b_i^{\prime 2}$ with the same index.

2. As a matter of fact all real points of a line l of S^3 are hyperbolic points of this surface with the exception of the two asymptotic points of this line showing a parabolic character; whilst each of these asymptotic points is point of contact of l with a conic lying on S^3, l touches in both points the parabolic curve S^{12}. If we apply this to each of the six lines a_i, imaged in the points A'_i, and if we consider that to a definite point P of a_i corresponds the point P' lying infinitely close to A'_i connected with A'_i by a line of definite direction (Versl., vol. I, pag. 143) we find immediately:

"The six basepoints A'_i of the linear system are fourfold points of the curve c^{12} of a particular character, consisting of the combination of two real cusps with conjugate imaginary cuspidal tangents, the cuspidal tangents of the curves out of the system with a cusp in A'_i".

The twelve points of intersection of the line c'_{ik} with c^{12} consist of the isolated points A'_i, A'_k counting four times and the real points of contact with two conics out of the pencil $(c_{ik}^{\prime 2})$ counting two times. Likewise do the 24 points of intersection of the conic $b_i^{\prime 2}$ with c^{12} consist of the five basepoints differing from A'_i counting four times and the imaginary points of contact with the tangents through A'_i counting two times.

3. From the investigations of F. Klein and H. G. Zeuthen dating from 1873 and 1875 it has become evident that the surface S^3 with 27 real right lines has ten openings and the parabolic curve s^{12} has ten oval branches. In connection with this we find:

"The locus c^{12} has ten oval branches."

We ask which situation of the six basepoints A'_i corresponds to the particular case of the "surface of diagonals" of Clebsch, in which the ten oval branches of the curve s^{12} have contracted to isolated points. In this case the fifteen lines with real asymptotic points, i.e. in our case the lines c'_{ik}, pass ten times three by three through a point; this is satisfied by the six points consisting of the five vertices of a regular pentagon and the centre of the circumscribed circle.

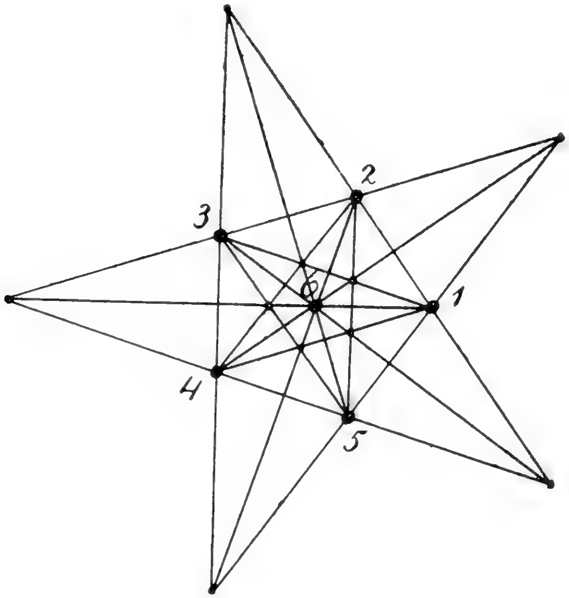

Fig. 1.

What is more, each six points having the indicated situation can be brought by central projection to this more regular shape. The ten meeting-points of the triplets of lines then form the vertices of two regular pentagons (fig. 1). The curve c^{12} corresponding to these six basepoints then consists of merely isolated points, namely of fourfold points in the six basepoints and twofold points in the ten meeting points of the triplets of lines.

The remark that the curve c^{12} belonging to the six basepoints of fig. 1 has the line c'_{16} as axis of symmetry and transforms itself into itself when rotating 72° around A'_6, enables us to deduce in a simple way its equation with respect to a rectangular system of coordinates with A'_6 as origin and c'_{16} as x-axis. The forms which pass into themselves by the indicated rotation are

$$\varrho^2 = x^2 + y^2,\quad P = x^5 - 10x^3y^2 + 5xy^4,\quad Q = 5x^4y - 10x^2y^3 + y^5.$$

If we pay attention to the axis of symmetry and to the identity $P^2 + Q^2 = \varrho^{10}$ the indicated equation can be written in the form

$$\varrho^4 + a\varrho^6 + b\varrho^8 + c\varrho^{10} + d\varrho^{12} + P(e + f\varrho^2 + g\varrho^4 + h\varrho^6) + P^2(i + k\varrho^2) = 0,$$

so that we have to determine only the ten coefficients $a, b, \ldots, k$. If now the common distance of the points $A'_1, A'_2, \ldots, A'_5$ to A'_6 is unity, then

$$x^4\left(x + \frac{3-e}{2}\right)^2 (x-1)^4 \left(x + \frac{3+e}{2}\right)^2 = 0,$$

where e stands for $\sqrt{5}$, represents the twelve points of intersection of the curve with the x-axis. By performing the multiplication this passes into

$$x^4\,(x^8 + 2x^7 - 7x^6 - 6x^5 + 20x^4 - 6x^3 - 7x^2 + 2x + 1) = 0.$$

From this follows

$$\begin{array}{llll} a = -7, & b = 20, & c + i = -7, & d + k = 1, \\ e = 2, & f = -6, & g = -6, & h = 2. \end{array}$$

So the equation

$$\varrho^4 - 7\varrho^6 + 20\varrho^8 - 7\varrho^{10} + \varrho^{12} + 2P(1 - 3\varrho^2 - 3\varrho^4 + \varrho^6) - Q^2(i + k\varrho^2) = 0$$

is determined, with the exception of the coefficients i and k still unknown. Now the parallel displacement of the system of coordinates to A'_1 as origin furnishes a new equation, of which the form

$$(4 - i - k)\,y^2 + 2\,(12 - 4i - 5k)xy^2 + x^4 + (54 - 28i - 45k)x^2y^2 + (5 + 4i + 3k)y^4$$

represents, after multiplication by 25, the terms of a lower order than five. The new origin being a fourfold point of c^{12} and the terms with y^2 and xy^2 having thus to vanish, we find

$$i = 8 \quad , \quad k = -4,$$

on account of which the indicated form passes into

$$(x^2 + 5y^2)^2.$$

The correctness of this result is evident from the following. Just as the two tangents in the old origin counting two times are represented by $x^2 + y^2 = 0$, and therefore coincide with the tangents out of A'_6 to the conic through the other basepoints, so $x^2 + 5y^2 = 0$ represents for the new origin A'_1 the pair of tangents out of A'_1 to the conic through the other basepoints. Or, if one likes, just as $x^2 + y^2$ is with the exception of a numerical factor, the fourth transformation ("Ueberschiebung") of the first member of the equation $Q = 0$ of the lines connecting A'_6 to the remaining basepoints, so $x^2 + 5y^2$ represents, likewise with the exception of a numerical factor, the fourth transformation of the first member of the equation $\frac{Py}{x} = 0$, which indicates with respect to the new origin A'_1 the five lines connecting A'_1 to the remaining basepoints.

Finally the equation of c^{12} is

$$\varrho^4(\varrho^8-7\varrho^6+20\varrho^4-7\varrho^2+1)+2P(\varrho^6-3\varrho^4-3\varrho^2+1)+4Q^2(\varrho^2-2)=0, \quad (1)$$

or entirely in polar coordinates (ϱ, φ)

$$4(\varrho^2-2)\varrho^5 \cos 5\varphi=(\varrho^2+1)(\varrho^4-4\varrho^2+1)\pm(\varrho^2-1)^2\sqrt{(\varrho^2-1)(4\varrho^2+1)(5\varrho^2-1)}. \quad (2)$$

It is easy to show that this curve admits of no real points differing from the six basepoints A'_i and the ten points of intersection of the triplets of connecting lines. If for brevity we write (2) in the form

$$L \cos 5\varphi = M \pm \sqrt{N},$$

then we find

$$- L^2 \sin^2 5\varphi = (M^2 + N - L^2) \pm 2M \sqrt{N} \quad . \quad . \quad . \quad (3)$$

and

$$\left.\begin{array}{l} M^2 + N - L^2 \equiv 2\,(\varrho^2-1)^2\,(2\varrho^2-1)(\varrho^8-6\varrho^6+14\varrho^4+2\varrho^2-1) \\ (M^2+N-L^2)^2 - 4M^2\,N \equiv 4\varrho^8\,(\varrho^2-1)^4\,(\varrho^2-2)^2\,(\varrho^4-7\varrho^2+1)^2 \end{array}\right\} \quad . \quad . \quad (4)$$

If now we moreover notice that N is negative and therefore $\cos 5\varphi$ complex when ϱ^2 lies between $\frac{1}{5}$ and 1, the following is immediately evident :

a. The first member of the second equation (4) tends to zero, when ϱ^2 assumes one of the values $0, 1, 2, \frac{1}{2}(7 \pm 3e)$; it is positive for all other values of ϱ^2.

b. If $\sqrt{N}$ is real and ϱ^2 differs from unity the second member of the first equation (4) is positive; for the equation

$$\varrho^8 - 6\varrho^6 + 14\varrho^4 + 2\varrho^2 - 1 = 0$$

has, as is evident when the roots ϱ^2 are diminished by $1\frac{1}{2}$, besides *one* real negative root only *one* real positive one between $\frac{1}{5}$ and 1.

c. If ϱ^2 differs from $0, 1, 2, \frac{1}{2}(7 \pm 3e)$ the second member of

(3) is positive when N is positive, and therefore φ is imaginary.

d. Neither does $\varrho^2 = 2$ give a real value for φ; for substitution in (1) furnishes for $\cos 5\varphi$ the result $\frac{3}{4}\sqrt{2}$.

e. So we find only the real points:

$\varrho = 0$, φ indefinite . . . . . . A'_6,
$\varrho = 1$, $\cos 5\varphi = 1$ . . . . . . A'_1, A'_2, A'_3, A'_4, A'_5,
$\varrho = \frac{3 \pm e}{2}$, $\cos 5\varphi = -1$ . . . the ten points of intersection of the fifteen connecting lines three by three.

4. We now consider a second case, in which the position of the six basepoints is likewise a very particular one, where namely these points form the vertices of a complete quadilateral. Through these six points not one genuine cubic with a cusp passes. For the three pairs of opposite vertices (A_1, A_2), (B_1, B_2), (C_1, C_2) of a complete quadilateral (fig. 2) form on each curve of order three, containing them, three pairs of conjugate points of the same system, and these do not occur on the cubic with a cusp, because through each point of such a curve only *one* tangent touching the curve elsewhere can be drawn. In this special case the locus of the cusps has broken

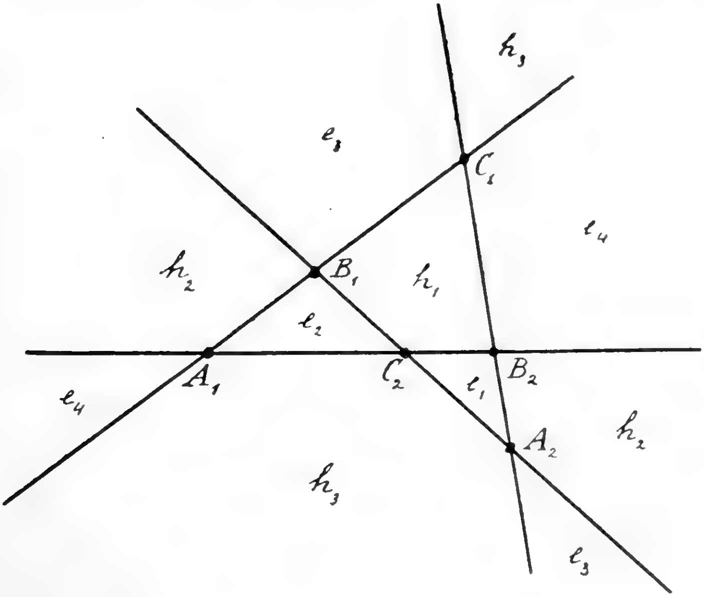

Fig. 2.

up into the four sides of the quadrilateral each of those lines counted three times. For it is clear that an arbitrary point of the line $A_1B_1C_1$ e. g., as a point of contact of this line with a conic passing through A_2, B_2, C_2, represents a cusp of the linear system of cubics. We can even expect that each of the four sides must be taken into account more than one time, because each of those points instead of being an ordinary cusp is a point, where two continuing branches touch each other. And finally the remark that the sides of the quadrilateral divide the plane into four triangles e with elliptic and three quadrangles h with four hyperbolic points, so that they continue to form the separation between those two domains, forces us to bring them an odd number of times into account, namely three times because we must arrive at a compound curve c^{12}.

Some more particulars with respect to the domains e and h. The nodal tangents of the cubic (fig. 3) passing through the three pairs of points (A_1, A_1), (B_1, B_2), (C_1, C_2) and having in P a node, are the double rays of the involution of the pairs of lines connecting

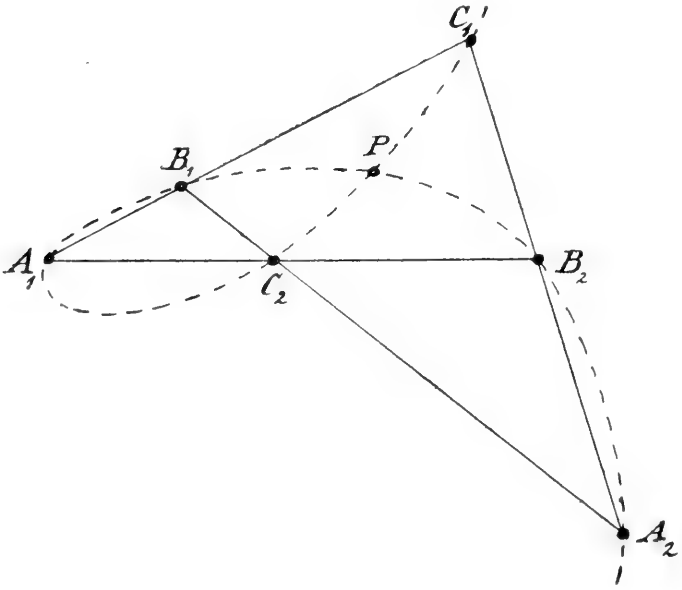

Fig. 3.

P with the three pairs of points mentioned, so also the tangents in P to the two conics of the tangential pencil with the sides of the quadrilateral as basetangents, passing through P; now, as these two conics are real or conjugate imaginary according to P lying in one of the three quadrangles h or in one of the four triangles e, what was assumed follows immediately.

To the case treated here of c^{12} broken up into four lines to be counted three times corresponds the parabolic curve of the surface S^3 with four nodes.

5. In the third place we consider still the special case of six basepoints lying on a conic, in which the linear system of cubics contains a net of curves degenerating into a conic and a right line; in this net of degenerated curves the conic is ever and again the conic c^2 through the six basepoints and the right line is an arbitrary right line of the plane.

This case can in a simple way be connected with a surface S^3 with a node O. If we project this surface out of this node O on a plane α not passing through this point, then the plane sections of the surface project as cubics passing through the six points of intersection of α with the lines of the surface passing through O; because these six lines lie on a quadratic cone, the six points of intersection with α lie on a conic. Besides, the sections with planes through O project as right lines; therefore the completing conic c^2 must evidently be regarded as the image of the node O. Of course we must here again think that c^2 corresponds point for point to the points of O^3 lying at infinite short distance from O^3; for c^2 is the section of α with the cone of the tangents to S^3 in O.

As c^2 with one of its tangents represents a curve of the linear system, this conic belongs at least twice to the locus of the cusps. Here too this locus of cusps improper with continuing branches must be accounted for three times, so that the locus proper is a curve c^6 of order six, touching c^2 in the six basepoints.

Let us suppose that c^2 is a circle and that the six basepoints on that circle (fig. 4) form the vertices of a regular hexagon, then the curve c^6 has the shape of a rosette with six leaves having the centre O' of the circle and the points at infinite distance of the diameters A_1A_4, A_2A_5, A_3A_6 as isolated points. Of the ten ovals there are four contracted to points, whilst the six remaining ones have joined into the circle of the basepoints and the curve c^6.

If we take point O' as origin and the line $O'A_1$ as x-axis of a rectangular system of coordinates, then if $O'A_1$ is unity of length we find for the equation of c^6

$$4y^2(y^2-3x^2)^2+9(x^2+y^2)^2-9(x^2+y^2)=0.$$

It is evident from this equation that the curve c^6 can really stand

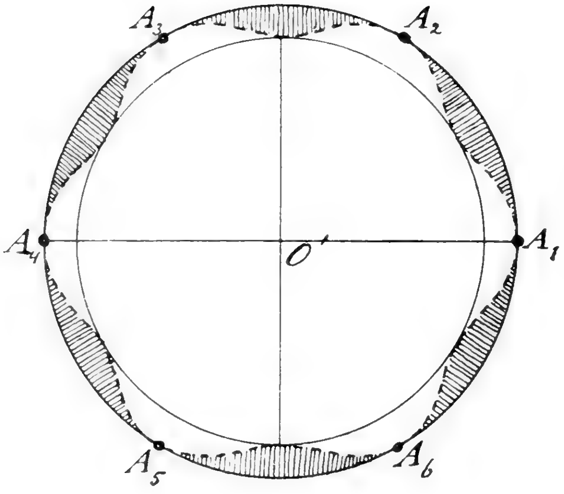

Fig. 4.

rotation of multiples of 60° round O', for then $x^2 + y^2$ and $y(y^2 - 3x^2$ are transformed into themselves.

Out of the equation

$$\sin 3\varphi = \pm \frac{3}{2r^2} \sqrt{1 - r^2}$$

on polar coordinates it is evident that the curve c^6 (with the exception of its four isolated points) is included between the circles described out of O' with the radii 1 and $\frac{1}{2}\sqrt{3}$.

If we pass from the locus of the cusps to the parabolic curve of S^3 we must notice that the last curve has the node O of S^3 as threefold point, because c^2 has separated itself three times from the locus c^{12}. So this parabolic curve is an s^9 of order nine, a result which will presently be arrived at in an other way.

We shall give — without wishing in the least to exhaust this case of the six basepoints situated on a conic — some degenerations of the remaining curve c^6 corresponding to some definite coincidences of the basepoints.

a) The cases (2, 2, 2), (4, 2), (6). If the six basepoints coincide two by two in three points of the conic, then c^6 consists of the sides of the triangle of the basepoints counted double, originating from compound cubics with a double line; there is not a locus proper. In reality the case (2, 2, 2) of a conic touching in three points cannot occur for a genuine cubic with a cusp.

The cases (4, 2) and (6) are to be regarded as included in the preceding. By allowing two of the vertices or the three vertices of the triangle just considered to coincide we find for case (4, 2) the connecting line of the two basepoints counted four times and the tangent to the conic in the basepoint of highest multiplicity counted two times, for case (6) the tangent to the conic in the point counting for six basepoints counted six times. That there can be no locus proper in the last case ensues also from the fact, that a genuine cubic with cusp allows of no sextactic point.

b) The case (3, 3). If the six basepoints coincide three by three in two points of the conic, then c^6 consists of a part improper, the connecting line of the two points counted four times, and a part proper, a conic touching the conic of the basepoints in these points. The new conic lies *outside* the conic of the basepoints.

c) The case (1, 5). This case agrees in many respects with the preceding. We find a part improper, the tangent in the point counting for five basepoints drawn to the conic of the basepoints, and a part proper, a conic touching the conic of the basepoints in these points. The new conic lies *inside* the conic of the basepoints.

6. Of course it is possible to call forth by the curve c^{12} successively all the different special cases which can put in an appearance by the parabolic curve s^{12} of the various surfaces S^3. As this would lead us here too far, we limit ourselves to a single remark, which can eventually facilitate an analytic investigation of this idea.

According to the general results with respect to a linear system of curves c^n obtained as early as 1879 by E. Caporali the locus $c^{4(2n-3)}$ of the cusps of this system has in each r-fold basepoint of the system a $4(2r-1)$ fold point and besides $6(n-1)^2-2\Sigma(3r^2-2r+1)$ nodes C. Each of those points C is characterized by the property that each curve of the system passing through this point is touched in this point by a definite line c.

For the case under observation, $n=3$ of the cubics, the number of points C is represented by $24-6p$, when p is the number of basepoints.

If we wish to investigate analytically what peculiarity the locus of the cusps shows in a basepoint of the system, or how a line through three basepoints separates from it, then the result — and this is the remark indicated — will be independent of the fact, whether the remaining basepoints occur or not, if in the former case, that some of these basepoints appear in a real or in an imaginary condition, we assume that these points both with respect to each other and to the former basepoints have not a particular position.

With the aid of this remark we can easily find the following theorems, with which we conclude:

"Both cusps of which the fourfold point of the curve c_{12} coinciding with a basepoint A'_i seems to consist and the two cusps of the curves of the system showing in this point a cusp, coincide in cuspidal tangents, but they turn their points to opposite sides."

"If the three basepoints A'_1, A'_2, A'_3 lie on a right line l, the locus proper of the cusps reduces itself to a curve c^9 touching the line l in A'_1. A'_2. A'_3. If the three remaining basepoints exist then the points of intersection of l with the sides of the triangle having those basepoints as vertices are points of c^9".

The last case answers to that of a surface S^3 with a double point; the parabolic curve having in this doublepoint a threefold point, because l separates itself three times from c^{12}, is as has been found above already a twisted curve of order nine.

Physics. — *"An investigation of some ultra-red metallic spectra."*

By W. J. H. Moll. (Communicated by Prof. W. H. Julius).

(Communicated in the meeting of December 29, 1906).

Among the spectra of known elements those of the alkali-metals, by their relatively simple structure, lend themselves particularly well to an investigation of their ultra-red parts. Many observers have consequently sought for emission lines of these metals in this region.

For the first part of the ultra-red spectrum the photographic plate may be sensitised; especially Lehmann 1) measured in this way various lines with wave-lengths ranging to almost 1 μ. By means of the bolometer Snow 2) could advance to 1.5 μ.

For the further region, however, nothing was known about these spectra. Coblentz 3), to be sure, was led by a series of observations in this respect, to the conclusion that the alkali-metals emit no specific radiation beyond 1.5 μ, but I had reason to doubt the validity of this conclusion.

In what follows I will briefly describe the method by which some ultra-red spectra were investigated, and the lines thus found. In an

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1) H. Lehmann. D.'s Ann. **5**. 633, 1901.

2) B. W. Snow. W.'s Ann. **47**, 208, 1892.

3) W. W. Coblentz. Investigations of Infra-red Spectra. Carnegie Inst. Washington. 1905.

academical thesis, which will soon be published, further details will be given.

For the investigation of the alkalies, the metallic salts were volatilised in the arc in the ordinary way. The very complicated band-spectrum, emitted by the arc when no metallic vapour is present, extends far into the ultra-red. But this interferes in no way with the investigation of the metals, since it is entirely superseded when the arc contains a sufficient quantity of metal. On the other hand the continuous spectrum, emitted by the incandescent particles in the arc, makes it somewhat difficult to observe some feebler lines; besides, the radiation of carbonic acid, the product of combustion of the carbons, (with a maximum near $4{,}44\,\mu$) persists with almost unchanged intensity.

The image of the arc is projected by a concave mirror on the slit of a reflecting-spectrometer; the rays are analysed by a rock-salt prism and part of the so formed spectrum falls on a linear thermopile. This thermopile, like that of RUBENS, is built up of iron and constantan; all the dimensions were chosen smaller than in the original pattern and a great sensitiveness was obtained. As well the emitting slit as the thermopile are mounted in fixed positions; in order to throw on this latter different parts of the spectrum in succession, the prism can be rotated through small angles. A WADWORTH combination of prism and plane mirror maintains minimum-deviation during rotation.

In chosing and designing the instruments, the desirability was kept in mind of replacing the very tiring reading of the galvanometer and the simultaneous noting of the corresponding position of the prism, by an automatical recording-device. I had in mind the splendid arrangement by which LANGLEY has for years recorded the intensity-curve of the ultra-red solar spectrum on a photographic plate. That this method has not been followed for recording heat-spectra instead of the time-absorbing visual observations, must be ascribed in the first place to a very complicated mechanism being required for obtaining complete correspondence between the linear displacement of the photographic plate and the rotation of the spectrometer, and secondly to the difficulty of keeping the surrounding temperature perfectly equal during the observations.

With very simple means I devised a method of recording, which avoids these two difficulties, while yet it warrants a sure "correspondence", and yields accurate results also when changes in the surrounding temperature cannot be prevented. For this purpose the continuous recording has been replaced by the marking of a series of dots, while for the continuous rotation of the spectrometer an intermittent one has been substituted. In this way for any recorded radiation-intensity the corresponding position of the prism can be found, not by *measuring* abscissae, but by *counting* dots. Since moreover not only the deflections of the galvanometer but each time also the zero-positions are recorded, it is possible to determine on the spectograms the radiation-intensities also when during the observations the surrounding temperature, and consequently the zero-position, was variable.

The principal advantages of this method of observation over the usual one are:

1. the absolute reliability of the observations,
2. the very short time required for a set of observations,
3. the accuracy with which interpolation is possible when the zero-position shifts,
4. the non-existence of disturbances, caused by the proximity of the observer,
5. the complete comparability of the different observations,
6. the possibility of estimating the probable error from the shape of the zero-line.

The short time in which a set of observations is made, is of importance when e.g. heat-sources are investigated which, like the arc, show slow changes in radiation-intensity. A spectrum, ranging from 0,7 to 6 μ was recorded with 200 displacements of the spectrometer in two hours.

In the spectrograms a spectral line is represented by 5 to 6 dots. With one displacement of the spectrometer namely the line is shifted over a distance amounting to $^2/_5$ of the breadth of the image of the slit, or of the equal breadth of the thermopile. Hence the same kind of radiation will strike the thermopile during five successive displacements. From the mutual position of the dots, the place where the radiation-intensity has its maximum may be accurately determined. In order to derive from this the place occupied by the line in the spectrum, it is sufficient to know one fixed point in the spectrum. This fixed point was as a rule taken from a comparison spectrum, for which the carbonic acid emission of a Bunsen flame was chosen, the maximum of which, according to very accurate measurements of PASCHEN, lies at 4.403 μ. Part of the flame spectrum was for this purpose recorded simultaneously with the spectrum to be studied.

A simple calculation then gives the refractive index for the unknown ray. In order to derive from this the wave-length of the line, a dispersion formula must be used. I became aware that the well-known dispersion curves of LANGLEY and of RUBENS show considerable differences, and although at first sight LANGLEY's determinations seem to be much preferable, yet on closer examination their excellence must be doubted, especially for the longer wave-lengths. To prefer one of the dispersion curves to the other seems to be at present a matter of arbitrary choice. So I have given in the tables besides the observed refractive indices, the wave-lengths, calculated from them as well by LANGLEY's as by RUBENS' formula. The refractive indices hold good for a temperature of 20°; their determination is based on the index 1.54429 for the D-line, a value, derived from very accurate determinations by LANGLEY.

The tables given below contain the lines of Na, K, Rb and Cs (I have been unable to obtain reliable results with Li in the arc) and of Hg. The results were derived from a large number of spectrograms (10 to 12 for each metal). For the investigation of the mercury spectrum a mercury arc-lamp was devised, furnished with a rock-salt window. The spectrum of mercury has been repeatedly investigated as far as 10μ; no measurable emission has been found beyond 1.7μ.

In the tables the first column gives the refractive index n of rock-salt, the second and third the wave-length μ of the line, according to the formulae of LANGLEY and RUBENS, and the fourth the approximate value I of the intensity.

For the lines of which the exact position was difficult to ascertain, the refractive index is only given in four decimals.

SODIUM.

n	μ(Langley)	μ (Rubens)	I
1.53529	0.819	0.816	240
.53062	1.14	1.13	180
.52961	1.27	1.25	15
.5286	1.44	1.42	5
.5281	1.57	1.54	5
.52711	1.85	1.80	25
.52613	2.21	2.16	45
.52589	2.31	2.25	35
.52455	2.90	2.84	20
.5234	3.42	3.36	5
1.52178	4.06	4.00	10

POTASSIUM.

n	μ(Langley)	μ (Rubens)	I
1.53654	0.771	0.768	620
.5325	0.97	0.96	10
.5310	1.11	1.10	20
.53030	1.18	1.17	320
.52972	1.25	1.24	200
.52823	1.53	1.50	95
.5261	2.24	2.18	5
.52486	2.76	2.70	20
.52401	3.14	3.08	20
.52263	3.73	3.67	15
1.52184	4.04	3.98	10

RUBIDIUM.

n	μ(Langley)	μ (Rubens)	I
1.53733	0.744	0.742	12
.53624	0.782	0.779	450
.5359	0.795	0.792	300
.5332	0.93	0.92	10
.53202	1.01	1.00	35
.5309	1.11	1.10	10
.52912	1.35	1.33	200
.52830	1.49	1.51	180
.52597	2.28	2.22	20
.52477	2.80	2.73	25
1.52186	4.03	3.97	10

CAESIUM.

n	μ(Langley)	μ (Rubens)	I
1.53566	0.803	0.801	40
.53451	0.855	0.851	250
.53375	0.895	0.891	200
.5333	0.920	0.914	75
.53202	1.01	1.00	90
.52902	1.37	1.35	70
.52846	1.48	1.45	80
.5275	1.74	1.70	5
.5264	2.08	2.03	5
.5257	2.41	2.35	5
.52433	3.00	2.93	50
.52315	3 .51	3.45	30
1.52203	3 97	3.91	10

MERCURY.

n	μ(Langley)	μ (Rubens)	I*
1.53198	1.01	1.00	28
.53076	1.13	1.11	8
.52907	1.36	1.34	11
.52828	1.52	1.49	5
1.52759	1.70	1.66	5

* The intensity of the green and yellow mercury lines has been put = 10.

Mathematics. — *"On the locus of the pairs of common points and the envelope of the common chords of the curves of three pencils."* 2nd part.: *Application to pencils of conics.* By Dr. F. Schuh. (Communicated by Prof. P. H. Schoute.)

(Communicated in the meeting of December 29, 1906).

9. If the pencils of curves are pencils of conics ($r = s = t = 2$) then in the case of there being no common base-points the locus is of order fifteen and the envelope of class six. In the following we

wish to treat the case more closely, that one of the pencils has two points in common with each of the two others, where we shall attain at results in another way, which will prove to agree to the general ones and complete these in some parts.

Let $ABCD$, $ABEF$ and $CDGH$ be the three pencils of conics. On one conic of the pencil $ABCD$ the two other pencils describe two quadratic involutions of which the connecting lines of the pairs of points pass through a point K of EF, resp. a point L of GH. The pair of common points PP' of these two involutions is thus determined by the right line KL. If the conic $ABCD$ describes the whole pencil, K and L describe projective series of points on EF and GH. For, if we take K arbitrarily on EF, the conic $ABCD$ is determined by it, as it must pass through the second point of intersection of CK with the conic $ABEFC$ (as likewise through the second point of intersection of DK and the conic $ABEFD$); by the conic $ABCD$ the point L is unequivocally determined. Reversely to a point L of GH now corresponds one point K. The projective series of points are however in general not perspective; *so the line KL or PP' envelops a conic N touching EF and GH.*

Of that conic three other tangents are easy to construct, namely by taking for the conic $ABCD$ in succession each of the three degenerations. If that conic is $AB \,.\, CD$ then the movable points of intersection with conics of the pencil $ABEF$ lie on CD so that K lies on CD, thus in the point of intersection K_1 of CD and EF; likewise does L coincide with the point of intersection L_1 of AB and GH. The line K_1L_1 is thus tangent to N. The construction becomes a little less simple if we take one of the other degenerations e.g. $AC \,.\, BD$. By cutting this by the degenerated conic $AE \,.\, BF$ of pencil $ABEF$ it is evident that K coincides with the point of intersection of EF with the line connecting the point of intersection of AE and BD with the point of intersection of BF and AC; in similar manner L is found.

To the locus of the points P and P' belongs the locus of the points of intersection of the conics of the pencil $ABCD$ with the projectively related series of tangents KL of the conic N. This locus (as is easily evident out of the points of intersection with an arbitrary right line or with an arbitrary conic of the pencil $ABCD$) is of order five with double points in A, B, C and D; further it passes through E, F, G and H, as K coincides with E when the conic $ABCD$ passes through E, etc. If we take for the conic of the pencil $ABCD$ the degeneration $AB \,.\, CD$, then KL passes into K_1L_1 which line cuts the conic $AB \,.\, CD$ in the points K_1 and L_1, which thus lie on the locus of the points of intersection too. By taking the two other degenerations we find four more points of C_5. Altogether there are 10 single and 4 double points by which C_5 is determined.

If we take the degeneration $AB \,.\, CD$, the particularity occurs, that the pair of points of the involution described by the pencil $ABEF$ can become indefinite on AB, if namely the conic $ABEF$ breaks up into $AB \,.\, EF$. By this the whole line AB (and of course the line CD too) will belong to the locus proper of P and P' [1]). To the part proper of the envelope of the lines PP' the pairs of points PP' lying on AB or CD contribute nothing but the lines AB and CD (which belong also to the part improper of the envelope, the points A, B, C and D), which does not give rise to a higher class.

So the locus proper of P and P' consists of the lines AB and CD and the curve C_5 and is thus in accordance to the general results of order seven. The line AB (CD) intersects C_5 in the points A and B (C and D) to be counted double and in L_1 (K_1). *The curve* C_7 *has three double points differing from the base-points* (of which E, F, G and H are single and A, B, C and D threefold points of C_7) *namely* K_1, L_1 *and the point of intersection* T *of* AB *and* CD. These form a triplet of double points belonging together of which we spoke in § 5. The conics of the three pencils passing through one of those double points, also pass through the two others; these conics are $AB \,.\, CD$, $AB \,.\, EF$ and $CD \,.\, GH$. To the branches TK_1 and TL_1 of C_7 passing through T correspond respectively the branches K_1T and L_1T passing through K_1 and L_1, whilst the branches of C_5 passing through K_1 and L_1 correspond mutually.

Summing up we find:

For the conics $ABCD$, $ABEF$ *and* $CDGH$ *the locus proper of the pairs of common points* PP' *consists of the lines* AB *and* CD *and a curve of order five, having in* A, B, C *and* D *double points and in* E, F, G *and* H *single points and further passing through the point of intersection* K_1 *of* CD *and* EF *and the point of intersection* L_1 *of* AB *and* GH. *The envelope proper of the lines* PP' *is a conic touching the lines* EF, GH *and* K_1L_1.

10. *If the points* A, B, C, D, E *and* F *lie on a conic,* the latter then belongs to the locus, so that the C_5 breaks up into that conic and a C_3 passing through A, B, C, D, G, H, K_1 and L_1. To each conic of the pencil $ABCD$ now belongs the same point K, namely K_1, as is immediately evident when we make the conic of

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[1]) More generally: if two base-points of one pencil lie with two base-points of another pencil on a right line, that line belongs to the locus proper.

the pencil $ABEF$ to pass through C and D. If we take $ABCDEF$ for the conic of the pencil $ABCD$, then K is indefinite on EF, whilst point L is to be found somewhere in L_2 on GH. The correspondence between the points K and L is of such a kind that to a point L differing from L_2 the same point K always corresponds, namely K_1, whilst when L coincides with L_2 point K is arbitrary on EF. *So the conic N breaks up into the two points K_1 and L_2.* The relation between the conics of the pencil $ABCD$ and the tangents KL or PP' of N is of such a kind, that to the conic $ABCDEF$ every line through L_2 corresponds and that, for the rest, between the conics $ABCD$ and the lines through K_1 a projective relation exists, in which to the conics $ABCDEF$, $ABCDG$, $ABCDH$ and the degenerated conic $AB . CD$ respectively K_1L_2, K_1G, K_1H and K_1L_1 correspond. From this is also evident, that *the curve C_5 breaks up into the conic $ABCDEF$ and a C_3 passing through A, B, C, D, G, H, K_1 and L_1* and farther that *C_3 passes through the points of intersection of K_1L_2 with the conic $ABCDEF$.*

The double points of $C_7 = AB . CD . ABCDEF . C_3$ differing from the base-points are K_1, L_1, T and the two points of intersection of K_1L_2 with $ABCDEF$. The latter two doublepoints do not furnish a triplet of points through which conics of the three pencils pass, but two coinciding pairs of points; the branches through one doublepoint correspond to the branches through the other and, it goes without saying, in such a way that the branches belonging to C_3 correspond mutually and likewise the branches belonging to the conic $ABCDEF$.

11. *If moreover the points A, B, C, D, G and H lie on a conic,* C_3 breaks up into that conic and the line K_1L_1 (L_2 then coincides with L_1) *so that the locus proper then consists of the conics $ABCDEF$ and $ABCDGH$ and the lines AB, CD and K_1L_1.* When conic $ABCD$ does not pass through E, and F neither through G and H, the point K coincides with K_1 and L with L_1; so that the pair of points PP' lying on that conic is always determined by the same line K_1L_1. Hence K_1L_1 forms part of the locus. The C_7 has now seven double points differing from the base-points, namely one triplet K_1, L_1, T, and two pairs, the two points of intersection of K_1L_1 with the conic $ABCDEF$ and those with the conic $ABCDGH$.

If the point K_1 coincides with L_1 and therefore also with T, i.o.w. *if the four lines AB, CD, EF and GH pass through one point,* on each conic of the pencil $ABCD$ the two involutions coincide. *The locus proper then becomes indefinite. If we bring through an arbi-*

trary point P a conic of each of the pencils, then those conics have another second common point, namely the second point of intersection of the line TP with the conic $ABCDP$. The envelope proper is then still definite and consists of two coinciding points T.

12. *If the points E and G coincide,* then if the conic of the pencil $ABCD$ passes through E the point K as well as the point L coincides with E. The series of points K and L are perspective, the lines KL all pass through a selfsame point U.

The conic N breaks up into two points E and U. As E belongs to the part improper of the envelope, *the envelope proper now consists only of point U.* By taking for the conic of the pencil $ABCD$ the degeneration $AB \cdot CD$ it is evident that U lies on the line $K_1 L_1$. Another line KL and by that the point U itself can be constructed in the way indicated in § 9 by allowing the conic $ABCD$ to break up into $AC \cdot BD$ or $AD \cdot BC$.

Between the lines KL or PP' through U and the conics of the pencil $ABCD$ exists a projective correspondence, where to the conics $ABCDE$, $ABCDF$, $ABCDH$ and $AB \cdot CD$ respectively the lines UE, UF, UH and $K_1 L_1$ correspond. *The locus of the points of intersection is a cubic through the points $A, B, C, D, U, E, F, H, K_1$ and L_1,* which is determined by these 10 points; the third points of intersection of that curve with AC, AD, BC and BD are easy to construct.

On the conic $ABCDE$ the two involutions coincide, so that that conic has separated from the C_5 of § 9 and has become improper. *The locus proper consists now of the lines AB and CD and the above-named C_3, so it is of order five.* Differing from the base-points the C_5 has three double points, K_1, L_1 and T (the point of intersection of AB and CD) forming a triplet.

If moreover the points A, B, C, D, E and F lie on a conic, no other particularity appears than *the point U coinciding with K_1.* Of the three points of intersection K_1, L_1 and U of $K_1 L_1$ with the C_3 the points K_1 and U now coincide, *so that the C_3 touches the line $K_1 L_1$ in K_1.* In comparison with § 10 the particularity that appears is this that the point L_2 coincides with E whilst the pencil of rays L_2 has passed into the part improper of the envelope and the conic $ABCDEF$ into the part improper of the locus.

13. The case treated in the preceding paragraph is of course not the only one in which the series of points K and L are perspective, the condition of that perspectivity being single, the condition of the

coincidence of E and G being double. The condition of perspectivity can be found out of the condition that the point of intersection V of EF and GH (as point K) corresponds to itself (as point L). Now the conic $ABCD$ belonging to V (as point K) passes through the second point of intersection W of CV with the conic $ABEFC$, whilst C, W is a pair of points of the involution described on the conic $ABCDW$ by the pencil $ABEF$. If this pair of points also belongs to the involution described on that same conic by the pencil $CDGH$, the point L coincides evidently with V. So this is the case *when the conic of the pencil $CDGH$ touching the conic $ABCDW$ in C passes through W.* This condition for the perspectivity of the series of points K and L (where of course it must be possible to interchange C with D and likewise AB resp. EF with CD resp. GH) is evidently satisfied when E and G coincide.

If U is the centre of perspectivity, there exists between the rays of the pencil U and the conics of the pencil $ABCD$ a projective correspondence, where to the conics $ABCDE$, $ABCDF$, $ABCDG$, $ABCDH$, $ABCDW$ and $AB \cdot CD$ correspond respectively the rays UE, UF, UG, UH, UV and $K_1 L_1$, whilst moreover to the conic $ABCDW$ all the rays of the pencil V correspond. So the C_5 of § 9 breaks up into the conic $ABCDW$, still belonging to the part proper of the locus, and a C_3 passing through the points $A, B, C, D, U, E, F, G, H, K_1$ and L_1, cutting the conic in A, B, C and D and the two points of intersection of UV with that conic.

The locus proper is thus a C_7 consisting of the lines AB and CD, the conic $ABCDW$ and the C_3 before mentioned. This C_7 has five double points differing from the base-points, namely, the triplet K_1, L_1, T and the pair formed by the points of intersection of UV with the conic $ABCDW$.

The C_3 is determined by the ten points, $A, B, C, D, E, F, G, H, K_1$ and L_1 so these ten points will have to lie on a C_3 if the above condition for the perspectivity is satisfied, and reversely it is easy to prove that when those ten points lie on a C_3 the series of points are perspective. Suppose namely that the series of points were not perspective. Then it would be possible by keeping the points A, B, C, D, E, F and G to construct on the line GH (thus by keeping the points K_1, L_1, V and W) by means of the former condition for perspectivity a point H' in such a manner that the series of points K and L are perspective; H' is then the second point of intersection of VG with the conic through C, D, G and W, touching the conic $ABCDW$ in C. So now the ten points A, B, C, D, E, F, G, K_1, L_1 and H' will lie on a C_3, however already determined by the nine former points [1]) and thus the same as C_3 through the ten points $A, B, C, D, E, F, G, K_1, L_1$ and H. The line VG would then however have four points G, L_1, H and H' in common with this C_3.

So we arrive at the following simple result:

If the ten points $A, B, C, D, E, F, G, H, K_1$ and L_1 lie on the same cubic, the series of points K and L are perspective, whilst the centre of perspectivity coincides with the third point of intersection U of K_1L_1 with C_3. The envelope proper breaks up into the point U and the point of intersection V of EF and GH. The locus proper consists of the lines AB and CD, the cubic just mentioned and the conic through A, B, C, D and the two points, in which the right line UV intersects moreover the C_3 besides in U.

If E and G coincide, we immediately see that the above condition is satisfied. The point V lies then in point E so that one point of intersection of UV with C_3 differing from U becomes the point E; the indicated conic is thus the conic $ABCDE$, which now however belongs to the part improper of the locus.

14. *If G coincides with E and H with F*, then the series of points K and L are connective with double points in E and F. The pair of points PP' on an arbitrary conic of the pencil $ABCD$ is now continually described by the same line EF, thus belonging to the locus proper. If the conic passes through E or F the two involutions coincide, so that the conics $ABCDE$ and $ABCDF$ belong to the locus, but to the part improper of it. Moreover the lines AB and CD belong to the locus proper, *so that the latter consists of the three lines AB, CD and EF.* An envelope proper is no more at hand, the line connecting P and P' coinciding with AB, CD or EF when P and P' differ from the base-points.

In comparison with § 12 the particularity appears that U coincides with F, that the pencil of rays U passes into the part improper of the envelope and that the C_3 breaks up into the conic $ABCDF$ becoming improper and the right line EF.

The case of the pencils of conics $ABCD$, $ABEF$ and $CDEF$ can be profitably used to define with the help of the principle of the permanency of the number the order of the locus of P and P' and the class of the envelope of PP' for the case of pencils of conics lying arbitrarily with respect to each other. Starting from this simplest

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[1]) The C_3 is only then not determined by these nine points if two of those points coincide in such a way that the connecting line is indefinite (e.g. G with E or K_1 with L_1). Then the ten points lie on a C_3, whilst it is easy to prove that the correspondence between K and L is perspective.

case, it is easy to reason that PP' coincides with AB, CD or EF and so the locus proper consists of these three lines and there is no envelope proper. The part improper of the locus however consists of six conics $ABCDE$, $ABCDF$, $ABEFC$, $ABEFD$, $CDEFA$ and $CDEFB$, the part improper of the envelope of the six points A, B, C, D, E and F. The total locus is thus of order fifteen, the total envelope of class six, so that for arbitrary position of the pencils of conics this same holds for the locus proper and the envelope proper.

Sneek, Nov. 1906.

Mathematics. — *"The locus of the pairs of common points of four pencils of surfaces."* By Dr. F. Schuh. (Communicated by Prof. P. H. Schoute).

(Communicated in the meeting of December 29, 1906).

1. Given four pencils of surfaces (F_r), (F_s), (F_t) and (F_u) respectively of order r, s, t and u. The base-curves of those pencils can have common points or they can in part coincide, in consequence of which of three arbitrary surfaces of the pencils (F_s), (F_t) and (F_u) the number of points of intersection differing from the base-curves can become less than $s\,t\,u$; we call this number a, calling it b for the pencils (F_r), (F_t) and (F_u), c for the pencils (F_r) (F_s) and (F_u) and d for the pencils (F_r), (F_s) and (F_t). We now put the question:

What is the order of the surface formed by the pairs of points P and P', through which a surface of each of the four pencils is possible?

If the points P and P' do not lie on the base-curves we call the locus formed by those points the *locus proper* L on which of course still curves of points P may lie for which the corresponding point P' lies on one of the base-curves. If *one* triplet of pencils furnishes at least several points of intersection which are situated for all surfaces of those pencils on one of the base-curves, then there is a surface that *does* satisfy the question but in such a manner that if we assume P arbitrarily on this surface the point P' belonging to it is to be found on one of the base-curves; this surface we call the *part improper* of the locus, whilst both surfaces together are called the *total locus*.

2. To determine the order n of the locus proper L we find the points of intersection with an arbitrary right line l. On l we take

an arbitrary point Q_{stu} and we bring through that point surfaces F_s, F_t and F_u of the pencils (F_s), (F_t) and (F_u). Through each of the $a-1$ points of intersection of those surfaces not situated on the base-curves of those surfaces we bring a surface F_r. These $a-1$ surfaces F_r intersect the right line l together in $(a-1)r$ points Q_r, which we make to correspond to the point Q_{stu}. The coincidences of this correspondence are: 1st the points Q_{rstu} determining four surfaces which intersect one another once more in a point not lying on the base-curves, thus the n points of intersection with the surface L, 2nd the points of intersection with the surface R_{stu} belonging to the pencils (F_s), (F_t) and (F_u), the locus of the points S determining three surfaces whose tangential planes in S pass through one line.

To find the number of coincidences we have to determine the number of points Q_{stu} corresponding to an arbitrary point Q_r of l. To this end we take on l a point Q_{tu} arbitrarily and bring through it an F_t and an F_u. Through each of the b points of intersection of these surfaces with the surface F_r through Q_r (not lying on the base-curves) we bring an F_s, which b surfaces F_s intersect together the line l in bs points Q_s which we make to correspond to Q_{tu}. To find the number of points Q_{tu} corresponding to an arbitrary point Q_s of l we take Q_u arbitrarily on l, we bring through Q_s an F_s and through Q_u an F_u and through each of the c points of intersection of those surfaces with F_r an F_t, which furnish c surfaces F_t cutting l in ct points Q_t; reversely to Q_t belong du points Q_u, so that we find between the points Q_u and Q_t a (ct, du)-correspondence, of which the $ct+du$ coincidences give the points Q_{tu} belonging to the point Q_s. So between the points Q_{tu} and Q_s exists a $(bs, ct+du)$-correspondence, of which the coincidences consist of the r points of intersection of l with the surface F_r through Q_r and of the points Q_{stu} corresponding to Q_r; the number of these thus amounts to $bs+ct+du-r$.

So between the points Q_{stu} and Q_r there is an $(ar-r, bs+ct+du-r)$-correspondence with $ar+bs+ct+du-2r$ coincidences. To find out of this the number of points Q_{rstu} we must first determine the order of the surface R_{stu}.

This surface may be regarded as the surface of contact of the surfaces of the pencil (F_s) with the movable curves of intersections C_{tu} of the surfaces of the pencils (F_t) and (F_u) [1]. So the question is:

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[1] We shall call this surface the surface of contact of the three pencils meaning by this that in a point of this "surface of contact" the surfaces of the pencils, though not touching one another, admit of a common tangent.

3. *To determine the order of the surface of contact of a twofold infinite system of twisted curves and a singly infinite system of surfaces.*

To this end we shall first suppose the two systems to be arbitrary.

To determine the order of the surface of contact we count its points of intersection with an arbitrary right line l. To this end we consider the envelope E_1 of the ∞^2 tangential planes of the curves of the system in their points of intersection with l and the envelope E_2 of the ∞^1 tangential planes of the surfaces of the system in their points of intersection with l.

The common tangential planes not passing through l of both envelopes indicate by means of their points of intersection with l the points of intersection of l with the surface of contact.

In order to find the class of the envelope E_1 (formed by the tangential planes of a regulus with l as directrix) we determine the class of the cone enveloped by the tangential planes passing through an arbitrary point Q of l. If the system of curves is such that φ curves pass through an arbitrary point and ψ curves touch a given plane in a point of a given right line, the tangential planes of E_1 through Q envelope the φ tangents in Q of the curves of the system through Q, and the line l counting ψ times; for each plane through l is to be regarded ψ times as tangential plane, there being ψ curves of the system cutting l and having a tangent situated in this plane. *The envelope E_1 is thus of class $\varphi + \psi$ and has l as ψ-fold line*[1].

To find the class of the envelope E_2 we determine the number of its tangential planes through an arbitrary point Q of l. If now the system has μ surfaces through a given point and ν surfaces touching a given right line, the tangential planes of the envelope passing through Q are the tangential planes in Q to the μ surfaces passing through Q and the tangential planes of the ν surfaces touching l. *So the envelope E_2 is of class $\mu + \nu$ with ν tangential planes through l.*

Hence both envelopes have $(\varphi + \psi)(\mu + \nu)$ common tangential planes. Each of the ν tangential planes of E_2 passing through l is however a ψ-fold tangential plane of E_1 and so it counts for ψ common tangential planes. So for the number of common tangential planes not passing through l, thus the number of points of intersection of l with the surface of contact we find:

$$(\varphi + \psi)(\mu + \nu) - \psi\nu = \varphi\nu + \psi\mu + \varphi\mu ,$$

therefore:

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[1] The regulus as locus of points has however line l as φ-fold line.

The surface of contact of a system (φ, ψ) *of* ∞^2 *twisted curves*[1]) *and a system* (μ, ν) *of* ∞^1 *surfaces*[2]) *is of order* $\varphi\nu + \psi\mu + \varphi\mu$[3]).

4. To determine the order of the surface of contact[4]) of the systems $\mu_1 , \nu_1)$, (μ_2 , ν_2) and (μ_3 , ν_3) each of ∞^1 surfaces, we regard the system (φ , ψ) of the curves of intersection of the systems (μ_1 , ν_1) and (μ_2 , ν_2). Of these curves of intersection $\mu_1\mu_2$ pass through a given point, so $\varphi = \mu_1\mu_2$. The ψ points, where the curves of intersection touch a given plane in a point of a given right line, are the points of intersection of that given line with the curve of contact of the systems (μ_1 , ν_1)[5]) and (μ_2 , ν_2) of plane curves, according to which the given plane intersects the systems of surfaces (μ_1 , ν_1) and (μ_2 , ν_2). This curve of contact is of order $\mu_1\nu_2 + \mu_2\nu_1 + \mu_1\mu_2$, thus:

$$\psi = \mu_1\nu_2 + \mu_2\nu_1 + \mu_1\mu_2 .$$

The surface of contact to be found is thus the surface of contact of a system $(\mu_1\mu_2 , \mu_1\nu_2 + \mu_2\nu_1 + \mu_1\mu_2)$ of ∞^2 twisted curves and a system (μ_3 , ν_3) of ∞^1 surfaces, so that we find:

The surface of contact of three systems (μ_1 , ν_1), (μ_2 , ν_2) *and* (μ_3 , ν_3) *of* ∞^1 *surfaces is of order*

$$\mu_2\mu_3\nu_1 + \mu_3\mu_1\nu_2 + \mu_1\mu_2\nu_3 + 2\mu_1\mu_2\mu_3 .$$

If the three systems are the pencils (F_s), (F_t) and (F_u) we have

$$\mu_1 = \mu_2 = \mu_3 = 1,$$

$$\nu_1 = 2(s - 1) \quad , \quad \nu_2 = 2(t-1) \quad , \quad \nu_3 = 2(u-1).$$

So we find:

The surface of contact F_{stu} *of the three pencils of surfaces* (F_s), (F_t) *and* (F_u) *is of order*

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[1]) System with φ curves through a given point and ψ curves cutting a given line and touching in the point of intersection a given plane through that line.

[2]) System with μ surfaces through a given point and ν surfaces touching a given right line.

[3]) This result is also immediately deducible from the Schubert formula

$$xp^2 = p'^3 . G + p'g'_e . p^2g_e + p'^3 . p^2g_e$$

(Kalkül der abzählenden Geometrie, formula 13, page 292) for the number of common elements with a point lying on a given line of a system Σ' of ∞^3 and a system Σ of ∞^4 right lines with a point on it. If we take for Σ' the tangents with point of contact of the system of curves (φ , ψ) and for Σ the tangents with point of contact of the system of surfaces (μ , ν), then

$$p'^3 = \varphi \quad , \quad p'g'_e = \psi \quad , \quad G = \nu \quad , \quad p^2g_e = \mu \, ,$$

whilst xp^2 is the order of the surface of contact.

[4]) Locus of the points, where the surfaces of the three systems have a common tangent.

[5]) System of ∞^1 curves of which μ_1 pass through a given point and ν_1 touch a given right line.

$$2(s+t+u-2).$$

5. To return to the question which gave rise to the preceding considerations we find for the number of points Q_{rstu} on the arbitrary line l, which are the points of intersection of l with the locus proper L:

$$ar+bs+ct+du-2r-2(s+t+u-2)=$$
$$=ar+bs+ct+du-2(r+s+t+u)+4.$$

So we find:

The locus L of the pairs consisting of two movable points common to a surface out of each of the pencils (F_r), (F_s), (F_t) and (F_u) of orders r, s, t and u, and not lying on the base-curves, is a surface of order

$$ar+bs+ct+du-2(r+s+t+u)+4.$$

Here a is the number of points of intersection not necessarily situated on the base-curves of the pencils (F_s), (F_t) and (F_u); b the analogous number for the pencils (F_r), (F_t) and (F_u), etc.

6. It the pencils have an arbitrary situation with respect to each other, then $a=stu$, etc., so that then the order of the locus becomes

$$4(rstu+1)-2(r+s+t+u).$$

That order is lowered when three of the base-curves have a common point or two of the base-curves have a common part, which lowering of the order can be explained by separation as long as the total locus is definite, i. e. as long as the four base-curves have no common point and no triplet of base-curves have a common part. For, if A_{rstu} is a common point of four base-curves then the surfaces of the four pencils passing through an entirely arbitrary point P have another second point in common, namely A_{rstu}; if B_{stu} is a curve forming part of the base-curves B_s, B_t and B_u of the pencils (F_s), (F_t) and (F_u), then the surfaces of the pencils passing through an arbitrary point P have moreover the points of intersection in common of B_{stu} with the surface F_r through P; so in both cases the arbitrary point P belongs to the total locus.

If the basecurves B_s, B_t and B_u have a common point A_{stu} then on account of that point the number a is diminished by unity without having any influence on b, c and d. The order of L is thus lowered by r on account of it, which is immediately explained by the fact that *the surface F_r passing through A_{stu} separates itself from the locus.*

If the base-curves B_t and B_u have a curve B_{tu} in common of which for convenience we suppose that it does not intersect the base-curves B_r and B_s, this B_{tu} has no influence on c and d, whilst a is lowered with sm and b with rm, where m represents the order of the curve B_{tu}: for, when F_s, F_t and F_u are three arbitrary surfaces always sm points of intersection lie on B_{tu}. The order of L is thus lowered with $2rsm$ by B_{tu}. This can be explained by the fact, that *the locus of the curves of intersection C_{rs} of surfaces F_r and F_s passing through a selfsame point of B_{tu}* [1]) *separates itself from the locus of P and P'*. That the locus of those curves of intersection is really of order $2rsm$ is easily evident from the points of intersection with an arbitrary line l. We can bring through an arbitrary point Q_r of l an F_r cutting B_{tu} in rm points; through each of those points of intersection we bring an F_s, which rm surfaces F_s cut the right line l in rsm points Q_s. To Q_r correspond rsm points Q_s and reversely. The $2rsm$ coincidences are the points of intersection of l with the locus of the curves of intersection C_{rs}.

7. The base-curves B_r, B_s, B_t and B_u of the pencils are morefold curves of the surface L. If A_r is a point of B_r but not of the other base-curves, then A_r is an $(a-1)$-fold point of L. For, the surfaces F_s, F_t and F_u through A_r intersect one another in $a-1$ points, not lying on the base-curves, each of which points furnishes together with A_r a pair of points satisfying the question. Each point of B_r is thus an $(a-1)$-fold point, i. o. w. *B_r is $(a-1)$-fold curve of the surface L.*

Let A_{rs} be a point of intersection of the base-curves B_r and B_s, but not a point of B_t and B_u. An arbitrary point P of the curve of intersection C_{tu} of the surfaces F_t and F_u through A_{rs} furnishes now together with A_{rs} a pair of points PP' satisfying the question properly, as A_{rs} is for each triplet of pencils a movable point of intersection not lying on the base-curves. If we let P describe the curve C_{tu}, then the tangent l_{rs} in A_{rs} to the curve of intersection of the surfaces F_r and F_s through P describes the cone of contact of L in the conic point A_{rs}. The tangents m_r and m_s in A_{rs} to B_r and B_s are $(a-1)$- resp. $(b-1)$-fold edges of the cone. This cone is cut by the plane through m_r and m_s only according to the line m_r counting $(a-1)$-times and the line m_s counting $(b-1)$-times, as another line l_{rs} lying in this plane would determine two surfaces

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[1]) If B_{tu} cuts the curve B_s in a point A_{stu}, then the surface F_r passing through A_{stu} separates itself from the locus of the curves of intersection C_{rs}.

F_r and F_s touching each other in A_{rs}, whose curve of intersection, however, does not cut the curve C_{tu}. *The tangential cone of* L *in* A_{rs} *is thus of order* $a+b-2$ [1]).

Let $A^{(1)}_{rs}$ be a point of a common part B_{rs} of the base-curves B_r and B_s but not a point of B_t and B_u. We get a pair of points PP' with a point P' coinciding with $A^{(1)}_{rs}$ when the surfaces F_r and F_s have in $A^{(1)}_{rs}$ a common tangential plane V_{rs} and pass through a selfsame point P of the curve of intersection C_{tu} of the surfaces F_t and F_u through $A^{(1)}_{rs}$. If we let P describe the curve C_{tu}, then on account of that between the planes V_r and V_s, touching in $A^{(1)}_{rs}$ the surfaces F_r and F_s through P, a correspondence is arranged, where to V_r correspond $b-1$ planes V_s and to V_s correspond $a-1$ planes V_r. One of the $a+b-2$ planes of coincidences is the plane through the tangents in $A^{(1)}_{rs}$ to B_{rs} and C_{tu}; this plane furnishes no plane V_{rs}. The remaining $a+b-3$ planes of coincidence are planes V_{rs} and indicate the tangential planes in $A^{(1)}_{rs}$ to the surface L. *So* B_{rs} *is an* $(a+b-3)$*-fold curve of* L.

8. Let us then consider a common point A_{rst} of the base-curves B_r, B_s and B_t. We get a pair of points PP' with a point P' coinciding with A_{rst}, when the tangential planes in A_{rst} to F_r, F_s and F_t pass through one line l_{rst} and these surfaces intersect one another again in a point P of the surface F_u passing through A_{rst}. There are ∞^1 such lines l_{rst}, forming the tangential cone of L in point A_{rst}. The tangents m_r, m_s and m_t in A_{rst} to B_r, B_s and B_t are $(a-1)$-, $(b-1)$- and $(c-1)$-fold edges of that cone. So the plane through m_r and m_s furnishes $a+b-2$ lines of intersection with the cone coinciding with m_r and m_s. Moreover $c-2$ other lines l_{rst} lie in this plane. For, the surfaces F_r and F_s touching this plane intersect F_u in $c-2$ points not lying on the base-curves; the surfaces F_t through those points intersect the plane through m_r and m_s according to curves whose tangents in A_{rst} are the mentioned

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[1]) The order of this cone can also be found out of the number of lines of intersection with an arbitrary plane ε through A_{rs}. If l_r and l_s are the lines of intersection of ε with the tangential planes in A_{rs} to the surfaces F_r and F_s through P, then to l_r correspond $b-1$ lines l_s and to l_s correspond $a-1$ lines l_r, so that in the plane ε lie $a+b-2$ lines l_{rs}.

lines l_{rst}. *So the tangential cone of L in A_{rst} is of order $a+b+c-4$* 1).

A point of intersection $A_{rst}^{(1)}$ of B_r with a common part B_{st} of the base-curves B_s and B_t is a conic point of L, the tangential cone of which is formed as in the previous case by ∞^1 lines l_{rst}. The tangents m_r and m_{st} in $A_{rst}^{(1)}$ to B_r and B_{st} are $(a-1)$ and $(b+c-3)$-fold edges of that cone. As no other lines l_{rst} lie in the plane through m_r and m_{st}, it is evident *that the tangential cone of L in $A_{rst}^{(1)}$ is likewise of order $a+b+c-4$* 1).

Let $A_{rst}^{(2)}$ be a point of a common part B_{rst} of the base-curves B_r, B_s and B_t. The point P' of the pair of points PP' coincides with $A_{rst}^{(2)}$ when the surfaces F_r, F_s and F_t have in $A_{rst}^{(2)}$ the same tangential plane V_{rst} and cut one another in another point P of the surface F_u through $A_{rst}^{(2)}$. If we now consider an F_r and an F_s having in $A_{rst}^{(2)}$ the same tangential plane V_{rs} and if we consider through each of the $c-1$ points of intersection of F_r, F_s and F_u not lying on the base-curves an F_t of which we indicate the tangential plane in $A_{rst}^{(2)}$ by V_t then to V_{rs} correspond $c-1$ planes V_t and to V_t correspond $a+b-1$ planes V_{rs} (as for given V_t a (b, a)-correspondence exists between V_r and V_s of which V_t is one of the planes of coincidence). Among the $a+b+c-2$ planes of coincidence $V_{rs}\,V_t$ there are however *three* which give no plane V_{rst}, namely the planes V_{rs}, for which the corresponding surfaces F_r and F_s furnish with F_u three points of intersection coinciding with $A_{rst}^{(2)}$. For this is necessary that F_u touches in $A_{rst}^{(2)}$ the movable intersection of F_r and F_s. Now the tangents of those intersections for all surfaces F_r and F_s touching each other in $A_{rst}^{(2)}$ form a cubic cone having for double edge the tangent m_{rst} to B_{rst} in point $A_{rst}^{(2)}$ 2). This cone is cut by the tangential plane in $A_{rst}^{(2)}$ to F_u according to three lines, furnishing with m_{rst} planes V_{rs} which are planes of coincidence

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1) This order can also be determined out of the number of lines l_{rst} in a plane ε passing through A_{rst}. In this plane we find a $(c-1,\ a+b-2)$-correspondence between lines l_{rs} and lines l_t of which however the line of intersection of ε with the tangential plane in A_{rst} to F_u is a line of coincidence, but no line l_{rst}.

2) This is immediately evident if we take for (F_r) a pencil of planes and for (F_s) a pencil of quadratic surfaces all passing through the axis B_r of the pencil of planes. The cone under consideration then becomes the cone of the generatrices of the quadratic surfaces passing through a given point of B_r. We can easily convince ourselves that the same result holds for arbitrary pencils of surfaces.

of V_{rs} and V_t, but not planes V_{rst}. So there are $a+b+c-5$ planes V_{rst}, which are the tangential planes of L in the point $A^{(2)}_{rst}$, i. o. w. B_{rst} *is* $(a+b+c-5)$*-fold curve of surface* L.

9. We then consider a common point A_{rstu} of the four base-curves. We get a pair of points PP' with point P' coinciding with A_{rstu} when F_r, F_s, F_t and F_u have in A_{rstu} a common tangent l_{rstu} and all pass once again through a selfsame point P. The ∞^1 lines l_{rstu} form the tangential cone of L in A_{rstu}. To determine the number of lines l_{rstu} in an arbitrary plane ε through A_{rstu} we take in this plane an arbitrary line l_{rst} through A_{rstu} and we bring through the $d-1$ points of intersection (not lying on the base-curves) of the surfaces F_r, F_s and F_t touching l_{rst} the surfaces F_u, whose tangential planes in A_{rstu} cut the plane ε according to lines, which we shall call l_u. To l_{rst} now correspond $d-1$ lines l_u and to l_u correspond $a+b+c-2$ lines l_{rst}, as there exists between l_{rs} and l_t when l_u is given a $(c, a+b)$-correspondence, of which l_u and the line of intersection of ε with the plane through the tangents in A_{rstu} to B_r and B_s are lines of coincidence, but not lines l_{rst}. So there are $a+b+c+d-3$ lines of coincidence $l_{rst}\,l_u$ of which however *three* are not lines l_{rstu}. The common tangents in A_{rstu} of the surfaces F_r, F_s and F_t possessing three points of intersection coinciding with A_{rstu} and where therefore the intersection of two of those surfaces shows a contact of order two to the third, form namely a cubic cone [1]) of which the lines of intersection with ε are lines of coincidence but not lines l_{rstu}. So in ε lie $a+b+c+d-6$ lines l_{rstu}, i. o. w. *the tangential cone of* L *in* A_{rstu} *is of order* $a+b+c+d-6$ [2]).

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[1]) This is again evident when taking for (F_r) and (F_s) pencils of planes with coplanar axes B_r and B_s and for (F_t) a pencil of quadratic surfaces passing through a line containing the point of intersection S of B_r and B_s. The line of intersection of the planes F_r and F_s shows only then a contact of order two to F_t when that line of intersection lies entirely on F_t, so that the cone under consideration becomes again the cone of the generatrices of the quadratic surfaces passing through S.

[2]) That order can also be found out of the lines of intersection with the plane V_{rs} through the tangents m_r and m in A_{rstu} to B_r and B_s. Those lines of intersection are: the line m_r, counting $(a-1)$-times, the line m_s counting $(b-1)$-times and $c+d-4$ other lines. This last amount we find by drawing in plane V_{rs} an arbitrary line l_t through A_{rstu}. The surface F_t touching l_t cuts the surfaces F_r and F_s touching V_{rs} in $d-1$ points (not lying on the base-curves) through which points we bring surfaces F_u whose tangential planes in A_{rstu} cut the plane V_{rs} according to lines to be called l_u. Between the lines l_t and l_u we now have a $(d-1, c-1)$-correspondence of which the nodal tangents in A_{rstu} of the intersection of the surfaces F_r and F_s touching V_{rs} are lines of coincidence. The remaining $c+d-4$ lines of coincidence are lines l_{rstu}.

The preceding considerations hold invariably for a point $A^{(1)}_{rstu}$ lying on the base-curves B_r and B_s and the common part B_{tu} of the base-curves B_t and B_u [1]).

In a point of intersection $A^{(2)}_{rstu}$ of B_{rs} and B_{tu} the tangential cone is likewise of order $a+b+c+d-6$ as that cone has the tangents m_{rs} and m_{tu} to B_{rs} and B_{tu} as $(a+b-3)$ and $(c+d-3)$ fold edges, whilst in the plane through m_{rs} and m_{tu} no other right lines l_{rstu} are lying.

A point of intersection $A^{(3)}_{rstu}$ of B_r and B_{stu} is also a $(a+b+c+d-6)$ fold point of L as m_r and m_{stu} are $(a-1)$- and $(b+c+d-5)$-fold edges of the tangential cone and the only lines of intersection of that cone with the plane through m_r and m_{stu}.

If finally $A^{(4)}_{rstu}$ is a point of a common part B_{rstu} of the four base-curves, then the point P' of the pair of points PP' coincides with $A^{(4)}_{rstu}$ when the surfaces F_r, F_s, F_t and F_u have in $A^{(4)}_{rstu}$ the same tangential plane V_{rstu} and all pass through a same point P. Let us now assume an arbitrary plane V_{rst} passing through the tangent m_{rstu} in $A^{(4)}_{rstu}$ to B_{rstu}. The surfaces F_r, F_s and F_t touching this plane in $A^{(4)}_{rstu}$ cut one another in $d-1$ points P, through which we bring surfaces F_u, of which we call the tangential planes in $A^{(4)}_{rstu}$ V_u. Thus we obtain a correspondence, where to V_{rst} correspond $d-1$ planes V_u and reversely to V_u correspond $a+b+c-1$ planes V_{rst}; for when V_u is given there is between V_{rs} and V_t a $(c, a+b)$ correspondence, of which V_u is plane of coincidence, but not a plane V_{rst}. So there are $a+b+c+d-2$ planes of coincidence $V_{rst}V_u$, of which however *five* are not planes V_{rstu}. These are namely the tangential planes of the surfaces F_r, F_s and F_t of which one more point of intersection coincides with $A^{(4)}_{rstu}$ which

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[1]) It is also easy to see from the lines of intersection with the plane V_{stu} through the tangents m_s and m_{tu} to B_s and B_{tu} that the tangential cone in $A^{(1)}_{rstu}$ is of order $a+b+c+d-6$. The line m_s counts for $b-1$ lines of intersection, the line m_{tu} for $c+d-3$. Further, the surfaces F_s, F_t and F_u touching V_{stu} cut one another in $a-2$ points not lying on the base-curves; through those points we bring surfaces F_r, whose tangential planes in $A^{(1)}_{rstu}$ cut the plane V_{stu} along to lines which lie on the tangential cone.

occurs five times [1]). So there remain $a+b+c+d-7$ planes Γ_{rstu} which are the tangential planes of L in the point $A^{(4)}_{rstu}$, so that B_{rstu} is a $(a+b+c+d-7)$ fold curve of L.

10. So we find:

Of the locus proper L of the pairs of points P and P' the base-curve B_r of the pencil (F_r) is $(a-1)$-fold curve, the common part B_{rs} of the base-curves B_r and B_s is $(a+b-3)$-fold curve, the common part B_{rst} of the base-curves B_r, B_s and B_t is $(a+b+c-5)$ fold curve and the common part B_{rstu} of the four base-curves is $(a+b+c+d-7)$-fold curve. The points of intersection of the base-curves are conic points of L, namely a point of intersection of B_r and B_s is $(a+b-2)$-fold point, a point of intersection of B_r, B_s and B_t or of B_r and B_{st} is $(a+b+c-4)$-fold point and a point of intersection of B_r, B_s, B_t and B_u or of B_r, B_s and B_{tu} or of B_{rs} and B_{tu} or of B_r and B_{stu} is $(a+b+c+d-6)$-fold point. [2])

11. The base-curves of the pencils are not the only singular curves of the surface L. There are namely ∞^1 triplets of points lying on a surface of each of the pencils. These triplets of points form a double curve of L. If P, P', P'' is such a triplet and if $P1$ and $P2$ are the sheets through P of the surface, then the sheets $P'1$ and $P''2$ correspond to them. Through P' passes another sheet $P'3$ and through P'' a sheet $P''3$ which sheets correspond mutually. The pair of points not lying on the base-curves is movable along the sheets $P1$, $P'1$, along the sheets $P2$, $P''2$ and along the sheets $P'3$, $P''3$; on the base-curve a third point then joins the pair.

Further there is still a finite number of quadruples of points,

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[1]) The number *five* is found in the following way. The tangents of the movable intersections of surfaces F_s and F_t touching each other in $A^{(4)}_{rstu}$ form a cubic cone having the tangent m_{rstu} to B_{rstu} as double line. Such an intersection shows to the surface F_r a contact of order two when it touches the movable intersection of F_r and F_t, so if its tangent in $A^{(4)}_{rstu}$ lies on the cubic cone belonging to the pencils (F_r) and (F_t). As this last cone has also m_{rstu} as double edge, both cones have $9-4=5$ lines of intersection differing from m_{rstu} which connected with m_{rstu} furnish the five planes under consideration.

[2]) If the total locus is not indefinite, i. o. w. if there is no point common to the four base-curves then B_r is a $(stu-1)$-fold curve and B_{rs} a $(stu+rtu-2)$ fold curve of the total locus whilst a point of intersection of B_r and B_s is a $(stu+rtu-2)$-fold point and a point of intersection of B_r, B_s and B_t or of B_r and B_{st} a $(stu+rtu+rsu-3)$-fold point of it.

through which passes a surface out of each of the pencils. Through the points P, P', P'' and P''' of such a quadruple pass three sheets of the surface L and three branches of the double curve. The 12 branches of the double curve through those four points we can call $P1, P2, P3, P'1, P'2, P'4, P''1, P''3, P''4, P'''2, P'''3, P'''4$, in such a way that the triplet of points is movable along the branches $P1, P'1, P''1$, along $P2, P'2, P'''2$, along $P3, P''3, P'''3$ and along $P'4, P''4, P'''4$. If the sheet of L passing through $P1$ and $P2$ is called $P12$, then the corresponding sheets (i. e. sheets along which the pair of points not lying on the double curve is movable) are $P12$ and $P'12$, $P13$ and $P''13$, etc.

Geophysics. — "*Current-measurements at various depths in the North Sea.*" (First communication). By Prof. C. H. Wind, Ltt. A. F. H. Dalhuisen and Dr. W. E. Ringer.

In the year 1904 accurate measurements of the currents in the North Sea [1]) were started by the naval lieutenant A. M. van Roosendaal, at the time detached to the "Rijksinstituut voor het Onderzoek der Zee", having been proposed and guided by the Dutch delegates to the International Council for the Study of the Sea.

By him four apparatus were put to the test, viz. 2 specimens of the current-meter of Pettersson [2]), one of that of Nansen [3]) and one of that of Ekman [4]), all destined to determine the direction and the velocity of the current at every depth.

The experiments were partly made on the light-ship "Haaks", where Dr. J. P. van der Stok, the Marine Superintendent of the Kon. Nederl. Meteorologisch Instituut, also took part in them. Other experiments were made in the harbour of Nieuwediep and further, from the research-steamer "Wodan", in the open North Sea at a station (H2) of the Dutch seasonal cruises [5]), situated at Lat. 53°44′ N. and Long. 4°28′ E.

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[1]) Cons. Perm. Intern. p. l'expl. de la mer, Publications de circonstance No. 26: A. M. van Roosendaal und C. H. Wind, Prüfung von Strommessern und Strommessungsversuche in der Nordsee. Copenhague, 1905.

[2]) Publ. de circ. No. 25.

[3]) „ „ „ No. 34.

[4]) „ „ „ No. 24.

[5]) Quarterly cruises of the countries taking part in the international study of the sea, along fixed routes, observations being made at definite points or "stations".

The apparatus of Nansen appeared to be unfit for the measurements on the North Sea; it was not calculated for the strong tidal currents occurring there (e.g. 60—100 cm/sec.), and also the putting out of the apparatus in unfavourable weather was hardly possible without doing harm to the instrument. In more quiet water, however, it seems to be very useful.

The apparatuses of Pettersson and Ekman appeared to be better fit for the observations in the North Sea. Some improvements in the construction were proposed, partly also put into practice, by Van Roosendaal and Wind, by which the instruments have gained in fitness. For a description of the construction of the current-meters used, and the experience made in using them, we may refer to the publications mentioned. The following few words may be sufficient here.

It appeared that pretty large oscillations, e. g. 15° to both sides round the longitudinal axis, did not yet render observation impossible. In 32 out of nearly 200 observations by Van Roosendaal as much as the figure 4 was noted for the motion of the sea, in 40 to 50 cases the oscillations amounted to 10 à 20° to either side, and yet the accuracy and certainty of these measurements were only exceptionally insufficient.

In the parallel-observations with the apparatus of Pettersson and Ekman the agreement in indicating the *velocity* appeared satisfactory. In one series of 23 measurements e. g. the average difference amounted to 4.8 cm/sec, whilst the smallest was 3.1, the greatest 6.3.

Nor did the indications of *direction*, as given by the two instruments, show great differences. The observations with Ekman's apparatus bear to some extent a check in themselves, as, by the construction of the instrument, every observation includes a series of consecutive readings at small intervals. In by far the greater part of the readings-observations these separate did not considerably vary. In 128 cases the direction of the current could be estimated from them:

To less than 10°	in 105 cases,
10—20	15
20—30	2
30—40	0
40—50	2
more than 50°	4.

Compared with the probable direction, as derived from the instrument of Ekman, that which was determined by means of Petterson's instrument deviated :

in 65	cases less than 10
37	10—20
15	20—30
5	30—40
1	40—50
8	more than 50°.

VAN ROOSENDAAL and WIND took from the whole of observations made at station H_2 the most probable values direction and velocity of current at the various depths and represented them graphically. They constructed for the different series of observations, each lasting 12 or 24 hours, in the first place *central vector-diagrams*, by drawing from a fixed point the successively determined currents as radii-vectores and connecting the terminal points by means of straight lines or of a curve, and in the second place *progressive vector-diagrams*, by drawing the current-vectors, this time interpolated for the successive full hours, one after and attached to the other. In the first kind of diagrams the periodical currents, and in the second the residual currents make themselves most apparent.

The measurements were continued at the station H2 during all the following seasonal cruises of the "Rijksinstituut", first by VAN ROOSENDAAL and afterwards by the naval lieutenant DALHUISEN, who succeeded the former in his detachment. At the more recent measurements the current-meter of EKMAN was always made use of.

The following table gives the dates of the series of observations and the number of measurements [1]).

N⁰.	Time.	Number of Measurements.	Depth (M.)	Apparatus.	Observer.
1.	from 16 Aug. '05 4.42 p.m. till 17 ,, ,, 4.54 »	56	5,20,35	EKMAN.	VAN ROOSENDAAL.
2.	from 7 Nov. '05 7.48 a.m. till 8 ,, ,, 12.34 p.m.	53	» » »	»	VAN ROOSENDAAL and DALHUISEN
3.	from 7 Febr. '06 7.20 p.m. till 8 ,, ,, 5.53 a.m.	18	» » »	»	DALHUISEN.
4.	from 2 May '06 6.35 a.m. till 3 ,, ,, 6.41 »	54	» » »	»	»

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[1]) A more detailed description of these observations forms the contents of the last issue of the "Publications de circonstance" No. 36.

At these researches wind and weather were on the whole favourable; the wind was in a few cases noted 7 at most, at which force, however, the observations had to be put a stop to in February 1906 [1]).

On the plate added, the new measurements are again represented graphically in central and progressive vector-diagrams. Also the central diagrams, have been constructed this time with the aid of values interpolated for full hours, the directly measured values however, having still been indicated by dots.

It is principally to give a full idea of the variability in direction and velocity of the currents, that these diagrams of the new series of observations have been reproduced fully here.

Comparing the values of the velocity near the surface and in the depth, we see that in 3 out of the 4 cases they show a rather distinct decrease at an increase of depth. Also at the former series of observations at H2 (3—4 Aug., 8—9 Aug. and 2—3 Nov. 1905 [2]), also 8—9 Febr. 1905 [3])) the same result was arrived at.

Also differences of phase in the periodical currents are noticed in most cases between the surface and the depth, though a distinct law may not immediately be obvious here.

The striking difference in amplitude of the tidal currents during the observations in August 1905 and February 1906 on the one side and that of November 1905 and May 1906 on the other, is certainly connected with the age of the tide, as it was with the first nearly spring-tide ($15^1/_2$ and 14 days after N. M.), with the last nearer to dead neap (10 and 0 days after N.M.).

The small number of series of observations that can be disposed of, does of course not allow at all to already think of a calculation of tidal constants, nor to give a correct description of the average variation of the currents. The unmistakable general agreement, however, between the different current-diagrams justifies sufficiently an attempt to compose them. As no doubt moon-tide will have played

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[1]) The reliability of the new observations is no doubt greater than that of the former, if we take into consideration, that in August and November 1905 and in February and May 1906 the Wodan lay moored, so that her motion was considerably smaller than on the former occasions, when she had cast only one anchor.

It may still be mentioned that an experimental and theoretical investigation was started about the influence of the movements of the ship upon the indications of the current-meter, which, however, has not yet led to a satisfactory result.

[2]) Publ. de Circ. N⁰. 26.

[3]) „ „ „ N⁰. 36.

the principal part, we have thought best for this purpose to compose for the successive full moon-hours the current-values as they follow by interpolation from the different diagrams. The averages thus obtained have been combined in new diagrams, which are represented on the plate, in the last column of figures, and that by black curved lines.

In order to complete the matter and to allow comparisons, in the same way average diagrams have been derived from the observations made in the past year at H2 (see above) and represented in the same figures on the plate by black-and-white curves.

The arrows drawn in these figures indicate: in the central diagrams the direction of the current at the moon's transit, in the progressive diagrams the total residual current during a half moon-day.

A comparison of the average current-diagrams for various depths or also of the newer with the older ones might give rise to all kinds of remarks. With a view to the small number of data, however, on which the diagrams are based, it would perhaps be inconsiderate to mention all of them here. We therefore confine ourselves to what follows.

Difference in Phase of the tide at different depths.

	August 1905 – May 1906		August—November 1904	
	20 M.—5 M.	35 M.—20 M.	20 M —70 M.	30 M.—20 M.
☾ Transit	18°	5°	0	3°
one hour after »	24	— 6	—13	14
2	23	— 3	— 8	5
3	20	5	— 3	6
4	25	— 2	5	14
5	26	0	18	— 5
6	25	8	3	22
5 » before »	19	17	0	17
4	25	15	— 9	17
3	8	— 6	— 3	25
2	4	10	— 6	24
1	6	11	— 6	11
Average	13°85′	4°30′	—1°50′	12°45

The tidal curve shows not only at different depths, but also in the older and newer observations, generally the same *shape*. Its *size*, on the other hand, both in the older and more recent observations, appears to be smaller near the bottom than near the surface. Also its *orientation* and the situation of the point in it, which relates to the moment of the moon's transit, or, more generally, the *phase* of the tidal current, seems to change in a definite sense as the depth increases. This last relation may be specially illustrated by the following table.

It appears from the table, that the tide is on the whole accelerated in the depth, compared with higher layers; but the table also proves that the phenomenon underlies varying influences, besides constant causes, among which perhaps may be reckonned the shape of the bottom of the sea and the rotation of the earth.

The residual current is by no means constant; at the new observations it has been much stronger than at the old; it shows considerable fluctuations also, when the progressive diagrams of the different days of observation are compared. At the new observations this residual current was on an average stronger near the surface than in deeper layers. This particular may perhaps be principally attributed to the action of persisting winds, which at least on the observations of August 1905 and May 1906 had a very marked influence, rendered quite obvious by the special diagrams for these dates.

The figures for the residual current as deduced from the newer observations are the following:

Depth.	Direction.	Velocity.
5 M.	N 304° E	1/4 mile p. hour
20	317	1/8
35	309°	1/9 ,

as deduced from the older:

7[1]) M.	N 319° E	1/19 mile p. hour
20	295°	1/26
30	323°	1/18 .

These results are worth comparing with the following table of values for the year-average of the residual current at the Noord-Hinder (Lat. 51°35′.5 N., Long. 2°37,E.), calculated by VAN DER STOK[2]) from current-estimations near the surface during five consecutive years.

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[1]) Average of depths of 1, 4, 5, 6, 10 M.; at a depth of 35 M. measurements were made by VAN ROOSENDAAL only in February 1905.

[2]) J. P. VAN DER STOK, Etudes des Phénomènes de Marée sur les côtes néerlandaises; Kon. Ned. Met. Inst. No. 90, II. p. 67, 1905.

Year.	Direction.	Velocity.
1890	N 16° E	0.024 miles p. hour.
91	15	62
92	16	35
93	29	47
94	27	47
Average	N 21° E	0.044 miles p. hour.

Here it appears that the average residual current, which — as we mention in passing — has at this point quite another direction than at H2, even from year to year does not at all remain constant in strength which may perhaps be an indication for differences in the quantity of Atlantic water, entering through the English Channel from year to year.

The question may be put, whether and how far the results attained by the current-measurements described, deviate from what is known from the charts, in general use, about the currents near the station H2, The subjoined table allows of a comparison with statements, borrowed from a chart, published by the British Admiralty 1), and shows

	From the Charts.		Observed.	
Hour.	Direction.	Velocity (m. p. h.).	Direction.	Velocity (m. p. h.).
5 before H.W.Dover	N 90° E	0,3—0,2	N 73° E	0,3
4	110	0,5—0,3	115	0,4
3	135	0,9—0,6	147	0,4
2	160	0,6—0,4	189	0,3
1	180	0,3—0,2	227	0.4
H. W Dover	—	0	266	0,5
1 after H.W. Dover	260	0,3—0,2	280	0,5
2	300	0,6—0,4	296	0,6
3	300	1,0—0,7	331	0,5
4	315	0,6—0,4	342	0,4
5	0	0,3—0,2	9	0,4
6	50	—	40	0,4

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1) Tidal Streams North Sea 1899.

that the deviations for a part considerably exceed the limits of accurateness of the statements.

It should be observed that the charts refer to currents near the surface, whereas the values of the table derived from our observations refer to a depth of 5 M.

Finally we may mention that the observations at station H2 up till now have been continued in the same way, that is to say, they are still made every quarter of a year, as far as possible, during 24 hours. Moreover, owing to the kind co-operation of His Excellency the Minister of Marine, a current-meter of PETTERSSON has been placed on the lightship "Noord-Hinder", with which since November 1906 daily, in so far as the state of the weather permits, with intervals of three hours, measurements at various depths are made by the ordinary staff of the lightship. The lists of observation are forwarded to the "Rijksinstituut" and promise to yield important material, especially for the inquiry into the way in which the tidal and residual currents differ in layers of different depth.

Mathematics. — "*The locus of the pairs of common points of $n+1$ pencils of $(n-1)$-dimensional varieties in a space of n dimensions.*" By Dr. F. SCHUH.

(Communicated by Prof. P. H. SCHOUTE).

1. Let $(V_i)\,(i=1,2,\ldots,n+1)$ be $n+1$ pencils of $(n-1)$-dimensional varieties in the space of operation Sp^n of n dimensions and let r_i be the order of the varieties V_i of the pencil (V_i). Let moreover a_i be the number of points of intersection of the n varieties $V_1, V_2, \ldots, V_{i-1}, V_{i+1}, V_{i+2}, \ldots, V_{n+1}$ not of necessity lying in the base-varieties.

When considering the locus of pairs of points P, P' through which a variety of each of the pencils passes we have exclusively such pairs in view of which neither of the two points lies of necessity on a base-variety of one of the pencils and we call the locus thus arrived at the *locus proper* L.

We determine the order of L out of its points of intersection with an arbitrary right line l. To this end we take on l an arbitrary point $Q_{12\ldots n}$ and we bring though it varieties $V_1, V_2, V_3, \ldots, V_n$, having $a_{n+1}-1$ points of intersection not lying on $Q_{12\ldots n}$ and the base-varieties. Through each of those points we bring a V_{n+1} and arrive in this way at $a_{n+1}-1$ varieties V_{n+1} intersecting together line l in $(a_{n+1}-1)\,r_{n+1}$ points Q_{n+1}. So to $Q_{12\ldots n}$ correspond $(a_{n+1}-1)\,r_{n+1}$ points Q_{n+1}.

To find reversely how many points $Q_{12\ldots n}$ correspond to Q_{n+1} we take arbitrarily on l the points $Q_{i+1}, Q_{i+2}, Q_{i+3}, \ldots, Q_{n+1}$ and we bring through those points respectively a $V_{i+1}, V_{i+2}, V_{i+3}, \ldots, V_{n+1}$. We now put the question how many points $Q_{123\ldots i}$ lie on l in such a way that the varieties mentioned $V_{i+1}, V_{i+2}, .., V_{n+1}$ and the varieties $V_1, V_2, .., V_i$ passing through $Q_{123\ldots i}$ have a common point not lying on the base-varieties. For $i < n$ the answer is: $a_1 r_1 + a_2 r_2 + \ldots + a_i r_i$.

To prove this we begin by noticing that the correctness is immediately evident for $i = 1$. If we now assume the correctness for $i = j$, we have only to show that the formula also holds for $i = j + 1$. Given the points $Q_{j+2}, Q_{j+3}, \ldots, Q_{n+1}$. To determine the number of points $Q_{123\ldots j+1}$ we take on l an arbitrary point $Q_{123\ldots j}$, we bring through it varieties $V_1, V_2, \ldots, V_j$ and then through each of the a_{j+1} points of intersection (not lying on the base-varieties) of these $V_1, V_2, \ldots, V_j$ and the varieties $V_{j+2}, V_{j+3}, \ldots, V_{n+1}$ resp. passing through $Q_{j+2}, Q_{j+3}, \ldots, Q_{n+1}$ we bring a variety V_{j+1}; these a_{j+1} varieties V_{j+1} cut l in $a_{j+1} r_{j+1}$ points Q_{j+1}. So to $Q_{123\ldots j}$ correspond $a_{j+1} r_{j+1}$ points Q_{j+1} and (according to the supposition that the formula holds for $i = j$) reversely to Q_{j+1} correspond $a_1 r_1 + a_2 r_2 + \ldots + a_j r_j$ points $Q_{123\ldots j}$. So there are $a_1 r_1 + a_2 r_2 + \ldots + a_j r_j + a_{j+1} r_{j+1}$ coincidences $Q_{123\ldots j}\, Q_{j+1}$; these are the points $Q_{12\ldots j\, j+1}$ belonging to the given points $Q_{j+2}, Q_{j+3}, \ldots, Q_{n+1}$; in this way the correctness of the formula has been indicated for $i = j + 1$.

When asking after the number of points $Q_{12\ldots n}$ corresponding to Q_{n+1} we have $i = n$, so that the formula furnishes $a_1 r_1 + a_2 r_2 + \ldots + a_n r_n$ for it. This number must however still be diminished by r_{n+1}, as each of the points of intersection of l with the V_{n+1} passing through Q_{n+1} is a point of coincidence $Q_{123\ldots n-1}\, Q_n$ but not one of the indicated points $Q_{12\ldots n}$.

So on l there exists between the points $Q_{12\ldots n}$ and Q_{n+1} an $(a_{n+1} r_{n+1} - r_{n+1}, a_1 r_1 + a_2 r_2 + \ldots + a_n r_n - r_{n+1})$ correspondence. The $a_1 r_1 + a_2 r_2 + \ldots + a_{n+1} r_{n+1} - 2 r_{n+1}$ coincidences are the points of intersection of l with the locus L to be found and the points of intersection of l with the $(n-1)$-dimensional variety of contact $R V_{12\ldots n}$ of the pencils $(V_1), (V_2), \ldots, (V_n)$; we understand by that *variety of contact* the locus of the points, where the varieties $V_1, V_2, \ldots, V_n$ passing through them have a common tangent, so where the $(n-1)$-dimensional tangential spaces of those varieties cut each other according to a line.

2. To determine the order of $R V_{12\ldots n}$ we must observe that $R V_{12\ldots n}$ is the locus of the points of contact of the varieties V_n with the curves of intersection $C_{12\ldots n-1}$ of the varieties $V_1, V_2, \ldots, V_{n-1}$. So the question has been reduced to that of the order of the variety of contact of a system of ∞^1 $(n-1)$-dimensional varieties and a system of ∞^{n-1} curves. That order can be determined out of the points of intersection with an arbitrary line l.

In a point of intersection of l with a variety of the system we bring the $(n-1)$-dimensional tangential space Sp^{n-1} and in a point of intersection of l with a curve of the system the ∞^{n-2} tangential spaces Sp^{n-1}. If we act in the same way with all varieties and curves of both systems, then the tangential spaces of the varieties furnish an *1-dimensional envelope* E_1 (i. e. a curve) of *class* $\mu + \nu$ (as is evident out of its osculating spaces Sp^{n-1} through an arbitrary point of l) *with* ν *osculating spaces* Sp^{n-1} *passing through* l; here μ is the number of varieties of the system passing through an arbitrary point, and ν that of the varieties touching an arbitrary right line. The tangential spaces of the curves in the points of intersection with l have an $(n-1)$-*dimensional envelope* E_2 *of class* $\varphi + \psi$ *with* l *as* ψ-*fold line,* where φ is the number of curves of the system passing through an arbitrary point and ψ that of the curves touching an arbitrary space Sp^{n-1} in a point of a given right line of that space; for, if we bring through a point Q of l an arbitrary Sp^{n-2}, then each of the φ curves of the system passing through Q furnishes a tangential space Sp^{n-1} passing through this Sp^{n-2} whilst the space Sp^{n-1} determined by l and Sp^{n-2} (just as every other Sp^{n-1} passing through l) is ψ times tangential space of the envelope.

Both envelopes have thus $(\mu + \nu)(\varphi + \psi)$ common tangential spaces Sp^{n-1}. Each of the ν osculating spaces Sp^{n-1} of E_1 passing through l is a ψ-fold tangential space of E_2, so it counts for ψ common tangential spaces; so that $\mu\varphi + \mu\psi + \nu\varphi$ common tangential spaces not passing through l are left; these indicate by their points of intersection with l the points of intersection of l with the variety of contact, so we find:

The $(n-1)$-*dimensional variety of contact of an* ∞^1 *system of* $(n-1)$-*dimensional varieties of which* μ *pass through a given point and* ν *touch a given right line, and an* ∞^{n-1} *system of curves of which* φ *pass through a given point and* ψ *touch a given space* Sp^{n-1} *in a point of a given right line of that space, is of order*

$$\mu\psi + \nu\varphi + \mu\varphi.$$

3. With the aid of this result it is easy to determine the order

of the variety of contact (locus of the points with common tangent) of n simple infinite systems (μ_1, ν_1), (μ_2, ν_2), $\ldots$, (μ_n, ν_n) of $(n-1)$-dimensional varieties.

This order is

$$\mu_1 \mu_2 \ldots \mu_n \left(\frac{\nu_1}{\mu_1} + \frac{\nu_2}{\mu_2} + \ldots + \frac{\nu_n}{\mu_n} + n - 1\right),$$

as can be shown by complete induction. The formula holds for $n = 2$. We assume the correctness of the formula for $n = i$ and out of this we must find the correctness for $n = i + 1$.

The variety of contact for $i + 1$ systems in Sp^{i+1} is the variety of contact of the system of varieties (μ_1, ν_1) and the system of curves formed by the intersections of the i remaining systems of varieties. So we have:

$$\mu = \mu_1 \quad , \quad \nu = \nu_1 \quad , \quad \varphi = \mu_2 \mu_3 \ldots \mu_{i+1}.$$

The points of contact of the curves of the system with a given space Sp^i form the $(i-1)$-dimensional variety of contact of the sections of Sp^i with the systems (μ_2, ν_2), (μ_3, ν_3), $\ldots$, (μ_{i+1}, ν_{i+1}); these sections are likewise systems (μ_2, ν_2), $\ldots$, (μ_{i+1}, ν_{i+1}), but of $(i-1)$-dimensional varieties. The variety of contact mentioned is according to supposition of order

$$\mu_2 \mu_3 \ldots \mu_{i+1} \left(\frac{\nu_2}{\mu_2} + \frac{\nu_3}{\mu_3} + \ldots + \frac{\nu_{i+1}}{\mu_{i+1}} + i - 1\right).$$

The points of intersection of that variety of contact with a right line l of Sp^i being the points of l in which Sp^i is touched by curves of the system, we have:

$$\psi = \mu_2 \mu_3 \ldots \mu_{i+1} \left(\frac{\nu_2}{\mu_2} + \frac{\nu_3}{\mu_3} + \ldots + \frac{\nu_{i+1}}{\mu_{i+1}} + i - 1\right).$$

Thus according to the formula $\mu\psi + \nu\varphi + \mu\varphi$ the order of the i-dimensional variety of contact of the $i + 1$ systems of varieties becomes

$$\mu_1 \mu_2 \ldots \mu_{i+1} \left(\frac{\nu_1}{\mu_1} + \frac{\nu_2}{\mu_2} + \ldots + \frac{\nu_{i+1}}{\mu_{i+1}} + i\right),$$

by which the correctness of the same formula for $n = i + 1$ has been demonstrated. So we find:

For n ∞^1 systems (μ_1, ν_1), (μ_2, ν_2), $\ldots$, (μ_n, ν_n) of $(n-1)$-dimensional varieties the locus of the points where the varieties of the systems passing through it have a common tangent is an $(n-1)$-dimensional variety (variety of contact) of order

$$\mu_1 \mu_2 \ldots \mu_n \left(\frac{\nu_1}{\mu_1} + \frac{\nu_2}{\mu_2} + \ldots + \frac{\nu_n}{\mu_n} + n - 1\right).$$

If the systems are pencils, then

$$\mu_i = 1 \quad , \quad \nu_i = 2\,(r_i - 1)\;;$$

thus *the order of the variety of contact* $RV_{12\ldots n}$ *is*:

$$2\,(r_1 + r_2 + \ldots + r_n) - n - 1.$$

4. Returning to the correspondence between the points $Q_{12\ldots n}$ and Q_{n+1} we find for the number of coincidences which are points of intersection of l with the demanded locus L, i. e. for the order of L:

$$a_1 r_1 + a_2 r_2 + \ldots + a_{n+1} r_{n+1} - 2\,(r_1 + r_2 + \ldots + r_{n+1}) + \\ + n + 1 = \sum_{i=1}^{i=n+1} \{(a_i - 2)\, r_i + 1\}.$$

It is easy to see that a base-variety B_i of the pencil (V_i) is an $(a_i - 1)$-fold variety of L. The tangential spaces Sp^{n-1} of L in a point P of B_i are the tangential spaces in P of the varieties V_i, which are laid successively through one of the $a_i - 1$ points of intersection (not lying on P and the base-varieties) of the varieties $V_1, V_2, \ldots, V_{i-1}, V_{i+1}, \ldots, V_{n+1}$ passing through P.

So we find:

Given $n+1$ *pencils* $(V_i)\,(i = 1, 2, \ldots, n+1)$ *of* $(n-1)$*-dimensional varieties in the space of operation* Sp^n. *Let* r_i *be the order of the varieties of the pencil* (V_i) *and* a_i *the number of the points of intersection (not lying on the base-varieties) of arbitrary varieties of the pencils* $(V_1), (V_2), \ldots, (V_{i-1}), (V_{i+1}), \ldots, (V_{n+1})$. *The locus proper of the pairs of points lying on varieties of each of the pencils is an* $(n-1)$*-dimensional variety of order*

$$\sum_{i=1}^{i=n+1} \{(a_i - 2)\, r_i + 1\},$$

having the $(n-2)$*-dimensional base-variety of pencil* (V_i) *as* $(a_i - 1)$*-fold variety.*

If $n > 3$, then also in the general case the base-varieties of the different pencils will intersect each other. In like manner as we have dealt with pencils of surfaces [1]) we can also determine the multiplicity of common points, curves etc. of base-varieties.

Sneek, Jan. 1907.

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[1]) See page 555.

Astromony. — *"On the astronomical refractions corresponding to a distribution of the temperature in the atmosphere derived from balloon ascents."* Preliminary paper by H. G. VAN DE SANDE BAKHUYZEN.

1. The various theories of the astronomical refraction in our atmosphere consider the atmosphere as composed of an infinite number of concentric spherical strata, each of uniform density, whose centre is the centre of the earth and whose densities or temperatures and refractive powers vary in a definite way.

The various relations between the temperature of the air and the height above the surface of the earth, assumed in the existing theories, are chosen so, that 1st they do not deviate too far from the suppositions on the distribution of the temperature in our atmosphere, made at the time when the theory was established, 2nd that the formula derived from this relation for the refraction in an infinitesimal thin layer at any altitude could be easily integrated.

At the time when the various theories were developed, only little was known about the variations of the temperature for increasing heights, and this little was derived from the results of a small number of balloon ascents and from the observations at a few mountain-stations. In the last decade, however, ascents of manned as well as of unmanned balloons with self-registering instruments have greatly increased in number, and our knowledge of the distribution of the atmospheric temperature has widened considerably, and has become much more accurate. Now I wish to investigate, whether by means of the data obtained, we can derive a better theory of refraction, or if it will be possible to correct the results of the existing theories.

2. The temperatures in our atmosphere at different heights have been derived from the following publications:

I. Ergebnisse der Arbeiten am aëronautischen Observatorium Tegel 1900—1902, Band I, II and III.

II. Travaux de la station Franco-scandinave de sondages aëriens à Halde par Teisserenc de Bord. 1902—1903.

III. Veröffentlichungen der internationalen Kommission für wissenschaftliche Luftschifffahrt.

From the last work I have only used the observations from December 1900 till the end of 1903.

I wished to investigate the distribution of the temperature up to the greatest heights, and therefore I used for my researches only the balloon ascents which reached at least an elevation of 5000 meters;

and, following **Hergesell**'s advice, I have used only the temperatures observed during the ascents, as during the descents aqueous vapour may condense on the instruments.

It is evident that for the determination of the refraction, as a correction to the results of the astronomical observations, we must know the variations of the temperature at different heights with a clear sky. For the temperatures, especially of the layers nearest to the surface of the earth, will not be the same with cloudy and uncloudy weather, as in the first case the radiation of the earth will lower the temperature of those layers, and so cause an abnormal distribution of temperature. It is even possible that in the lower strata the temperature rises with increasing height, instead of lowering, as is usual.

For this reason I have divided the balloon ascents into two groups, 1st those with a cloudy sky, 2nd those with a clear or a partly clouded sky.

In working out the observations, I have supposed that for each successive kilometer's height the temperature varies proportionally to the height, and after the example of meteorologists, I have determined the changes of temperature from kilometer to kilometer. For this purpose, I have selected from the observations, made during each ascent, the temperature-readings on those heights, which corresponded as nearly as possible with a round number of kilometers, and I have derived the variations of temperature per kilometer through division.

The available differences of height were often less than a kilometer, especially at the greatest elevations; in those cases I adopted for the weight of the gradient a number proportional to the difference of heights. Sometimes on the same day, at short, intervals several ascents have been made at the same station, or at neighbouring stations, from which the variations of temperature at the same heights could be deduced. In these cases I have used the mean of the results obtained, but I assumed for that mean result the same weight as for a single observation, as the deviations of the daily results from the normal distribution of temperature are only for a small part due to the instrumental errors, and for the greater part to meteorological influences.

3. The observations which I have used, were the following: from publication I, 31 ascents of which 12 had been made in pairs on the same day, so that 25 results were obtained; from publication II, 38 ascents all on different days; and from publication III, 170

ascents distributed over 119 different days; — I have disregarded the observations marked as uncertain in this work. On the whole I have obtained the results on 182 different days, of which 58 with unclouded and 124 with clouded sky.

The temperature gradients for each month were derived from this material, and to obtain a greater precision, I have combined them in four groups, each of three successive months, December, January and February (winter), March, April and May, (spring), June, July and August, (summer), September, October, November, (autumn).

TABLE I.

Variations of temperatures per kilometer.

(V.T. Variation of temperature per kilometer; N. Number of observations).

A. Clear sky.

	Winter.		Spring.		Summer.		Autumn		Mean.	
Kil	V.T.	N.	V.T.	N.	V.T.	N.	V.T.	N.	V.T.	N.
0— 1	+ 1°.2	10	— 3°.6	15	— 2°.8	18	+ 0°.6	15	— 0°.6	58
1— 2	— 4.2	10	— 5.4	15	— 4.3	18	— 3.2	15	— 4.3	58
2— 3	— 5.2	10	— 4.9	15	— 4.4	18	— 4.6	15	— 4.7	58
3— 4	— 5.4	10	— 5.8	15	— 5.4	18	— 5.3	15	— 5.5	58
4— 5	— 5.3	10	— 6.7	14.3	— 5.9	18	— 5.7	14.9	— 5.9	57.2
5— 6	— 5.6	8.9	— 7.1	13.6	— 6.0	18	— 7.3	13.8	— 6.5	54.3
6— 7	— 5.8	8	— 7.5	12.7	— 6.6	17.3	— 6.7	10.1	— 6.7	48.1
7— 8	— 6.8	7	— 7.8	10.8	— 7.5	14.6	— 8.0	8	— 7.5	40.4
8— 9	— 7.6	5	— 6.4	7.8	— 7.4	13.3	— 8.1	8	— 7.3	34.1
9—10	— 5.9	4	— 4.4	5.7	— 7.2	13	— 6.9	7	— 6.4	29.7
10—11	— 3.8	2.9	— 2.5	5	— 6.8	10.4	— 6.1	6.8	— 5.4	25.1
11—12	— 6.2	2	— 2.4	2.6	— 5.9	5.2	— 2.0	5.9	— 3.5	15.7
12—13	— 1.6	2	+ 2.0	1	— 1.1	2	— 1.0	4.9	— 0.7	9.9
13—14			+ 7.0	1	+ 1.0	2	— 4.0	1.6	— 0.8	4.6
14—15					+ 0.7	1.6	— 5.1	1	— 1.5	2.6
15—16					+ 0.8	1			+ 0.8	1

B. Cloudy sky.

	Winter.		Spring.		Summer.		Autumn.		Mean.	
Kil.	V.T.	N.	V.T.	N.	V.T.	N.	V.T.	N.	V.T.	N.
0— 1	— 1°.8	27	— 5°.5	33	— 3°.7	24	— 3°.9	40	— 3°.8	124
1— 2	— 3.0	27	— 5.6	32.5	— 5.1	24	— 3.7	49	— 4.3	123.5
2— 3	— 4.5	27	— 4.8	33	— 5.1	24	— 4.3	40	— 4.5	124
3— 3	— 5.8	27	— 5.5	33	— 5.1	23.8	— 5.8	39.5	— 5.6	123.3
4— 5	— 6.8	27	— 6.7	33	— 6.1	23	— 6.1	39	— 6.4	12.2
5— 6	— 6.9	26	— 6.7	30.7	— 6.7	21.5	— 6.2	36.5	— 6.6	114.7
6— 7	— 6.8	25.4	— 6.7	25	— 6.6	17.7	— 7.3	27.8	— 6.9	95.9
7— 8	— 6.9	19.7	— 7.2	20.3	— 7.2	16.8	— 5.9	21.6	— 6.8	78.4
8— 9	— 6.1	14.2	— 6.0	16.2	— 7.9	14.1	— 7.9	13	— 6.9	57.5
9—10	— 6.2	12.3	— 3.9	12.9	— 8.4	12.1	— 7.5	11.4	— 6.5	48.7
10—11	— 5.4	9.4	— 1.8	9.6	— 5.9	8.1	— 5.4	8.5	— 4.5	35.6
11—12	— 2.5	7.6	+ 1.0	8.3	— 2.1	5.1	— 1.9	6.8	— 1.2	27.8
12—13	— 1.3	5	+ 1.2	6.7	+ 0.2	1.9	— 0.5	4.1	+ 0.1	17.7
13—14	— 0.9	2.7	— 3.9	1			+ 1.7	1.4	— 0.8	5.1
14—15	+ 1.9	1.9	— 3.2	1					+ 0.2	2.9
15—16	— 0.6	1	— 3.2	0.5					— 1.5	1.5
16—17	+ 0.1	0.8							+ 0.1	0.8

We may derive from these tables that the mean variation of temperature with clear and with cloudy weather only differs in the lower strata, but is nearly the same in the higher ones.

In order to deduce from the numbers in this table the temperatures themselves from kilometer to kilometer, I have also derived from the data the following mean temperatures at the surface of the earth:

	clouded sky	clear sky
Winter	+ 0°.1	— 0°.9
Spring	+ 6 .4	+ 5 .1
Summer	+ 14 .4	+ 14 .7
Autumn	+ 9 .0	+ 7 .9

By means of these initial temperatures and the gradients of table I

C. Cloudy and uncloudy sky.

	Winter.			Spring.			Summer.			Autumn.			Mean.		
Kil.	V.T.	N.	Hann.	V.T.	N.	Hann.	V.T.	N.	Hann.	V.T.	N.	Hann.	V.T.	N.	Hann.
0— 1	−1°.0	37	+0°.5	−3°.8	48	−3°.1	−3°.3	42	−4°.1	−2°.7	55	−2°.1	−2°.8	182	−2°.2
1— 2	−3.3	37	−2.2	−5.6	47.5	−5.5	−4.7	42	−5.6	−3.6	55	−4.1	−4.3	181.5	−4.4
2— 3	−4.7	37	−5.0	−4.9	48	−5.1	−4.8	42	−5.1	−4.4	55	−4.8	−4.7	182	−5.0
3— 4	−5.7	37	−5.8	−5.6	48	−5.8	−5.2	41.8	−5.6	−5.6	54.5	−5.8	−5.5	181.3	−5.7
4— 5	−6.4	37	−6.7	−6.7	47.3	−6.7	−6.0	41	−5.9	−6.0	53.9	−5.9	−6.2	179.2	−6.3
5— 6	−6.7	34.9	−6.7	−6.8	44.3	−7.3	−6.4	39.5	−6.4	−6.5	50.3	−6.8	−6.6	169	−6.8
6— 7	−6.6	33.4	−6.7	−7.0	37.7	−7.2	−6.6	35	−7.2	−7.1	37.9	−7.1	−6.9	144	−7.0
7— 8	−6.9	26.7	−7.2	−7.4	31.1	−6.3	−7.4	31.4	−7.7	−6.4	29.6	−7.3	−7.3	118.8	−7.1
8— 9	−6.5	19.2	−6.9	−6.1	24	−6.4	−7.6	27.4	−7.6	−7.9	21	−7.6	−7.1	91.6	−7.1
9—10	−6.2	16.3	−6.4	−4.0	18.6	−4.8	−7.8	25.1	−6.9	−7.4	18.4	−6.6	−6.5	78.4	−6.3
10—11	−5.0	12.3	−3.9	−2.0	14.6	−0.9	−6.4	18.5	−5.0	−5.7	15.3	−6.1	−4.9	60.7	−4.0
11—12	−2.6	9.6	0.0	−0.2	10.	+0.5	−4.0	10.3	−2.4	−1.9	12.7	−2.7	−2.1	43.5	−1.2
12—13	−1.2	7		+1.3	7.7		−0.5	3.9		−0.5	9		−0.2	27.6	
13—14	−0.9	2.7		−1.6	2		+1.0	2		−1.3	3		−0.8	9.7	
14—15	+1.9	1.9		−3.2	1		+0.7	1.6		−5.1	1		−0.6	5.5	
15—16	−0.6	1		−3.2	0.5		+0.8	1					−0.6	2.5	
16—17	+0.1	0.8											+0.1	0.8	

which in a few cases have been slightly altered, I have derived the following list of temperatures for clear weather from kilometer to kilometer.

Although the adopted values for the temperature of the air above 13 kilometer are not very certain, yet the observations indicate that at these heights the temperature decreases slowly with increasing height. The refraction in those higher strata being only a small part of the computed refraction, nearly $^1/_{10}$, an error in the adopted distribution of temperature will have only a slight influence on my results.

I must remark that almost all the observations have been made during the day, generally in the morning. It is evident that the variation of temperature, especially near the surface of the earth, is not the same during the day and during the night, but the number of

TABLE II.

Temperatures at heights from 0 to 16 kilometer for clear weather.

	Winter.		Spring.		Summer.		Autumn.		Mean.	
Height.	Temp.	Diff.	Temp.	Diff.	Temp.	Diff.	Temp.	Diff.	Temp.	Diff.
0	— 1°.9		+ 5°.1		+14°.7		+ 7°.9		+ 6°.4	
		+1.2		—3.6		—2.8		+0.6		—1.1
1	— 0.7		+ 1.5		+11.9		+ 8.5		+ 5.3	
		—4.2		—5.4		—4.3		—3.2		—4.3
2	— 4.9		— 3.9		+ 7.6		+ 5.3		+ 1.0	
		—5.2		—4.9		—4.4		—4.6		—4.8
3	—10.1		— 8.8		+ 3.2		+ 0.7		— 3.8	
		—5.4		—5.8		—5.4		—5.6		—5.5
4	—15.5		—14.6		— 2.2		— 4.9		— 9.3	
		—5.8		—6.7		—5.9		—6.1		—6.1
5	—21.3		—21.3		— 8.1		—11.0		—15.4	
		—6.0		—6.7		—6.0		—6.9		—6.4
6	—27.3		—28.0		—14.1		—17.9		—21.8	
		—6.2		—6.9		—6.6		—7.2		—6.7
7	—33.5		—34.9		—20.7		—25.1		—28.5	
		—6.8		—7.3		—7.3		—7.7		—7.3
8	—40.3		—42.2		—28.0		—32.8		—35.8	
		—7.3		—6.9		—7.6		—7.6		—7.4
9	—47.6		—49.1		—35.6		—40.4		—43.2	
		—6.4		—5.4		—7.2		—6.9		—6.4
10	—54.0		—54.5		—42.8		—47.3		—49.6	
		—4.9		—2.5		—6.8		—6.1		—5.1
11	—58.9		—57.0		—49.6		—53.4		—54.7	
		—2.1		—1.0		—4.0		—2.0		—2.3
12	—61.0		—58.0		—53.6		—55.4		—57.0	
		—1.0		—1.0		—1.0		—1.0		—1.0
13	—62.0		—59.0		—54.6		—56.4		—58.0	
		—0.6		—0.6		—0.6		—0.6		—0.6
14	—62.6		—59.6		—55.2		—57.0		—58.6	
		—0.4		—0.4		—0.4		—0.4		—0.4
15	—63.0		—60.0		—55.6		—57.4		—59.0	
		—0.2		—0.2		—0.2		—0.2		—0.2
16	—63.2		—60.2		—55.8		—57.6		—59.2	

observations was not great enough for a *reliable* determination of this difference. Lastly I remark that the various balloon ascents have been made from different stations, Halde (in Danemark), Berlin, Paris, Strasbourg and Vienna and consequently the given values do not hold for one definite place, but for the mean of the *area* enclosed by those stations.

After I had derived the temperatures given in table II, I got notice of two papers, treating of about the same subject, namely: J. HANN, Ueber die Temperaturabnahme mit der Höhe bis zu 10 Km. nach den Ergebnissen der internationalen Ballonaufstiege. Sitzungsberichte der mathematisch-naturwissenschaftlichen Klasse der K. K. Akademie der Wissenschaften Wien. Band 93, Abth. IIa, S. 571; and S.

GRENANDER. Les gradients verticaux de la température dans les minima et les maxima barométriques. Arkiv för Matematik, Astronomi och Fysik. Band 2. Hefte 1—2 Upsala, Stockholm.

Of the results which HANN has given, up to a height of 12 kil., I have taken the means of groups of 3 months, which are printed in table I by the side of the values I had obtained; the agreement of the two results, which for the greater part have been deduced from different observations, is very satisfactory.

GRENANDER in his paper chiefly considers the relation between the changes of temperature and the barometer readings; his results cannot therefore be compared with mine directly, but probably we are most justified in comparing the variations of temperature at barometer maxima, with those which I have computed for clear weather. For great elevations, till nearly 16 kil., GRENANDER also obtains with increasing height a small decrease of temperature.

It is difficult to state with what degree of precision the temperatures of table II represent the mean values for the different seasons; the deviations, especially at great heights, may perhaps amount to some degrees, but certainly they represent the mean distribution of temperature better than the values adopted in the various theories of refraction, and we can therefore derive from them more accurate values for the refraction.

4. It is hardly possible to represent the relation between the temperatures in table II and the heights by a simple formula, and to form a differential equation between the refraction, the zenith distance and the density of the atmosphere at a given height, which can be easily integrated.

Therefore I have followed another method to determine the refraction corresponding to the distribution of temperature I had assumed.

According to RADAU's notations (Essai sur les réfractions astronomiques. Annales de l'Observatoire de Paris. Mémoires Tome XIX), the differential equation of the refraction, neglecting small quantities, is:

$$ds = \alpha'' \frac{\left(1 - \frac{l_0}{R}(y - 3\,\varepsilon\omega)\right) d\omega}{\sqrt{\left\{cot^2 z + 2\frac{l_0}{R}(y - \varepsilon\omega) - \left(\frac{l_0}{R}y - 2\frac{l_0}{R}\varepsilon\omega\right)^2\right\}}} \,. \qquad \text{(I)}$$

Here is:

R radius of the earth for 45° latitude,

r_0 radius of the earth for a given point,

h height above the surface of the earth,

$r = r_0 + h$,

μ_0 index of refraction at the surface of the earth,

μ ,, ,, ,, ,, ,, height h,

ϱ_0 density of the air at the surface of the earth,

ϱ density at the height h,

t_0 temperature at the surface of the earth,

l_0 height of a column of air of uniform density at 45° latitude, of a temperature t_0, which will be in equilibrium with the pressure of one atmosphere, the gravity being the same at different heights. According to REGNAULT's constants, we have $l_0 = 7993\ (1 + \alpha t_0)$ meter, if α represents the coefficient of expansion of the air.

Between these quantities exist the following relations:

$$\mu^2 = 1 + 2\,c\varrho \quad (c \text{ being a constant}), \quad \omega = 1 - \frac{\varrho}{\varrho_0}$$

$$\alpha = \frac{c\varrho_0}{1+2c\varrho_0} \qquad \alpha'' = \frac{\alpha}{\sin 1''} \qquad \varepsilon = \frac{R}{l_0}\,\alpha \qquad y = \frac{Rh}{(r_0+h)l_0}\,.$$

To determine the value of ds at each height, we require a relation between ω and y or between ω and h, which can be obtained when we assume that the temperature varies according to IVORY's theory, or that the temperature varies as represented in table II. For the same given values of z and ω, the two values of ds in formula (I) can be computed by means of the first and by means of the second supposition, and the differences of these two values of ds can be found. By means of mechanical quadrature, we can then determine the differences Δs of the refractions s according to IVORY's theory and according to table II.

The relations between y and ω may be found in the following manner.

5. If in a given horizontal initial plane, at a distance r_0 from the centre of the earth, the pressure is p_0, the temperature t_0 and the density of the air ϱ_0, and in another horizontal plane, h kil. above the former, the pressure is p, the temperature t, the distance from the centre of the earth r, and the density of the air ϱ, then we have (see RADAU):

$$l_0\, d\left(\frac{p}{p_0}\right) = -\frac{\varrho}{\varrho_0}\left(\frac{R}{r}\right)^2 dh = -\frac{\varrho}{\varrho_0}\frac{R}{r_0}\, d\left(\frac{Rh}{r}\right), \text{ or } \frac{r_0}{R}\, d\left(\frac{p}{p_0}\right) = -\frac{\varrho}{\varrho_0}\, d\left(\frac{Rh}{l_0 r}\right),$$

or, putting $\dfrac{\varrho}{\varrho_0} = \eta$ and $\dfrac{Rh}{(r_0+h)\,l_0} = y$:

$$\frac{r_0}{R}\, d\left(\frac{p}{p_0}\right) = -\,\eta\, dy\,; \qquad \text{. . . . . . .} \qquad \text{(II)}$$

further is:

$$\frac{p}{p_0} = \frac{1+at}{1+at_0}\,\eta = \left(1 - \frac{a\,(t_0-t)}{1+at_0}\right)\eta = (1-\vartheta)\,\eta, \quad . \quad . \quad \text{(III)}$$

if we put $\frac{a\,(t_0-t)}{1+at_0} = \vartheta$.

When dividing equation (II) by (III), we get:

$$\frac{r_0}{R}\,\frac{d\left(\frac{p}{p_0}\right)}{\frac{p}{p_0}} = -\frac{dy}{1-\vartheta},$$

while by differentiating logarithmically we find:

$$\frac{d\left(\frac{p}{p_0}\right)}{\frac{p}{p_0}} = -\frac{d\vartheta}{1-\vartheta} + \frac{d\eta}{\eta}.$$

From the two last equations follows:

$$dy = \frac{r_0}{R}\left\{d\vartheta - (1-\vartheta)\frac{d\eta}{\eta}\right\} = \frac{r_0}{R}\left\{d\vartheta + (1-\vartheta)\frac{d\omega}{1-\omega}\right\}. \quad . \quad \text{(IV)}$$

According to IVORY's theory $\vartheta = f\omega$, where f is a constant value (RADAU assumes 0,2); if we introduce this relation into the equation (III) we obtain after integration:

$$y = 0{,}4\,\frac{r_0}{R}\,\omega - 1{,}8420681\,\frac{r_0}{R}\,Br.\,log\,(1-\omega) \quad . \quad . \quad . \quad \text{(V)}$$

By substituting (V) in (I) we can therefore calculate for each value of ω the value of ds according to IVORY's theory.

6. Now I proceed to determine the relation between ω and y according to the temperature table II.

Of two horizontal planes, one above the other, the first is situated n kil. (n a whole number), the second n' kil. ($n' =$ or $< n+1$) above the surface of the earth; their distances from the centre of the earth are r_n and $r_{n'}$, their temperatures t_n and $t_{n'}$ and the values of y, y_n and $y_{n'}$. The temperature between n and n' varies regularly with the height and, to simplify the formulae, I suppose $t_n - t_{n'}$ proportional to $y_{n'} - y_n$, so that, if $\vartheta_n = \frac{a\,(t_n - t_{n'})}{1+at_n}$:

$$\frac{R}{r_n}\,(y_{n'} - y_n) = c_n\,\vartheta_n\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(VI)}$$

Hence follows $\frac{R}{r_n}\,dy = c_n\,d\vartheta$ and after substitution of dy in (IV) and integration

$$(c_n - 1)\, lg\, (1 - \vartheta_n) = lg\, (1 - \omega) \quad . \quad . \quad . \quad . \qquad (VII)$$

in which $1 - \omega$ represents the ratio of the densities in the two horizontal planes.

If we substitute $n + 1$ for n', we can find in table II the temperature for the two planes and hence also ϑ_n; as y_n and y_{n+1} are also known, we can derive from (VI) the value of c_n and we can deduce from (VII) the ratio of the densities in those planes. By putting for n successively 0, 1, 2, etc. we can construct a table containing the densities of the air, D_1, D_2, D_3 etc. at the height of 1, 2, 3, etc. kil. above the surface of the earth, the density at the surface being unity.

It is easy to derive from this table the height of a layer of a given density d. If $d < D_n$ and $> D_{n+1}$, the layer must be situated between n and $n + 1$ kil., and we only want to know in which manner, within this kil., the density varies with the height h above the lower plane.

We may assume:

$$\frac{d}{D_n} = 10^{-ah}.$$

For $h = 1$ kil., $d = D_{n+1}$, hence $a = -\, lg\, \frac{D_{n+1}}{D_n}$.

a being known, we may determine for each value of d, h and also y. By substitution in (I) we find then for each value of ω the value of ds.

7. Now we are able to form the differences of ds after the theory of Ivory and after the table of temperatures II, for values of ω which increase with equal amounts, and then determine the whole difference of the refraction for both cases.

For great values of z and small values of y and ω the coefficients of $d\omega$ in (I) will become rather large, which derogates from the precision of the results.

This will also be the case when the differences of the successive values of ω are large; small differences are therefore to be preferred, but they render the computation longer.

Both these difficulties can be partly avoided if, according to Radau's remark, we introduce $\sqrt{\omega}$ as a variable quantity instead of ω; the value of ds thus becomes:

$$ds = \frac{a''}{\sqrt{\frac{l_0}{2R}}} \frac{\left(1 - \frac{l_0}{R}(y - 3\,\varepsilon\omega)\right) d\sqrt{\omega}}{\sqrt{\left\{\frac{\frac{R}{2l_0}\cot^2 z + y}{\omega} - \varepsilon - \frac{l_0}{2R\omega}(y - 2\varepsilon\omega)^2\right\}}} \qquad \text{(VIII)}$$

or approximately:

$$ds = \frac{a''}{\sqrt{\frac{l_0}{2R}}} \frac{d\sqrt{\omega}}{\sqrt{\left\{\frac{\frac{R}{2l_0}\cot^2 z + y}{\omega} - \varepsilon\right\}}}$$

It is evident that for small values of ω the coefficient of $d\sqrt{\omega}$ in (VIII) is smaller than that of $d\omega$ in (I), and that also the refraction in the lower strata will be found more accurately by means of the formula (VIII) than by means of (I). For if we increase $\sqrt{\omega}$ in formula (VIII) and ω in formula (I) with equal quantities, beginning with zero, we find, that, from $\omega = 0$ to $\omega = 0{,}2$, the number of values in the first case is twice as great as in the second case, hence the integration by means of quadrature will give more accurate results in the first case.

Therefore I have used the formula (VIII) and computed the coefficient of $d\sqrt{\omega}$ for values of $\sqrt{\omega}$, 0, 0,05, 0,10, 0,15 . . . to 0,95.

The density of the air which corresponds to $\sqrt{\omega} = 0{,}95$, occurs at the height of about 18 kil. From the observations at my disposal I could not deduce reliable values for the temperature at heights above 16 kil.; yet it is probable that the gradients at those heights are small and I have assumed the temperature at heights of 17 and 18 kil. to be equal to that at a height of 16 kilometers.

In this way I have determined by means of mechanic quadrature, and an approximate computation of the refraction between $\sqrt{\omega} = 0.925$ and $\sqrt{\omega} = 0.95$, the differences Δs of the two values of the refraction corresponding to IVORY's theory and corresponding to the table of temperature II in the part of the atmosphere between the earth's surface and a layer at a height of about 18 kil. where $\sqrt{\omega}$ is 0.95. I have worked out this comptuation for the zenith distances 85°, 86°, 87°, 88°, 88°30′, 89°, 89°20′, 89°40′ and 90°.

An investigation, made for the purpose, showed me that in formula (VIII) the terms $\frac{lo}{R}(y - 3\varepsilon\omega)$ in the numerator and $\frac{lo}{2R\omega}(y - 2\varepsilon\omega)^2$ in the denominator may be neglected for all zenith distances except $z = 90°$; therefore I have taken them into account in the computation of the horizontal refraction only.

The results which I have obtained for the differences :

$\Delta s =$ Ivory—table of temperatures

are the following:

TABLE III.

Refraction after Ivory — Refractions after the table of temperatures II.

Zenith distance	Winter	Spring	Summer	Autumn	Annual mean	Annual mean — Winter	Annual mean — Spring	Annual mean — Summer	Annual mean — Autumn
85°	+ 0″21	+ 0″78	+ 0″66	+ 0″31	+ 0″49	+ 0″28	— 0″29	— 0″17	+ 0″18
86°	+ 0.13	+ 1.26	+ 0.95	+ 0.30	+ 0.66	+ 0 53	— 0.60	— 0.29	+ 0.36
87°	— 0.47	+ 2.08	+ 1.31	— 0.20	+ 0 66	+ 1 13	— 1.42	— 0.65	+ 0.86
88°	— 3 93	+ 3.10	+ 0.95	— 3.29	— 0.83	+ 3 10	— 3.93	— 1.78	+ 2.46
88°30′	— 9.64	+ 3.06	— 0.67	— 8.51	— 3.95	+ 5.69	— 7.01	— 3.28	+ 4.56
89°	—23.69	+ 1.08	— 5.45	—21.15	—12.31	+11.38	—13.39	— 6 86	+ 8.84
89°20′	—43.80	— 3.17	—12 68	—38.77	—24.51	+19.29	—21 34	—11.83	+14.26
89°40′	—1′ 21″97	—13.07	—25.25	—1′ 11″16	—27.74	+34.23	—34.67	—22.49	+23.42
90°	—2 32.4	—33.1	—52.9	—2 9.6	—1′ 30″9	+1′ 1″5	—57.8	—38.0	+38.7

To test the computations, we may compare the mean of the values of Δs for the four seasons, and the values of Δs in column 6 which have been computed, independently the former, for the mean yearly temperatures, which are almost equal to the mean of the temperatures in the four seasons. Only for $z = 89^\circ 40'$ and $z = 90^\circ$ do these values show deviations exceeding 0″.1.

From table III follows, 1 that for a distribution of temperature, as derived by me from observations, the refraction deviates perceptibly from that deduced from Ivory's theory, 2 that the differences in the refraction in the different seasons are about of the same order as the deviations themselves. I want it to be distinctly understood, 1 that the adopted distribution of temperature above 13 kil. and especially from 16 to 18 kil. is uncertain, and 2 that I have not taken into account the refraction in the layers which are lying more than 18 kil. above the surface of the earth, in other words those layers where the density, as compared to that of the surface of the earth, is less than $1 - 0{,}95^2$, or less than 0,0975.

Physiology. — *"An investigation on the quantitative relation between vagus stimulation and cardiac action, on account of an experimental investigation of* Mr. P. Wolterson"[1]). By Prof. H. Zwaardemaker.

(Communicated in the meeting of December 29, 1906).

The experiments were performed on Emys orbicularis, whose right nervus vagus was stimulated by means of condensator charges and non-polarising electrodes of Donders[2]), while auricle and ventricle were recorded by the suspension method. The mica-condensators had a capacity of 0,02, 0,2 and 1 microfarad, the voltage varied from a fraction of a volt to 12 volts, occasionally even more. From this the intensity of the stimulus was calculated in ergs (or in coulombs by Hoorweg's method). Only a part of this energy, passing through the nerve, when it is charged, acts as a stimulus. What part this is remains unknown, but it is supposed not to vary too much in the same set of experiments. In the typical experiments a summation took place of ten stimuli, succeeding each other in tempos of $^1/_2$ second; in particular experiments single stimuli or other summations were investigated. Of fatigue little evidence is found with our mode of experimenting, rather a somewhat increased sensitiveness of the vagus system towards the end of a set of experiments.

Stimulation of the right vagus produces in the tortoise in the first place lengthening of the duration of a cardiac period[3]), in such a way that in the second period, after a stimulus, starting during the cardiac pause, the diastolic half of the period is considerably retarded, while in some subsequent periods a decreasing retardation of the diastolic part of the period is noticed.

Then stimulation of the vagus causes contraction to become feebler, this phenomenon becoming gradually more distinct and reaching its maximum some periods after stimulation. This decrease of contractile power is primary, since it may also occur when any change in the automatic action is absent (e.g. when the stimulus consists of one condensator charge and when the left vagus is stimulated). Finally vagus stimulation as a rule produces slackening of the tonus, rarely tonic heightening. Changes in conductivity were only observed once.

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[1]) For details we refer to the author's academical thesis, which will be published ere long.

[2]) Onderzoekingen Phys. Lab. Utrecht (3) Vol. I p. 4, Pl. I, fig. 1, 1872.

[3]) The duration of a cardiac period is reckoned from the foot-point of a sinusal contraction or if this is not visible, of an auricular contraction, to the foot-point of the next following sinusal resp. auricular contraction.

The negative chronotropy holds good for sinus, auricle and ventricle to the same extent, the negative inotropy exists exclusively for the sinus and the auricle, is mostly positive for the ventricle, if it is found; the tonotropy is met with in auricle and ventricle.

A latent stage of the phenomenon, measured by the time-difference between vagus stimulation and vagus action, was always observed. It is smallest for the inotropy; already the first period often shows an enfeeblement of the contraction, which in the subsequent periods increases still further. The latent stage of the chronotropy is greater, for only in the second, sometimes in the third period, a retardation is noticeable; on the other hand this phenomenon reaches its maximum at once. Inotropy and tonotropy do not coincide. On the contrary, the maxima of effect form the following series as to time: first maximum of chronotropy, then maximum of tonotropy, finally maximum of inotropy.

In regard to the sensitiveness for vagus stimuli, we remark that for the inotropy the "threshold value" lies below that for the chronotropy and for this latter lower again than for the tonotropy. So we have:

Threshold value for inotropy $<$ idem for chronotropy $<$ idem for tonotropy.

From the fact that dromotropy did not occur in our experiments, one would infer that the threshold value of the dromotropy lies higher still in the present case.

Physiologists are generally convinced that the rhythmic processes at the bottom of the cardiac pulsations, are based on chemical actions in the cardiac muscle. Leaving apart the founder of the myogenic theory TH. W. ENGELMANN, we mention some authoritative writers, FANO and BOTAZZI in RICHET's Dictionnaire and HOFMANN in NAGEL's Handbuch, who embrace this point of view [1]).

Also experimental results may be adduced in support of this theory. SNYDER [2]) showed that the frequency of the contractions with respect to temperature follows exactly the law, formulated by VAN 'T HOFF and ARRHENIUS for chemical reactions [3]) and experiments, independently made by J. GEWIN, entirely confirmed this. [4]) Whereas the influence of temperature is considerable, that of pressure is very small. This agrees with the small significance of external pressure for so-called condensed systems, i. e. systems in which no gaseous phases occur.

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[1]) FANO and BOTAZZI, RICHET's Dict. de physiologie t. IV. p. 316.

[2]) SNYDER, Univ. of California Publications II. p. 125. 1905.

[3]) E. COHEN, Voordrachten. Blz. 236 1901.

[4]) J. GEWIN, Onderzoekingen Physiol. Lab. Utrecht (5). Dl. VII, p. 222.

For the automatism it seems to me to be settled, that it must be based on chemical processes.

For the remaining cardiac properties: conductivity, local sensitiveness to stimuli, contractile power and tonicity the decision is more difficult. The law of VAN 'T HOFF-ARRHENIUS concerning the relation between reaction-velocity and temperature can only be applied if the duration of the reaction is known. Now the velocity of conduction, measured with this purpose, increases with temperature up to a certain optimum [1]) whereas correspondingly the duration of the contractions is diminished [2]). The local excitability, however, has not been studied yet from this point of view, while also for the contractile power the time factor is still lacking. But the contraction of a muscle and also that of the cardiac muscle is so universally considered a truly chemical process, that the reader will not object to classing it among chemical phenomena without further arguments. As to the tonicity we are absolutely in the dark, although we know that rise of temperature chiefly brings about a change, in which the tonus is definitely abolished.

In preparing his thesis Mr. WOLTERSON had chiefly to deal with:

1. changes in the automatism (chronotropy);
2. changes in the contractile power (inotropy).

Both these changes are purely chemical phenomena, as was shown above.

For chemical processes the law of GULDBERG and WAAGE holds [3]), and we may apply this law to the processes here dealt with. For this purpose we shall have to give a nearer definition for our special case of the conception "times of equal change".

By "times of equal change" we mean the times in which a definite reaction has taken place between two accurately fixed and in the corresponding cases analogous terminal points. The total duration of a cardiac period is such a characteristic time element, the beginning and end of which cannot be determined with the balance after chemical analysis, but still are determined by biological characteristics. The time between the beginning and the end of a cardiac period may be looked upon as a time of equal change provided no

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[1]) TH. W. ENGELMANN. Onderz. Physiol. Lab. Utrecht (3d series) III p. 98. Above the optimum the conductive velocity diminishes again.

[2]) HOFMANN l. c. p. 247. Recently confirmed by V. E. NIERSTRASZ; vide acad. thesis, Utrecht 1907, p. 145, fig. 22: a fall in temperature of 9° gave an increase of the duration of the systole to the double value.

[3]) E. COHEN. Ned. Tijdschr. v. Geneesk. 1901, Vol. I, p. 58. Cf. also ZWAARDEMAKER, ibidem, 1906. Vol. II. p. 868.

inotropic changes occur [1]) and the mechanical resistance which the heart has to overcome, has remained the same.

These premisses made, we may at once apply the fundamental equation of GULDBERG and WAAGE's law;

$$\varphi = kC^n$$

Here k is a constant, the constant of the reactional velocity, C is the quantity of the substance, taking part in the reaction, n is the exponent, determining the so-called order of the reaction, while φ indicates the reactional velocity. About the exponent n nothing can be stated a priori for the heart. Toxicological experiments, in which the quantity of the reacting substance diminishes, might perhaps teach us something in this respect; perhaps also experiments on fatigue might give us some clue; at present, however, no data at all are available. Whether there are intermediate reactions and in what number, cannot be ascertained. Under these circumstances I assume, quite arbitrarily, that the present case is the simplest and that the exponent is unity. If later this assumption turns out to be wrong, our calculations will still apply, mutatis mutandis, without losing their meaning. In this simple case the formula runs:

$$\varphi = k\,C.$$

When the vagus is stimulated a very marked alteration of the times of equal change is noticed. The reactional velocity of the hypothetical chemical process, which lies at the bottom of the automatism, must consequently undergo a very considerable change. Such a change cannot take place unless either k or C are modified. In the literature on the subject both views are put forth, but only the conception that k changes, leads to a clear explanation without further auxiliary hypotheses. It also fits in best with a recent paper of MARTIN [2]), according to which vagus-inhibition is ascribed to the action of K-ions and is counter-acted by rise of temperature. The significance of the ions of the alkalies and alkaline earths for the cardiac muscle is indeed by no means fully explained, even after the mumerous investigations of J. LOEB and his followers and critics — they are regarded by some as the cause of the continually excited condition of the cardiac muscle, as the stimulus for the automatism [3]), by others as the condition, necessary for keeping the

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[1]) In the ventricle vagus-stimulation produces no inotropy.

[2]) MARTIN. Amer. Journal of Physiol. Vol. XI, p. 370, 1904 (MARTIN himself seems to assume a compound of K-ions with C).

[3]) WENCKEBACH. Die Arythmie etc. Eine physiol.-klinische Studie. Leipzig. 1904.

active substances in solution [1]) — they certainly do not enter into simple chemical combination with the cardiac substance, by which this latter would become unfit. If this latter were the case, the life-prolonging influence of RINGER's solution and the remarkable antagonism of Na and K on one hand and Ca on the other, would be entirely unexplainable.

By placing the principal weight on the hypothesis that the vagus alters the constant of velocity, of reaction we were led to the application of the formula for the catalytic acceleration of a chemical reaction. The catalytic acceleration is here negative. The explanation of the formula will be found in G. BREDIG's work. It runs:

$$\beta = k' - k = \frac{1}{(t'_2 - t'_1)} - \frac{1}{(t_2 - t_1)}.$$

By application to our experiments, the normal duration of the period being indicated by $(t_2 - t_1)$ the altered one during the principal retardation by $(t'_2 - t'_1)$, a relation became evident which appears to be constantly found between the intensity of the vagus stimulus on one hand and the retardation, indicated by β on the other. (An examination of the curves, recorded by the heart would show that the retardation affects principally the diastolic part of the process, but since for this part, taken separately, the times of equal change cannot be sharply determined, our calculations enclose the whole process).

When the vagus stimulus increases the retardation increases also very gradually, until a definite degree is reached; from this moment the reactional velocity of the hypothetical process of the automatism remains the same, independent of any rise in the intensity of the stimulus. Only by increase of the duration of the vagus stimulus, a new retardation may be produced, which is pretty well proportional to the extension of the duration of the stimulus. For a warmed heart all this holds without any alteration.

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[1]) H. J. HAMBURGER. Osmotischer Druck und Ionenlehre. Bd. III, p. 127.

Exp. 8, VI. 1906. Emys orbicularis. Right nervus vagus stimulated on non-polarising electrodes with charging currents. Capac. of the condensator 1 microfarad. Number of stimuli 10 (2 per second). Between the series of stimuli pauses of 4 minutes; external temperature 18° C.

Micro-coulomb	Ergs	Initial retard. in %	Total retard. in %	β
0.80	3.20	13	23	—0.0392
0.82	3.36	92	143	—0.1662
0.84	3.53	95	133	—0.1694
0.86	3.69	282	347	—0.2555
0.88	3.87	320	385	—0.2716
0.90	4.05	320	364	—0.2635
0.92	4.23	322	360	—0.2648
0.94	4.42	346	364	—0.2765
0.96	4.61	337	366	—0.2575
0.98	4.80	337	398	—0.2667
1.00	5.00	343	398	—0.2679
1.04	5.41	333	394	—0.2570
1.08	5.83	346	410	—0.2765
1.12	6.27	333	367	—0.2661
1.20	7.20	330	322	—0.2480
1.28	8.19	346	373	—0.2592
1.36	9.25	336	370	—0.2575
1.52	11.50	343	374	—0.2679
1.68	14.11	360	421	—0.2790
1.84	16.93	340	377	—0.2673
3.68	67.71	371	405	—0.2723
5.52	152.35	371	418	—0.2723
7.36	270.85	371	411	—0.2723
9.20	423.20	357	377	—0.2702
11.04	609.40	333	347	—0.2661
0.80	3.20	330	343	—0.2654

Exp. 15, VI. 1906. Emys orbicularis, Right nervus vagus. Non-polarising electrodes. Charging currents. Capac. 0.2 microfarad. Number of stimuli 10; (2 per second). Resting pauses between the series of stimuli 2 minutes. Experimental animal in 0.6% Na Cl solution, heated to 28° C.

Micro-coulombs	Ergs	First visible retardation noticeable in the second period of the stimulus in %	2nd idem in the 3rd period	Total retardation	β col. 3	β col. 4
0.48	5.76	13	139	224	—0.0785	—0.3889
0.496	6.15	20	99	155	—0.1111	—0.3334
0.504	6.35	20	139	205	—0.1111	—0.3889
0.52	6.76	26	152	224	—0.1404	—0.4035
0.552	7.61	26	152	224	—0.1404	—0.4035
0.616	9.48	26	152	218	—9.1404	—0.4035
0.744	13.83	28	199	270	—0.1587	—0.4762
1.116	31.13	21	157	270	—0.1261	—0.4579
5.58	155.65	28	157	284	—0.1587	—0.4579

Two particulars deserve notice:

1. that the greatest retardation falls not in the second but in the third period.

2. With stimulation with 7,61, 9,48, 13,83 ergs turbulent motions occur in the ventricle, followed by the post-undulatory pause, namely in the first systole after the preliminary retardation.

The relation brought to light in both these cases might be explained by assuming with LANGLEY that the vagus fibres do not reach the heart directly, but first pass a station of the intra-cardial ganglia. If this be the case the stimulated condition of the prae-ganglionic fibres will only be communicated to the post-ganglionic by contact in the ganglion cells. But then the quantitative coercion of WEBER's law holds for these ganglion cells and a relation as sketched above is not astonishing. To this conception may be objected that probably with stimulation of the post-ganglionic fibres (in the so-called n. coronarius ¹) the same relation will be found in its principal features. If on this point not only preliminary, but decisive experiments will have been made, it will be found that the just-mentioned explanation

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¹) On the n. coronarius as a post-ganglionic nerve vide J. GEWIN, l. c. 82.

is untenable. Mr. WOLTERSON accordingly gives an alternating explanation which, in my opinion possesses some probability, and which agrees with MARTIN's hypothesis on the nature of the vagus action.

Let us suppose that by the action of the vagus some catalytic substance — say MARTIN's K-ions — is produced in the receptive substance of the cardiac muscle, then the above stated quantitative relation will be explained, if we may assume that the substance, produced by vagus action, is only to a limited extent soluble in the medium. For with a small production of the catalyser this latter will be dissolved and will increase the retardation, but when the medium has become saturated with the catalyser, further secretion is without effect. It must further be assumed that the newly formed catalyser is at once removed from the substance by diffusion or is deposited in the form of indifferent compound, for the vagus action is known to cease after a short time. Only when the duration of the stimulus is increased and catalytic substance is again and again produced, the disappearance of the catalyser may be compensated and the retardation may be lasting.

The second chemical process we meet in Mr. WOLTERSON's thesis, that of the contractility, cannot be submitted to the above followed treatment, since the time-factor is wanting. We tried to introduce this latter by seeking the relation between the intensity of the vagus stimulation and the duration of the inotropic action, but this latter is not itself a chemical reaction, but only a modification of the conditions under which periodically recurring reactions take place. The negative inotropy may at the utmost be regarded as a diminution of the quantity C in the formula $\varphi = kC$, which amounts to the assumption that by vagus stimulation the quantity of the just mentioned substance, undergoing chemical change, is diminished. But this also is uncertain, for in the chemical reaction of the automatism C represents part of LANGLEY's receptive substance, which is different from the contractile substance. So I prefer to keep the two chemism apart and to consider the inotropy entirely by itself.

Placing ourselves on this point of view, we notice: 1. that with feeble and increasing vagus stimuli the inotropic effect on the sinus and auricle gradually increases with the intensity of the stimulus, until a certain degree of inotropy has been reached, after which it does not increase further for any intensity of the stimulus; 2. that an analogous relation holds good for the duration of the inotropic effect; 3. that the pessimum of contractility is found about the end of the first third or fourth part of the total duration, for which the inotropy exists.

Summarising we arrive at the following conclusions:

A. the chronotropy, produced by stimulation of the vagus, may be reduced to a negatively catalytic action on a chemical process which lies at the bottom of the pulsation.

B. the inotropy admits by analogy of a similar interpretation, but it is impossible to prove this, since at present no times of equal change can be determined here.

As secondary results we mention:

a. the existence of twofold negatively chronotropic fibres in the right vagus of the tortoise.

b. a particularly great sensitiveness of the heart of the tortoise for inotropy of the auricle by vagus stimulation, in such a degree that a single condensator discharge may produce the stated modification and that also with cumulative stimulation it appears sooner and lasts longer than the chronotropy.

c. the occasional occurrence of spontaneous cardiac turbulence in a warmed tortoise heart, immediately after a principal retardation brought about by vagus stimulation.

ERRATUM.

In the Proceedings of the meeting of December 29, 1906.

p. 504, line 13 from the bottom: for 2 read 4
p. 511, line 5 from the top: for 0.052 read 0.104

(February 21, 1907).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday February 23, 1907.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 23 Februari 1907, Dl. XV).

CONTENTS.

Chemistry. — *"Contribution to the knowledge of the action of absolute nitric acid on heterocyclic compounds."* By Prof. A. P. N. FRANCHIMONT.

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

When searching about twenty years ago for the rules according to which nitric acid [1]) acts on hydrogen compounds, not only on those which contain the hydrogen in combination with carbon, but also on those which contain it in combination with nitrogen, I found that the hydrogen combined with nitrogen to the atomic group NH, does *not* act on nitric acid, when, in cyclic compounds, this group is placed between two groups of CO, but it *does* act if placed therein between the group CO and a saturated hydrocarbon residue [2]), and it may be added: *not* if placed therein between two saturated hydrocarbon residues, although I have not mentioned this previously.

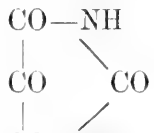
It is a peculiar fact that the hydrogen of the group NH does not act on nitric acid if this group is placed between two similar groups such as CO, or saturated hydrocarbon residues, but it does act if placed between two dissimilar ones; so that it might be thought that a tautomeric form is essential for the reaction.

There are, therefore, in reality three rules, which, when considered more closely, apply also to acyclic compounds and which, although the cycle also exerts an influence, appear to spring mainly from the nature of the substance in which the group NH is placed: viz. secondary amine, amide or imide. In acyclic amides it was found that not only the acyl group in particular, but also the alkyl group exerts an influence on the reaction; we may, therefore, expect something similar in the cyclic ones.

The first of the above rules was mainly deduced from the behaviour of penta- and hexa-atomic cyclic urea derivatives, but was confirmed also in the case of other compounds. For instance

parabanic acid

and



alloxan

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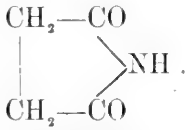
[1]) Namely the real (absolute) acid which may be obtained by distilling a mixture of nitric acid 1.42 with twice its weight of sulphuric acid at a gentle heat under reduced pressure (Recueil XVI. p. 386).

[2]) Which, however, need *not* be the group CH_2 as stated wrongly by HARRIES (Annalen **327**. p. 358). The pages of the Recueil referred to by him contain exactly the proof of the contrary. I have also never spoken of "höchst concentrirter Salpetersäure" as he says, and of which he thinks he must "den Begriff festlegen", and for which he then recommends something which in many cases cannot give a good result.

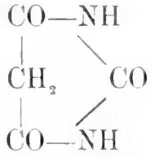
could be evaporated with nitric acid on a boiling waterbath without suffering any decomposition,

and also



succinimide

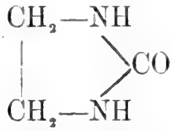
The



malonureide

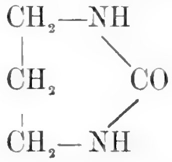
gives a nitroderivative, but with the nitro-group attached to the carbon; the two NH-groups do not act.

The second rule is also based mainly on the behaviour of penta- and hexa-atomic cyclic urea derivatives. For instance



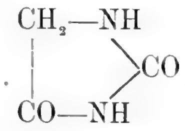
ethyleneureïne

gave a dinitroderivative, which on boiling with water yielded carbon dioxide and ethylenedinitramine. To this I may now add:



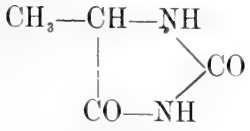
Trimethyleneureïne

of which I have stated recently with Dr. FRIEDMANN that it gives directly a *dinitroderivative*, which on boiling with water yields carbon dioxide and trimethylenedinitramine.

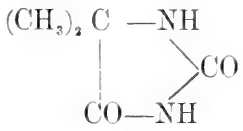


and its methyl derivatives

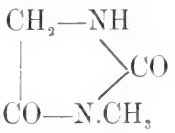
Hydantoin



α lactylurea

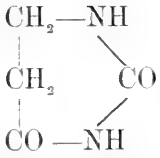


acetonylurea



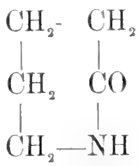
1 Nmethylhydantoïn

gave mononitroderivatives, which on boiling with water were decomposed with evolution of 1 mol. of carbon dioxide and formation of a nitramino-amide; for instance nitrohydantoïn yields nitramino-acetamide.

To this I may add the  recently investigated with Dr. Friedmann, which yields, equally readily, a *mononitroderivative*[1]), which on boiling with water yields, in an analogous manner, carbon dioxide and β *nitraminopropionamide,* from which we have prepared β *nitraminopropionic acid,* also its barium and silver salt.

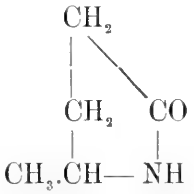
hydro-uracil
(β *lactylurea*)

This decomposition proves the position of the nitrogroup, and at the same time these substances are all a confirmation of the first rule because the group NH, which is placed between the two CO-groups, has not taken part in the reaction.



α *Piperidone*

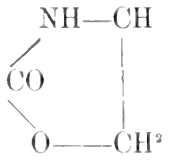
and



α *methylpyrrolidone*

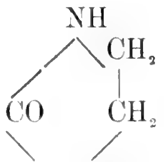
gave with nitric acid N_2O, presumably derived from a nitro-compound unstable towards nitric acid at the ordinary temperature; for it has been shown that some nitramides are decomposed by nitric acid at the ordinary temperature with evolution of nitrous oxide; whilst others may be evaporated with this acid on a boiling waterbath with impunity.

The rule was confirmed five years ago with cycles in which oxygen takes part, for instance



μ. *céto tetrahydro-oxazole.*

and



μ. *céto pentoxazolidine*

gave on evaporation with nitric acid, mononitroderivatives, which on

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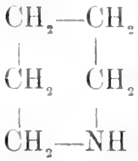
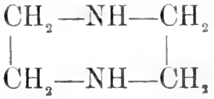
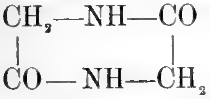
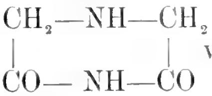
[1]) Tafel stated about this substance (Ber. d. D. ch. G. 33 p. 3385) that it is not affected even by prolonged boiling with concentrated nitric acid; evidently he has not used absolute nitric acid

boiling with water were decomposed with formation of carbon dioxide and a nitramino-alcohol.

The third rule is derived from the behaviour of  *piperidine* which yields with nitric acid a nitrate, but not directly a nitro-compound. This, however, may be prepared from a number of piperidides, to which we added recently the piperidides of *sulphuric* and *succinic acids*, or from the nitrate with acetic anhydride as found by BAMBERGER.

I have noticed recently that  *piperazine.* behaves in the same manner.

The above cited new investigations and those which follow originated in a research by Mr. A. DONK. He had prepared for practice  *glycocol anhydride* and we treated this with nitric acid. But even on evaporation on a boiling waterbath it gave no evolution of nitrous oxide, no nitroderivative, but a nitrate. I had expected this behaviour sooner from the unknown  *iminodiacetic imide* which is one of its isomeres, and in which one NH-group is placed between two CO-groups and the other between two saturated hydrocarbon residues, but not from glycocol anhydride in which each NH-group is placed between CO and a hydrocarbon residue, and about whose structure no doubt could be entertained. At most, we might suspect here a tautomer which does not react with nitric acid, or in all other cases in which nitric acid does act we might assume a tautomer and not here. [1])

Mr. DONK's nitrate, a very loose compound, appeared to be a mononitrate, and on applying BAMBERGER's method for amines (treatment

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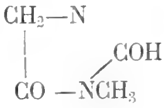
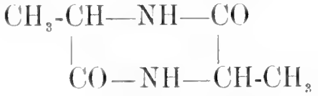
[1]) HARRIES l. c. suspects in 1 N methylhydantoïn a tautomer  which, however, yields with nitric acid the same nitromethylhydantoïn.

of the nitrate with acetic anhydride) he obtained a *mononitroderivative*, of which he proved the structure by acting on it with methylalcoholic potassium hydroxide, which yielded a properly crystallised acid, namely $NO_2\,NH\,CH_2\,CO\,NH\,CH_2\,CO_2\,H$.

nitraminoacetylaminoacetic acid

The reaction therefore took place as in all other cases where NO_2 and CO are both linked to a nitrogen atom; by absorbing the elements of water H and OH the group CO leaves the nitrogen whilst NO_2 remains attached to it.

After the departure of Mr. Donk, who did not wish to prosecute this matter, Dr. Friedmann took it up and obtained the *dinitro-compound* from glycocol anhydride by treatment with excess of nitric acid and acetic anhydride. By the action of ammonia on dinitroglycocol anhydride nitroaminoacetamide was obtained, and by means of sodium hydroxide nitraminoacetic acid was formed in such a quantity that the formation of two molecules was no longer doubtful. The position of the two nitro-groups on the nitrogen atoms has, therefore been sufficiently proved.



Alanine-anhydride

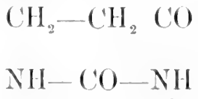
when evaporated with nitric acid also gave a nitrate only, which on treatment with acetic anhydride yielded a *dinitroalanine anhydride*.

These results, which formed a first deviation from the rule previously laid down, incited to further research. For it was shown plainly that besides the placing of the group NH between CO and a saturated hydrocarbon residue, the other part of the molecule may also influence the reaction in such a manner that a direct nitration is prevented, even on warming, although nitro-compounds actually exist.

The question, therefore, arose as to the behaviour of those isomers of glycocol anhydride, which possess the same atom-groups, but arranged in another order.

There may be eleven cyclic compounds which consist of two groups of NH, two groups of CO and two groups of CH_2, of whom however three only are described in the literature, namely:

glycocol anhydride



hydro-uracil

and

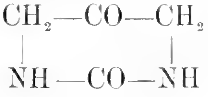
ethyleneoxamide

The last one, however, only in an impure condition, as described by Hoffmann in 1872, and which we have not yet succeeded in obtaining in a pure state.

This substance had a special importance. It has the two groups

NH, also between CO and CH_2, and, according to the rule, it ought to yield readily a dinitro-derivative; either stable or unstable. Still it might be that it was not attacked at all by absolute nitric acid, for if we remember that diacetamide, although slowly, still evolves N_2O with nitric acid and, therefore, presumably forms an unstable nitro-compound under those circumstances, and if we compare this with the cyclic succinimide, which is not attacked at all even on warming and which is connected with it in such a manner that it contains two hydrogen atoms less, and thus causes the cyclic combination, one feels inclined to attribute to the cyclic combination the prevention of the action of the nitric acid. We might also compare ethyleneoxamide to dimethyloxamide which is readily nitrated, and is related to it in the same manner as diacetamide to succinimide, and if the cycle formation has the same effect here as it has in the other case, ethyleneoxamide should not be attacked.

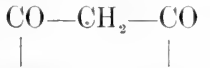
Preliminary experiments with the impure substance showed that no stable dinitro-derivate appears to be formed; at most, one which is at once decomposed by nitric acid, or it is not attacked at all. A very slow evolution of N_2O and CO_2 takes place, but this may be due to the impurity.

Of the eleven possible isomers there are only two urea derivatives namely hydro-uracil, which, as stated, conforms to the rule and gives a mononitroderivative. The second is 

$$\begin{array}{ccc} CH_2\text{—}CO\text{—}CH_2 \\ |\qquad\qquad\quad | \\ NH\text{—}CO\text{—}NH \end{array}$$

acetoneureïne

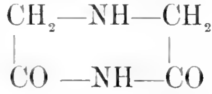
. RÜGHEIMER thought in 1892 that he had obtained this substance by the action of chloro-formic ester on diaminoacetone, but it was merely a surmise; no analysis was made and the properties were not investigated; and from our investigations it is extremely doubtful whether he had this substance in hand, for although we made the experiments in various ways we could obtain nothing else but *acetondiurethane*, from which a *dinitro-derivative* was readily obtained. A number of other methods for preparing acetonureine from diaminoacetone were tried but always without good result. In the meanwhile we are continuing our experiments for, we attach great importance to this substance as a second urea derivative, seeing that the first one conforms to the rule.

A fifth isomer would be 

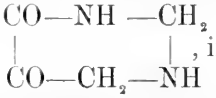
$$\begin{array}{ccc} CO\text{—}CH_2\text{—}CO \\ |\qquad\qquad\quad | \\ NH\text{—}CH_2\text{—}NH \end{array}$$

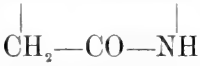
methylenemalonamide

which we have tried in vain to prepare from malonamide and formaldehyde. In this case it is the group CH_2 of the malonic acid which appears to react principally; but even with the amide of dimethylmalonic acid and formaldehyde we have not arrived at the desired result. Methylenemalonamide is of importance for this reason, that the CH_2-group of malonic acid might give a nitroderivative, whilst this may be equally expected from the two NH-groups.

A sixth isomer is the already quoted  $\begin{array}{ccccc} CH_2 & - & NH & - & CH_2 \\ | & & & & | \\ CO & - & NH & - & CO \end{array}$ *iminodiaceticimide* of which one might expect that it should yield with nitric acid only a nitrate, but not a nitro-derivative.

On heating the diamide of iminodiacetic acid in vacuo, Mr. JONGKEES obtained a substance which sublimes and has the composition of the imide. This, however, does not behave as was expected, but when evaporated with nitric acid, seems to give a nitro-derivative, whose properties are, however, somewhat different from the usual ones of nitramines or nitramides.

The last isomer of some significance for the problem under consideration, for the preparation of which no experiments have, as yet, been made, would be  $\begin{array}{ccccc} CO & - & NH & - & CH_2 \\ | & & & & | \\ CO & - & CH_2 & - & NH \end{array}$, in which one NH-group between CO and CH_2 renders probable a nitro-compound, whereas the second, placed between two CH_2, could only yield a nitrate.

The other four are derivatives of hydrazine, and are of no importance for our problem, because the two NH-groups contained therein are in a state of combination. One of those  $\begin{array}{ccccc} CH_2 & - & CO & - & NH \\ | & & & & | \\ CH_2 & - & CO & - & NH \end{array}$ has been prepared by Dr. FRIEDMANN and, when it was brought in contact with nitric acid a violent evolution of red vapours was noticed, evidently caused by oxidation.

The details of these researches which of course, are being continued will appear in the "Recueil des Travaux chimiques des Pays-Bas."

But it is evident that the second rule will have to be altered, namely in that sense that the direct nitration (if any) of the heterocyclic compounds, which contain NH placed between CO and C_nH_{2n} depends also on the manner in which the groups, between which the group NH is placed, are combined; therefore it is the same as has been noticed with acyclic compounds. In how far the cycle itself plays a rôle has not yet been satisfactorily made out but we may point, provisionally, to one peculiarity, namely, that the three compounds which do not seem to conform to the previously established rule contain the NH-groups in the *para* position in regard to each other.

Chemistry. — *"On a tetracomponent system with two liquid phases."* By Prof. F. A. H. SCHREINEMAKERS.

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

Although in the systems of three components with two and three liquid phases there may occur many cases which have been predicted by theory, but have not yet been realised by experiment, I have still thought it would be as well to investigate a few systems with four components to have a glance at this as yet quite unknown, region.

I will now describe more fully a few of those systems built up from the substances: water, ethyl alcohol, lithium sulphate and ammonium sulphate.

We may represent the equilibria with the aid of a regular tetrahedron as in Fig. 1; the angular points represent the four components:

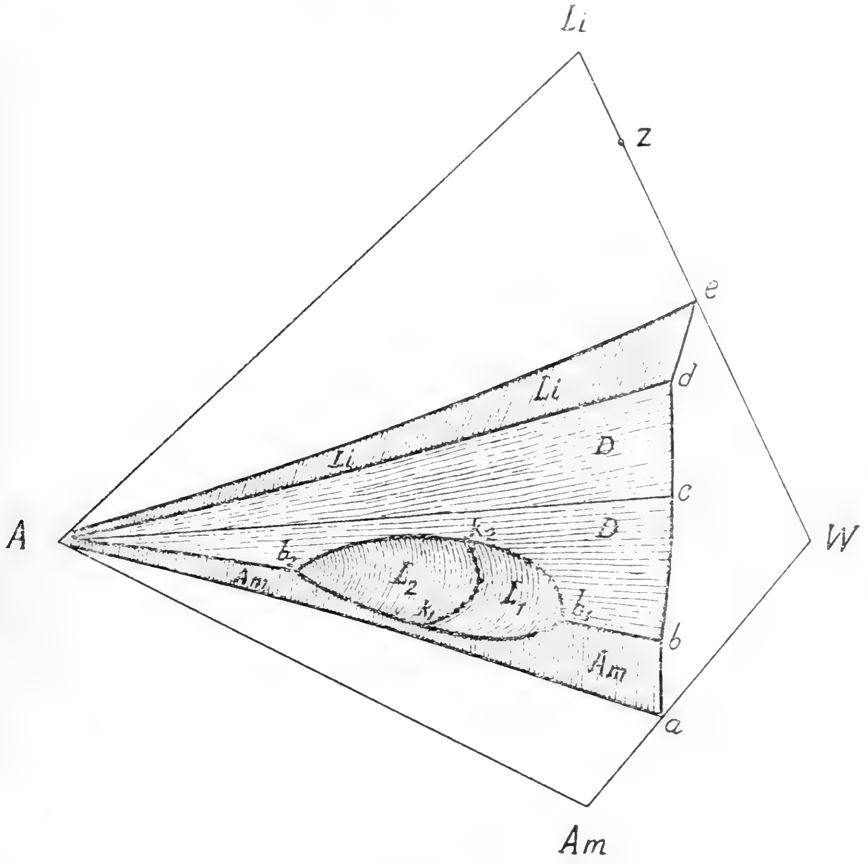


Fig. 1.

W = water, *A* = alcohol, *Li* = lithium sulphate, *Am* = Ammonium sulphate. The side *AW* being invisible has been left out, also the side *Li Am*.

$Li_2SO_4 . H_2O$ and the double salt $LiNH_4SO_4$ may also occur as solid phases besides Li_2SO_4 and $(NH_4)_2SO_4$. The first is represented by a point *Z* on the side *Li W*, the second by a point *D*, not indicated, on the side *Li Am*.

The equilibria occurring at 6°5 are represented schematically by Fig. 1. The solubilities of the $(NH_4)_2SO_4$ and of the $Li_2SO_4 . H_2O$ in water are indicated by the points *a* and *e*; point *c* indicates the solubility in water of the double salt and must, therefore, be situated on the line *WD* (the point *D* is on the side *Li Am*). As Li_2SO_4, $(NH_4)_2SO_4$ and $LiNH_4SO_4$ are practically insoluble in alcohol, their solubility may be represented practically by the point *A*.

The curve *aA* is the saturation line of the $(NH_4)_2SO_4$; it indicates the aqueous-alcoholic solutions which are saturated with solid $(NH_4)_2SO_4$.

The aqueous-alcoholic solutions saturated with Li_2SO_4 and $Li_2SO.H_2O_1$ are represented by the curve *eA* which, however, must show a discontinuity in the immediate vicinity of the point *A*, for the curve consists of two branches, of which the one to the right indicates the solutions saturated with $Li_2SO_4 . H_2O$ and the one to the left those saturated with anhydrous Li_2SO_4.

The equilibria in the ternary system: water, lithium sulphate and ammonium sulphate are represented by the curves *ab*, *bcd* and *de*, which are situated in the side plane of the tetrahedron. *ab* is the saturation line of the ammonium sulphate, *bcd* that of the double salt $LiNH_4SO_4$, *de* that of $Li_2SO_4 . H_2O$. In my opinion, however, this latter is not quite correct, for, according to several analyses, Lithium sulphate seems to mix with the ammonium sulphate, although only to the extent of a few per cent, so that branch *de* indicates solutions saturated with mixed crystals. As, however, I have not accurately investigated this mixing, I will continue to speak in future of lithium sulphate monohydrate $Li_2SO_4 . H_2O$.

Let us now look at the equilibria in the quaternary system. The surface *Am* or $Aabb_1k_1b_2A$ represents solutions saturated with solid ammonium sulphate; surface *D* or $Ab_2k_2b_1bcdA$ represents the solutions saturated with $LiNH_4SO_4$; the curve *Ac* of this surface has as pecial significance, because it indicates the solubility of $LiNH_4SO_4$ in aqueous-alcoholic mixtures. The points of the surface *D* facing the curve *Ac* represent solutions which, in relation to the double salt, contain an excess of $(NH_4)_2SO_4$; the points behind this line show solutions containing an excess of Li_2SO_4.

The curve Ac must therefore, be situated in the plane passing through AW and the point D of the side $Li\ Am$. The surface Li or Ade indicates the liquid saturated with Li_2SO_4 or $Li_2SO_4H_2O$, or with the above mentioned mixed crystals; it must, therefore, consist of different parts which however, are not further indicated in the figure. At the temperature mentioned here (6°5) systems of two liquid phases may occur also; in the figure these are represented by the surface L_1L_2 or $b_1K_1b_2K_2$ which we may call the binodal surface; this binodal surface is divided by the line K_1K_2 into two parts L_1 and L_2 in such a manner that each point of L_1 is conjugated with a point of L_2. Two conjugated points indicate two solutions in equilibrium with each other: with each solution of the surface L_1 a definite solution of the surface L_2 may be in equilibrium.

Instead of a critical point, such as occurs with ternary mixtures at a constant temperature and pressure, a critical line is formed here, represented by K_1K_2. Each point of this line represents, therefore, a solution which is formed because in the system of two liquid phases $L_1 + L_2$ the two liquid phases become identical. Let us now look at the sections of the different surfaces: Ad then represents the solutions saturated with $LiNH_4SO_4$ as well as with $Li_2SO_4H_2O$; Ab_2 and b_1b indicate the liquids saturated with $LiNH_4SO_4$ and $(NH_4)_2SO_4$.

The intersection of the binodal surface with the surface Am namely, the curve $b_1K_1b_2$ indicates the system: $L_1 + L_2 + (NH_4)_2SO_4$ namely, two liquid phases saturated with solid ammonium sulphate. With each point of the curve b_1K_1 a point of b_2K_1 is conjugated. Each liquid of b_1K_1 may, therefore, be in equilibrium with a definite liquid of b_2K_1 while both are saturated with solid $(NH_4)_2SO_4$.

The intersection of the binodal surface with the surface D, namely, the curve $b_1k_2b_2$ represents the solutions of the system $L_1 + L_2 + Li\ NH_4SO_4$. With each liquid of b_1k_2 another one of b_2k_2 may, therefore, be in equilibrium while both are saturated with solid $Li\ NH_4SO_4$.

The points of intersection b_1 and b_2 of these two curves give the system: $L_1 + L_2 + (NH_4)_2SO_4 + Li\ NH_4SO_4$, namely two liquids both saturated with ammonium sulphate and lithium ammonium sulphate which may be in equilibrium with each other.

The points k_1 and k_2 have a special significance; both are critical liquids which, however, are distinguished from the other critical liquids of the critical curve k_1k_2 in that they are also saturated with a solid substance: k_1 is saturated with ammonium sulphate and k_2 with lithium ammonium sulphate.

If the temperature is raised the heterogeneous sphere is extended;

at about ± 8° the point k_1 arrives on the side $AWAm$, so that above this temperature a separation of water-alcohol-ammonium sulphate may occur in the ternary system.

I have further closely investigated at 30° the equilibria occurring in this quaternary system; the results are represented by the schematic figure 2.

The saturation surface Am which at 6°.5 still consists of a coherent whole, now consists (experimentally) of two parts separated from each other: this is because the binodal surface $L_1 L_2$ now terminates on the side plane $AWAm$ in the curve $a_1 k_1 a_2$.

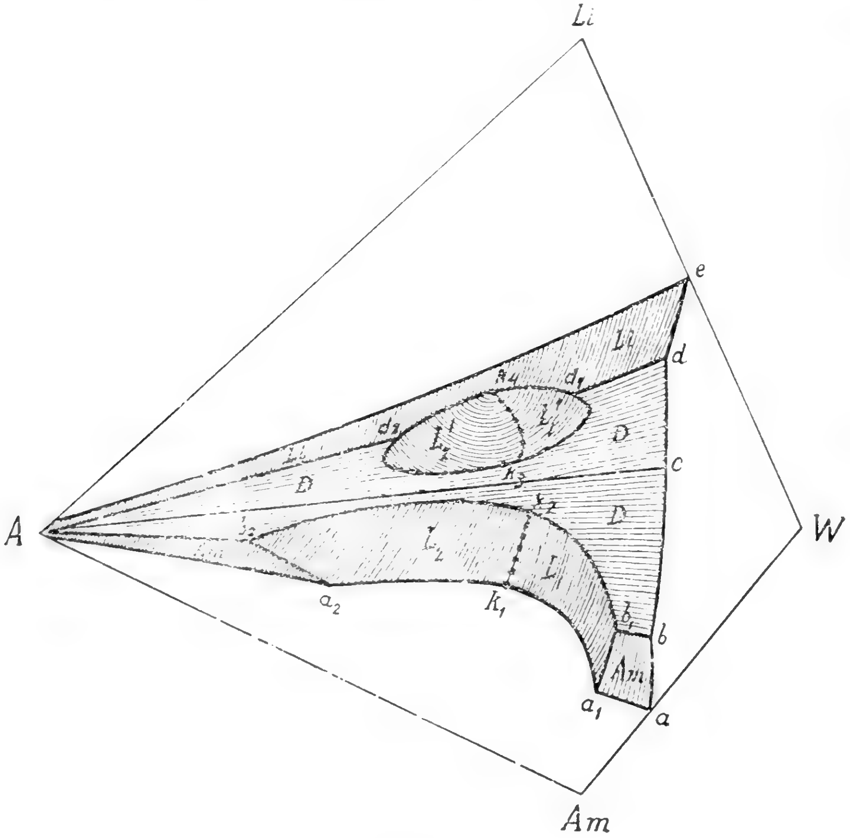


Fig. 2.

Of the critical line $k_1 k_2$ the terminal point k_1 represents a ternary critical liquid; all other liquids of this line are quaternary critical ones, of which k_2 is saturated with solid lithium ammonium sulphate.

The phenomenon of the existence of a second heterogeneous region at this temperature was quite unexpected; it is represented in the figure by the binodal surface $L_1{}^1 L_2{}^1$ or $d_1 k_4 d_2 k_3$ with the critical line $k_3 k_4$. I have not further investigated at what temperature this is formed; it is sure to be present at about 18°.

The binodal surface $L_1 L_2$ intersects the saturation surfaces Am and D; we have, therefore, one series of two liquid phases, saturated with solid $(NH_4)_2SO_4$, and one series saturated with solid $LiNH_4SO_4$. The binodal surface $L_1{}^1 L_2{}^1$ intersects the two saturation surfaces D and Li. We have, therefore, one series of two liquid phases saturated with $LiNH_4SO_4$ (curve $k_3 d_1$ and $k_3 d_2$), and one series saturated with $Li_2SO_4 . H_2O$ (curve $k_4 d_1$ and $k_4 d_2$). By d_1 and d_2 are represented two liquid phases which are in equilibrium with each other and saturated with $LiNH_4SO_4$ and $Li_2SO_4 . H_2O$. Of the series of the critical liquids represented by the curve $k_3 k_4$, k_3 is saturated with $LiNH_4SO_4$ and k_4 with $Li_2SO_4 . H_2O$.

The curve Ac which indicates the liquids saturated with $LiNH_4SO_4$ without any excess of either of the components runs between the two heterogeneous regions. From this it follows that this double salt at 30° cannot give two liquid phases with water-alcohol mixtures.

We, therefore, have at 30° the following equilibria in the quaternary system.

liquids saturated with

1. $(NH_4)_2SO_4$, represented by the surface Am
2. $LiNH_4SO_2$, ,, ,, ,, ,, D
3. $Li_2SO_4H_2O$, ,, ,, ,, ,, Li
4. $(NH_4)_2SO_4$ and $LiNH_4SO_4$,, ,, the curves: bb_1 and b_2A
5. $Li_2SO_4H_2O$ and $LiNH_4SO_4$,, ,, ,, ,, dd_1 and d_2A

system of two liquid phases:

6. in itself represented by the surface L_1L_2
7. ,, ,, ,, ,, ,, ,, $L_1'L_2'$
8. saturated with $(NH_4)_2SO_4$, represented by the curves a_1b_1 and a_2b_2
9. ,, ,, $LiNH_4SO_4$, ,, ,, ,, ,, b_1K_2 and b_2K_2
10. ,, ,, $LiNH_4SO_4$, ,, ,, ,, ,, d_1K_3 and d_2K_3
11. ,, ,, $Li_2SO_4H_2O$, ,, ,, ,, ,, d_1K_4 and d_2K_4

two liquid phases saturated with:

12. $(NH_4)_2SO_4$ and $LiNH_4SO_4$, represented by the points: b_1 and b_2
13. $Li_2SO_4H_2O$ and $LiNH_4SO_4$, ,, ,, ,, ,, d_1 and d_2

critical liquids:

14. one series represented by the curve K_1K_2
15. ,, ,, ,, ,, ,, ,, K_3K_4
16. one critical liq. saturated with $LiNH_4SO_4$, represented by the point K_2
17. ,, ,, ,, ,, ,, $LiNH_4SO_4$, ,, ,, ,, ,, K_3
18. ,, ,, ,, ,, ,, $Li_2SO_4H_2O$, ,, ,, ,, ,, K_4

On raising the temperature over 30° the two heterogeneous regions gradually approach each other and finally unite; at what temperature this happens has not been determined, but from the experiments it is shown that this is already the case below 40°; I have also not been able to determine whether this point of confluence is situated in front or behind the curve *Ac*, or perhaps accidentally on the same.

I have closely investigated the equilibria occurring at 50° and represented the same by figure 3; any further explanation is superfluous. I must, however, say something as to the points c_1 and c_2, namely the intersecting points of the curve *Ac* with the saturating curve of the two liquid phases: b_1d_1 and b_2d_2. At first sight we might think that these two liquids may be in equilibrium with each other. That possibility, of course, exists. Suppose we take a water-alcohol mixture of such composition that two liquid phases occur on saturating with $LiNH_4SO_4$. Both liquids will now contain Li_2SO_4

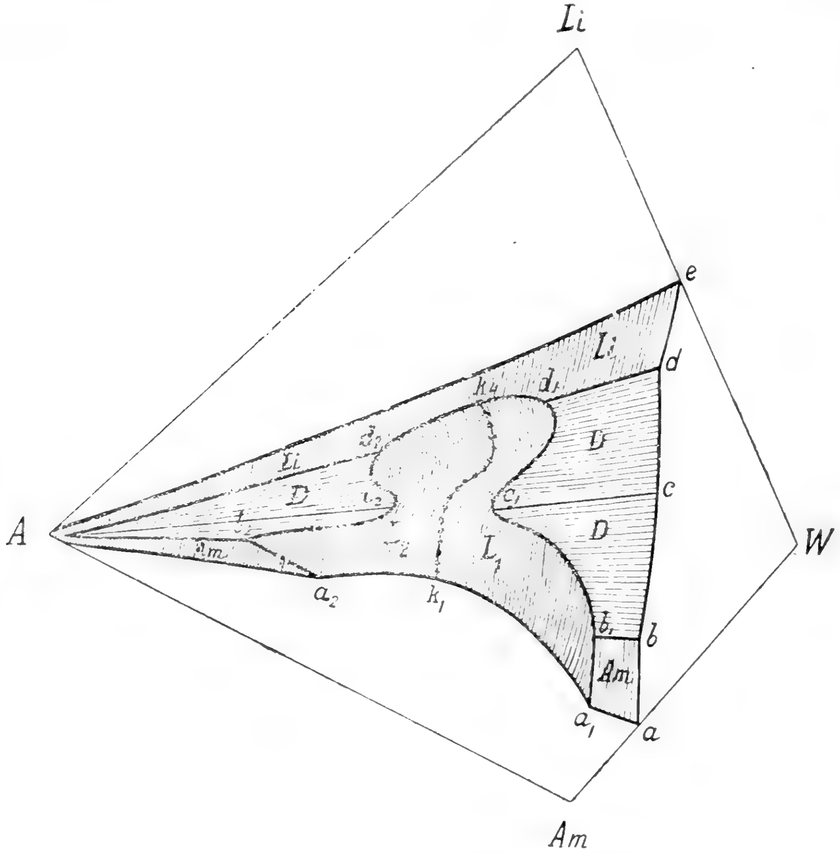


Fig. 3.

and $(NH_4)_2SO_4$ and it is evident that two cases may occur. It may be that the two liquids contain the two components in the same proportion as they occur in the double salt; it is then as if the double salt dissolves in both liquids without decomposition. If this is the case the liquids c_1 and c_2 will be in equilibrium with each other.

The second possibility is that one of the liquids has in regard to the double salt an excess of Li_2SO_4 and the other, therefore, an excess of $(NH_4)_2SO_4$; in this case, c_1 and c_2 cannot be in equilibrium with each other. The experiment now shows such to be the case. When I saturated a water-alcohol mixture with $LiNH_4SO_4$ at 50°, the alcoholic layer contained a small excess of Li_2SO_4 and the aqueous layer a small excess of $(NH_4)_2SO_4$. From this it follows that the conjugation line does not coincide with the surface DAW but intersects it; the part to the right of the line must be situated in front of the plane and the left part behind it. The alcoholic solution c_2 of the double salt cannot, therefore, be in equilibrium with the aqueous solution c_1 of this double salt, but may be so with a solution containing an excess of $(NH_4)_2SO_4$.

Chemistry. "*On catalytic reactions connected with the transformation of yellow phosphorus into the red modification.*" By Dr. J. BÖESEKEN. (Communicated by Prof. A. F. HOLLEMAN).

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

I.

From the researches of HITTORF (Pogg. Ann. 126 pag. 193) LEMOINE (Ann. Ch. Ph. [4] 24. 129) TROOST and HAUTEFEUILLE (Ann. Ch. Ph. [5] 2 pag. 153), R. SCHENCK (B. Ch. G. 1902 p. 351 and 1903 p. 970) and the treatises of NAUMANN (B. Ch. G. 187 2p. 646), SCHAUM (Lieb. Ann. 1898. 300 p. 221), WEGSCHEIDER and KAUFLER (Cent. Blatt 1901 I p. 1035) and ROOZEBOOM (Das heterogene Gleichgewicht I p. 171 and 177) it appears highly probable that red phosphorus is a polymer of the yellow variety, which polymerism is, however, restricted exclusively to the liquid and the solid conditions: the vapour (below 1000°) always consists of the monomer P_4.

From the above considerations it moreover follows that the yellow phosphorus is metastable at all temperatures below the melting point of the red phosphorus (630°); it may, therefore, be expected that it will endeavour to pass into the red variety below 630°.

Although there are many instances where a similar transformation, as with phosphorus at a low temperature, proceeds exceedingly slowly, the velocity in this case is certainly strikingly small. Even at 200°, when the metastable substance possesses a considerable vapour tension, it is still immeasurably small even though red phosphorus may be present.[1] This extraordinary slowness, notwithstanding the considerable heat quantities liberated during the transformation, and the complete alteration of properties caused thereby, have a long time since established the conviction that the two modifications of phosphorus are each other's polymers and that the red one has a much more complex molecule than the yellow one, but the real cause of that slowness is not elucidated thereby.

As regards the question *how* this condensation takes place, SCHENCK (l.c.) was the first to endeavour to answer this experimentally. On boiling yellow phosphorus with an excess of PBr_3, he succeeded in changing it to the red modification at 172° with measurable velocity; and from his first investigations he concluded that the order of this reaction was a bimolecular one:

$$2\,P_4 \rightarrow P_8.$$

This was meant to represent the first phase, for SCHENCK pointed out that red phosphorus had no doubt a higher molecular weight than P_8, which subsequent condensation should then take place with great velocity; in other words he arrived at the rather improbable result that the condensation of P_8 to P_n would take place much more rapidly than that of the simple P_4 molecules to P_8.

At a repetition of these measurements with one of his pupils (E. BUCK), they came indeed to the conclusion that the reaction is monomolecular (B. Ch. G. 1903 p. 5208). He remarks "Daraus geht mit Sicherheit hervor, dass die Reaction der Umwandlung des weissen Phosphors in rothen monomolekular verläuft."

He, however, adds "Daraus könnte man den Schluss ziehen, dass die Molekular-gewichte des weissen und rothen Phosphors identisch sind."

It strikes me that SCHENCK arrives here at a less happy conclusion. From the occurrence of a mono-molecular reaction we need not necessarily come to the conclusion that the *entire* process proceeds in this manner.

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[1] ROOZEBOOM (l.c.) compares this to the retardation of the crystallisation of strongly undercooled fusions as 200° is more than 400° below the melting point of red phosphorus; I am, however, of opinion that this view is untenable on account of the relatively high temperature, and particularly the very great mobility of the yellow phosphorus (ROOZEBOOM l.c. p. 89). The cause of the phenomena must be looked for elsewhere.

On the contrary as in so many other chemical transformations, we must assume that the measurements executed only apply to a subdivision of the reaction, namely to that with the smallest velocity.

In this case it is only natural to suppose that the velocity determinations of SCHENCK and BUCK apply to the decomposition of the P_4 molecule[1]) into more simple fragments (P_2 of P), then at once condense to the red modification so that we may represent the whole process in this manner for instance:

$$P_4 \text{ (yellow)} \rightarrow 2P_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$nP_2 \qquad \rightarrow P_{2n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which the reaction velocity of (2) is very much larger than that of (1).

(We might also suppose, as a primary reaction the transformation of the metastable phosphorus into a *labile* P_4; this, however, I do not think so probable because, in the determination of the vapour density above 1000°, a *splitting* has been indeed observed).

It cannot be a matter of surprise that this decomposition velocity at 200°, (without catalyst) will still be extremely small, looking at the great stability of P_4 in the state of vapour; and if this decomposition, as I suppose, must precede the condensation, the separation of the red phophorus at that temperature will proceed at least equally slowly.

There is also nothing very improbable in the very rapid transformation of the dissociated P_2 or P into red phosphorus.

The fact that the allotropic transformation takes place particularly under the influence of sunlight is certainly not in conflict with the idea of a primary splitting, as we know that the actinic rays accelerate the decompositions (such as of HJ, AgBr, C_2J_2, etc.).

I wish also to point out that a primary splitting is also accepted in other monomolecular reactions, such as in the decomposition of AsH_3 (VAN 'T HOFF's Vorlesungen), of CO (SCHENCK B. Ch. G. 1903 p. 1231 and SMITS and WOLFF. (These Proc. 1902 p. 417).[2])

The monomolecular splitting of C_2J_2 into C and C_2J_2 SCHENK and

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[1]) Although the size of the molecule of the liquid yellow phosphorus is not known with certainty, the identity with that of the vapour is however very probable; for the rest it does not affect the argument.

[2]) I omit purposely the beautiful researches of M. BODENSTEIN, although for the union of S and H. he also arrives at the conclusion that a primary splitting of the S_8 molecule precedes the union with H_2, because we are dealing here with heterogeneous systems in which solubility velocities play an important rôle. It is not impossible, that in all cases in which *amorphous* substances separate we are dealing with such solubility velocities.

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SITZENDORFF B. 1905, p. 3459, may be interpreted in the simplest manner by the succession of the reactions:

$$C_2J_2 \rightarrow C + CJ_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$nC \rightarrow C_n \text{ and } 2\ CJ_2 \rightarrow C_2J_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

II.

The measurements of SCHENCK and BUCK have been made at the boiling point of PBr_3. As this is situated at 172°, it appears that the solvent exerts a considerable accelerating influence on the transformation, as pure yellow phosphorus at 200° remains practically unaltered.

The solvent, therefore, acts catalytically; a still more powerful influence has $AlCl_3$. If this is brought together with phosphorus in vacuum tubes, the transformation takes place even below 100°.

The catalyst is at once covered with a layer of pale red phosphorus, which it is rather difficult to remove by shaking, so that it is necessary to add now and then a fresh quantity of $AlCl_3$. The action proceeds much more regularly if benzene (and particularly PCl_3) is added as a solvent. At the boiling point of this, the transformation is completed after a few hours (respectively, minutes); the product is SCHENCK's scarlet-red phosphorus but much contaminated with benzene and condensation products, which are retained with great obstinacy.

In connection with the explanation in part I. I believe that the observations of SCHENCK and of myself throw some light on catalytic actions in general.

For it is very probable that in this allotropic transformation a splitting occurs first; we notice that the transformation, consequently the splitting, is accelerated by PBr_3 or $AlCl_3$. Will this not occur generally in catalysis? As a dissociation precedes most reactions it is probable that this question must be answered in the affirmative. (I wish, however, to lay stress on the fact, that in answering this question we do not penetrate into the real nature of catalysis. The reason *why* the dissociation acceleration occurs, whether this is connected with a temporary combination of the catalyst with the active molecules, or whether the catalyst removes the cause which impedes the dissociation, remains unexplained and need not be discussed here any further.)

As far as I have been able to ascertain, this conception is not antagonistic to the facts observed; in fact a number of cases are known where a catalyst causes *directly* a splitting or considerably accelerates the same.

Platinum, for instance, powerfully accelerates the decomposition of hydrogen peroxide, ozone, nitric acid, hydrazine etc.

Aluminium chloride causes a direct splitting of the homologues of benzene, of the very stable polyhalogen derivatives, of aromatic ethers, of sulphuryl chloride, etc. The number of these decompositions is so considerable that, in other cases where we cannot prove a direct dissociation by the catalyst, we may still argue that it takes place primarily, or rather that an already present but exceedingly small dissociation is accelerated in such a manner that a system attains the stable condition of equilibrium much sooner than without the catalyst.

The great evolution of heat in the process

$$HCCl_3 + 3\,C_6H_6 + (AlCl_3) = (C_6H_5)_3\,CH + 3\,HCl + (AlCl_3)$$

points to the fact that the system to the right is more stable than that to the left. I attribute its slow progress when no $AlCl_3$ is used to the small dissociation velocity of chloroform: the catalyst accelerates this dissociation so that the stable condition of equilibrium is attained in a short time. This reaction gets continuously more violent (the temperature being kept constant). This phenomenon may be readily explained if we bear in mind that the reaction proceeds in different stages ($C_6H_5\,CHCl_2$, $CHCl\,(C_6H_5)_2$ and $CH(C_6H_5)_3$ are formed in succession) and that the chlorinated intermediate products are decomposed much more readily than $CHCl_3$.

If sulphur is boiled with benzene and aluminium chloride we obtain almost exclusively $(C_6H_5)_2\,S$, $(C_6H_4)_2\,S_2$ and H_2S. Without the catalyst hardly any action takes place because the dissociation of S_8 in benzene solution at 80° is negliglible: (if sulphur is boiled with toluene H_2S and condensation products are formed without $AlCl_3$ being present) the aluminium chloride accelerates the reaction $S_8 \rightarrow 4\,S_2$, and consequently the formation of the condensation products. This explanation is therefore quite the same as that given for the reaction of P_4 with benzene and aluminium chloride; the sole difference is that in the latter the second stage of the reaction consists exclusively in the condensation of P_2 to red phosphorus, a condensation to which sulphur does not seem to be liable to the same extent, so that the dissociated sulphur forms with benzene the above products.

I consider the formation of a compound of the catalyst with one of the reacting substances of importance for the taking place of the reaction in so far only that one phase can be formed; otherwise it rather obstructs the reaction, because the catalyst becomes to a certain extent paralysed. One of the most powerful catalysts, platinum, is actually characterised because it does *not* (or at least with great difficulty) unite with the reacting molecules, but forms a kind of solid solution. Carbon tetrachloride which forms no compound with aluminium chloride is certainly attacked by benzene in presence of that catalyst not less easily than benzoyl chloride which does form an additive product; whilst also the chlorine atom in the acid chloride is certainly not less "mobile" than that of CCl_4.

Gustavson imagines that the formation of compounds, such as $C_6H_3(C_2H_5)_3\,Al_2Cl_6$ is necessary for the action of C_2H_5Cl on benzene; these were separated from the bottom liquid layer which forms during the action of C_2H_5Cl on benzene and aluminium chloride; if, however, the formation of this layer is prevented as much as possible, the yield of ethylated benzene improves. Therefore I do not call its formation *necessary*. That it may act favourably perhaps is because the catalyst and also the two reacting molecules are soluble in the same, thus allowing them to react on each other in concentrated solutions.

As has been observed above, there is something unsatisfactory in assuming intermediate reactions in order to explain catalytic phenomena. I will try to explain this matter more clearly.

As is known, we may express the reaction velocity of a condition change by the ratio: $\frac{\text{impelling force}}{\text{resistance}}$ in which the impelling force for that change in condition possesses a definite value which a catalyst cannot alter in the least; the resistance, however, is dependent on influences for the greater part unknown. Therefore, the resistance must be lessened by the catalyst and the question to be solved is: "On what does this decrease in resistance depend?"

If we suppose that intermediate reactions take place we divide the process into a series of others of which each one considered by itself is propelled by a force less impelling than the total change; the resistance of each of those division processes must, therefore, be much less, and the question then becomes: How is it that those intermediate reactions proceed much more rapidly than the main reaction? which is in fact nothing else but a circumlocution of the first question: how is it that the catalyst decreases the original resistance? Therefore, by assuming intermediate products, we have not been much enlightened, on the contrary we have made the problem more intricate, because, instead of having to account for a single increase of velocity, we have to look for that of at least two.

I call to mind the theory of Ostwald who supposes each process to be a succession of condition changes, which will be all possible if they occur with potential diminution. If, however, the first of those changes can commence only with absorption of free energy, the process will not take place unless a catalyst is added; this, therefore, opens another road . . . Now, in my opinion too much attention is paid to the milestones on that road and too little to the opening itself.

This is chiefly caused by the fact that we know so little of the so-called ,,passive resistances'', for instance we cannot give a satisfactory explanation of the fact that iodine acts much more rapidly at low temperatures on metals than does oxygen, although the potential decline is much smaller. Still, I think that we must look for this mainly in the ready dissociation of the iodine molecule, always supposing that atoms react more rapidly than molecules, a supposition, moreover nearly a century old.

If this should be so, the action of a catalyst must be sought for in the increase of this dissociation.

Now, we know of a number of reactions where the catalyst forms undoubtedly a compound with one of the reacting molecules, which additive product then reacts with the second molecule to form the final product, with liberation of the catalyst, but even in such a case, which is called by many "pseudo-catalysis" (WAGNER, Z. Phys. Ch. 28 p. 48), I do not consider the *formation* of this compound as something essential without which the acceleration would not take place.

I certainly do not consider the formation of such an additive product as being without any significance, as it is an indication that the catalyst can exercise a particular influence on one of the molecules; the real increase of velocity is, in my opinion, due more to that influence than to the formation of the additive product, and in view of what precedes this, that influence consists presumably of an increase of the dissociation (and through this of the active mass).

It is, of course, obvious that a catalyst will act all the more energetically when the additive products are more labile. I have already mentioned platinum and now point also to the H-ions with which the formation of additive products, for instance when accelerating saponification, is far from probable. As a very lucid example, I mention the different catalytic influence which iodine and $AlCl_3$ exert on the transformation of yellow into red phosphorus.

From the researches of Brodie (Ann. de Ch. Ph. 1853 p. 592) which I have found fully confirmed, a small quantity of iodine can convert a large quantity of yellow phosphorus very rapidly into red phosphorus at 140°. (As in many other cases, there is a limit because the catalyst is precipitated by the colloidal phosphorus formed.

The velocity at the ordinary temperature is very small but becomes plainly perceptible at 80°. We are undoubtedly dealing here with a case where the catalyst combines with the phosphorus to P_2I_4; this substance commences at 80° to dissociate measurably [so that its vapour density can only be determined at a low temperature (TROOST CR 95 293)] with separation of *red* phosphorus. We may, therefore give here a fairly positive answer to the question: How is it that the second division process proceeds more rapidly than the original? Because P_2I_4 dissociates much more rapidly than P_4.

But this is after all but a lucky circumstance, the real cause must be sought in the fact that in order to obtain P_2I_4 the P_4 molecule must be dissociated to begin with. With $AlCl_3$ I have not been able to find an additive product, only some indications that, besides the allotropic transformation, a trace of PCl_3 is formed (even with perfectly dry substances the manometer, after a few hours' heating to 100°, showed a slight increase of the vapour pressure).

The fact that the red phosphorus formed has in a high degree the property of coprecipitating the catalyst might perhaps indicate the possibility of a compound being formed between yellow phosphorus and $AlCl_3$; from the above it follows that there is a possibility of a certain reciprocal influence[1]) but I attribute this coprecipitation to the colloid properties of the red phosphorus, which, when obtained from solvents and also under the influence of rays of light, carries with it a certain quantity.

But even if an additive product is found, the existence of this substance is no more the cause of the acceleration than it is in the case of P_2I_4.

On the contrary, I consider the formation of a compound of the catalyst to be a case of "poisoning", caused by one of the reacting molecules, just as arsenic and prussic acid are poisons for platinum, because in combining with it, they prevent the entrance of O_2 and H_2 (respectively SO_2); just as ether is a poison for $AlCl_3$, because it unites with it to a firm compound, which does not decompose until over 100°, the temperature at which the catalyst again recovers itself.

Now, I cannot deny that we have not advanced much further with this dissociation theory (which is also not absolutely novel) for the question is now: How is it that a catalyst accelerates the dissociation? But my object was to point out that the formation (and eventually the admitting of the formation) of intermediate products can certainly never lead to an explanation of the catalytic phenomena.

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[1]) I have also found a similar reciprocal influence in the action of C_2H_5 Br on $AlCl_3$ in which C_2H_5Cl and $AlBr_3$ are formed; it undoubtedly points to a dissociation.

Physics. — *"Contribution to the theory of binary mixtures."* By Prof. J. D. VAN DER WAALS.

The theory of binary mixtures, as developed in the "Théorie moléculaire", has given rise to numerous experimental and theoretical investigations, which have undoubtedly greatly contributed to obtain a clearer insight into the phenomena which present themselves for the mixtures. Still, many questions have remained unanswered, and among them very important ones. Among these still unanswered questions I count that bearing on a classification of the different groups of ψ-surfaces. For some binary systems the plait of the ψ-surface has a simple shape. For others it is complex, or there exists a second plait. And nobody has as yet succeeded in pointing out the cause for those different forms, not even in bringing them in connection with other properties of the special groups of mixtures. It is true that in theory the equation of the spinodal curve which bounds the plait, has been given, and when this is known with perfect accuracy, it must be possible to analysis to make the classification. But the equation appears to be very complicated, and it is, especially for small volumes, only correct by approximation, on account of our imperfect knowledge of the equation of state. Led by this consideration I have tried to find a method of treatment of the theory which is easier to follow than the analytical one, and which, as the result proved, enables us to point out a cause for the different shape of the plaits, and which in general throws new light upon other already more or less known phenomena.

Theory teaches that for coexisting phases at given temperature three quantities viz. $-\left(\frac{d\psi}{dv}\right)_{xT}$, $\left(\frac{d\psi}{dx}\right)_{vT}$ and $\psi - v\left(\frac{d\psi}{dv}\right)_{xT} - x\left(\frac{d\psi}{dx}\right)_{vT}$ must be equal. The first of these quantities is the pressure, which we represent by p; the second is the difference of the molecular potentials or $M_2\mu_2 - M_1\mu_1$, which we shall by analogy represent by q. The third of these quantities is the molecular potential of the first component, which we shall represent by $M_1\mu_1$. Now the points for equal value of p lie on a curve which is continuously transformed with change of the value of p, so that, if we think all the p-curves to be drawn, the whole v,x-diagram is taken up by them. In the same way the points for given value of q lie on a curve which continuously changes its shape with change of the value of q: and again when all the q-lines have been drawn, the whole v,x-diagram is taken up. Both the p-lines and the q-lines have the property, that through a given point only one p-line, or only one

q-line can be drawn. One single p-line, however, intersects an infinite number of lines of the q-system, and every q-line an infinite number of lines of the p-system. One and the same p-line intersects a given q-line even in several points. However, it will, of course, be necessary, that if two points indicate coexisting phases, both the p-line and the q-line which passes through the first point, passes also through the second point. If we choose a p-line for two coexisting phases, not every arbitrarily chosen value for a q-line will satisfy the condition of coexistence in its intersections with the p-line, because a third condition must be satisfied, viz. that $M_1 \mu_1$ must have the same value. The result comes to this: when all the p-lines and all the q-lines have been drawn and provided with their indices there is one more rule required to determine the points which belong together as indicating coexisting points. So in the following pages I shall have to show, when this method for the determination of coexisting phases is followed: 1. What the shape of the p-lines is, and how this shape depends on the choice of the components. 2. What the shape of the q-lines is, and how this shape depends on the choice of the components. 3. What rule exists to find the pair or pairs of points representing coexisting phases from the infinite number of pairs of points which have the same value of q, when p has been given — or when on the other hand the value of q is chosen beforehand, to find the value of p required for coexistence.

But for the determination of the shape of the spinodal curve the application of the rule in question is not necessary. For this the drawing of the p- and the q-lines suffices. There is viz. a point of the spinodal curve wherever a p-line touches a q-line. We have viz. from $\frac{d^2\psi}{dv^2}\left(\frac{dv}{dx}\right)_p + \frac{d^2\psi}{dvdx} = 0$, and from $\frac{d^2\psi}{dxdv}\left(\frac{dv}{dx}\right)_q + \frac{d^2\psi}{dx^2} = 0$ for $\left(\frac{dv}{dx}\right)_p$ the value $-\dfrac{\frac{d^2\psi}{dxdv}}{\frac{d^2\psi}{dv^2}}$ and for $\left(\frac{dv}{dx}\right)_q$ the value $-\dfrac{\frac{d^2\psi}{dx^2}}{\frac{d^2\psi}{dxdv}}$, and so we may write the equation of the spinodal curve:

$$\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q .$$

So if we are able to derive from the properties of the components of a mixture what the course of the p- and of the q-lines is, we can derive much, if not everything, about the shape of the spinodal curve. And even when the course of these lines can only be predicted qualitatively, and the quantitatively accurate knowledge is wanting, the quantitatively accurate shape of the spinodal curve will, indeed, not be known, but yet in large traits the reasons may be stated, why in many cases the shape of the plait is so simple as we are used to consider as the normal course, whereas in other cases the plait is more complex, and there are even cases that there is a second plait.

Particularly with regard to the p-lines, it is possible to forecast the course of these lines from the properties of the components. With regard to the q-lines this is not possible to the same extent, but if there is some uncertainty about them, we shall generally have to choose between but few possibilities.

THE COURSE OF THE p-LINES.

In fact the most essential features of the course of the p-lines were already published by me in "Ternary Systems" — and only little need be added to enable us to determine this course in any given case of two arbitrarily chosen components. As $p = -\frac{d\psi}{dv_{xT}}$ and $\left(\frac{dv}{dx}\right)_p = -\frac{\left(\frac{dp}{dx}\right)_{vT}}{\left(\frac{dp}{dv}\right)_{xT}}$, it is required for indicating the course of these p-lines to know the course of the curves $\left(\frac{dp}{dv}\right)_{xT} = 0$ and $\left(\frac{dp}{dx}\right)_{vT} = 0$.

The former curve has a continuous liquid branch, and a continuous gas branch, at least when T lies below every possible T_k, when we denote by T_k the critical temperature for every mixture taken as homogeneous that occurs in the diagram. If there should be a minimum value of T_k for certain value of x, and T is higher than this minimum T_k, the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$ has split up into two separate curves. In either of them the gas and the liquid branch have joined at a value of $v = v_k$. In this case a tangent may then be traced // to the v-axis to each of these two parts of the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$.

The second curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ is one which has two asymptotes, and which may be roughly compared to one half of a hyperbola. The shape of this curve derived from the equation of state follows from the equation:

$$\frac{MRT\dfrac{db}{dx}}{(v-b)^2}-\frac{\dfrac{da}{dx}}{v^2}=0.$$

If we now always take as second component that with the greatest value of b, so that $\frac{db}{dx}$ is always positive, it appears from the given equation that the curve $\left(\frac{dp}{dx}\right)_{vT}=0$ cannot possess points for these values of x, for which $\frac{da}{dx}$ is negative. Only at that value of x for which $\frac{da}{dx}=0$, this possibility begins, but then only if $T=0$. If T has a definite value $\frac{da}{dx}$ must be positive, for points of this curve to be possible. For $v=\infty$, $\frac{da}{dx}$ must be $=MRT\frac{db}{dx}$. And the value of x which satisfies this equation, indicates one asymptote of the discussed curve by a line // to the v-axis. If this asymptote has been drawn, we may think the mixtures with decreasing critical temperature to be placed on its left side. And on the right the mixtures with increasing critical temperature do not yet immediately follow. For a separation between the mixtures with decreasing and those with increasing T_k, $\frac{da}{dx}$ must be $=\frac{a}{b}\frac{db}{dx}$; only when $MRT=\frac{a}{b}$ T_k would immediately ascend again on the right of this asymptote; but then T would have to be chosen so high, that it was $^{27}/_{8}$ T_k, and for the present at least we shall choose T far below that limit.

That the line $x=c$, where c has the value which follows from $\frac{da}{dx}=MRT\frac{db}{dx}$, is an asymptote, is seen when we think the equation of the curve $\left(\frac{dp}{dx}\right)_{vT}=0$ written as follows: $\frac{v^2}{(v-b)^2}=\frac{\dfrac{da}{dx}}{MRT\dfrac{db}{dx}}$. As the value of $\frac{da}{dx}$ becomes larger from left to right, $\frac{v}{v-b}$ must increase from left to right, or $\frac{v}{b}$ decrease. For the value of x, following from $\frac{da}{dx}=MRT\frac{db}{dx}$, $\frac{v}{b}$ is infinite; for larger values of x, $\frac{v}{b}$ decreases more and more, and as $\frac{v}{b}$ can never become $= 1$, because $\frac{da}{dx}$ cannot become infinite, the curve $v = b$ is the second asymptote. So if x is made to increase more and more, also beyond the values which for a given pair of components are possible in order to examine the circumstances which may occur with all possible systems for which with positive value of $\frac{db}{dx}$ increasing value of T_k is always found, a minimum volume must occur on the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$. So for this point $\left(\frac{d^2p}{dx^2}\right)_{vT} = 0$.

Now that we have described in general outlines the two curves which control the course of the p-lines, we shall have to show in what way they do so.

From

$$\left(\frac{dv}{dx}\right)_{pT} = -\frac{\left(\frac{dp}{dx}\right)_{vT}}{\left(\frac{dp}{dv}\right)_{xT}}$$

follows that to a p-line a tangent may be drawn // x-axis when it passes through the curve $\left(\frac{dp}{dx}\right)_{vT}$, and a tangent // v-axis, when it passes through the curve $\left(\frac{dp}{dv}\right)_{xT}$. But though these are important properties they would be inadequate for a determination of the course of the isobars, if not in general outlines the shape of one of these lines could be given. The line $\left(\frac{dp}{dx}\right)_{vT} = 0$ viz. intersects the line $\left(\frac{dp}{dv}\right)_{xT} = 0$ in two points, and it is these two points which are of fundamental significance for the course of the p-lines. The point of intersection with the liquid branch is viz. for a definite p-line a double point, the second point of intersection being such an isolated point that it may be considered as a p-curve that has contracted to a single point. The surface $p = f(x, v)$ is namely convex-concave in the neighbourhood of the first mentioned point. Seen from below a section // v-axis is convex, and a section // x-axis is concave. A plane, parallel to the v, x-plane touching the p-surface intersects, therefore, this surface in two real lines, according to which p has the same value. But for the second point of intersection the two sections are concave seen from below — and there are no real lines of intersection. This second point is a real point of maximum pressure. With all these properties, and also with those mentioned before or still to be mentioned, $\frac{d^2a}{dx^2}$ is assumed to be positive. ¹)

Now the curve $p =$ constant passing through the first point of intersection which the curves $\left(\frac{dp}{dv}\right)_{xT} = 0$ and $\left(\frac{dp}{dx}\right)_{vT} = 0$ have in common, is the isobar whose shape we can give, which shape at the same time is decisive for all those following, either for larger or smaller value of p. In the adjoined figure 1 its course is represented. Coming from the left it retains its direction to the right also in the point of intersection with the curve $\left(\frac{dp}{dx}\right)_v = 0$, the convex side all the time turned to the x-axis till it is directed straight downward in the point where it meets the vapour branch of the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$. There it has a tangent // v-axis, and from there it has turned its concave side to the x-axis. When it meets the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$, $\left(\frac{dv}{dx}\right)_p$ is equal to 0 for this as for all isobars. Passing again through the curve $\left(\frac{dp}{dv}\right)_{xT}$, $\left(\frac{dv}{dx}\right)_p$ is again infinitely large, and pursuing its course, it passes for the second time through the double point, and further moves to the right, always passing to smaller values of v, till it has again a tangent // to the axis of x, when it meets the curve $\left(\frac{dp}{dx}\right) = 0$ once more, after which it proceeds to larger value of v. It is clear that in the path it describes from the double point till it passes through this point for the second time, it has passed round the point we have called the second point

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¹) That the characters of the two points of intersection of the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ with the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$ are different appears among others from this that when these points of intersection coincide as is the case when these curves touch each other, the quantity $\frac{d^2p}{dv^2}\frac{d^2p}{dx^2} - \left(\frac{d^2p}{dx\,dv}\right)^2 = 0$. The character of the points of intersection depends on this quantity being positive or negative.

of intersection with the curve $\left(\frac{dp}{dv}\right)_{xT}=0$, and where maximum pressure is found. In fig. 1 some more isobars have now been drawn besides this one. We obtain the course of the isobars for lower value of p by drawing a curve starting from the left at higher value of v, bearing in mind that two p-lines of different value of p can never intersect, because the p is univalent for given value of x and v. Such an isobar cuts the curve $\left(\frac{dp}{dv}\right)_{xT}=0$ on the left of the isobar with the double point in two points, where $\left(\frac{dv}{dx}\right)_{p}=\infty$, then passes through the curve $\left(\frac{dp}{dx}\right)_{vT}=0$ in a point where $\left(\frac{dv}{dx}\right)_{pT}=0$, and has then also on the right of the said isobar again two points of intersection with the curve $\left(\frac{dp}{dv}\right)_{xT}=0$, in which points of intersection again $\left(\frac{dv}{dx}\right)_{pT}=\infty$.

An isobar of somewhat higher value of p has split up into two isolated branches. One of them starts on the right at somewhat smaller value of v; further this branch follows the course of the isobar with the loop, but must not cut it. Arrived in the neighbourhood of the double point it is always obliged to remain at small volumes; there it meets the curve $\left(\frac{dp}{dx}\right)_{v}=0$, and it has $\left(\frac{dv}{dx}\right)_{p}=0$. From this point it proceeds to smaller volumes, till a new meeting-point with the same curve causes this branch again to turn to larger volumes. But the second branch of this isobar of higher value of p is entirely inclosed within the loop of the loop-isobar. Such a branch forms a closed curve surrounding the point which we have called the second point of intersection of the curves $\left(\frac{dp}{dv}\right)_{x}=0$ and $\left(\frac{dp}{dx}\right)_{v}=0$. Such a closed branch passes twice through $\left(\frac{dp}{dx}\right)_{v}=0$, and also twice through $\left(\frac{dp}{dv}\right)_{x}=0$, and has again in the first cases $\left(\frac{dv}{dx}\right)_{p}=0$, in the second points of intersection $\left(\frac{dv}{dx}\right)_{p}=\infty$.

With ascending value of p the detached portion of the p-line contracts more and more, till it has contracted to a single point. So at still higher value of p only one single branch of the p-line remains.

A similar remark must be made for the curves of lower value of p. The smallest value of p for gas volumes is of course $p=0$; but this limit does not exist for the minimum pressure of the mixtures with given value of x. For this we know that also values of p may occur which are strongly negative. For values of p which are negative, the p-line has again divided into two disjointed portions, viz. a portion lying on the left in the diagram, which is restricted to volumes somewhat larger and somewhat smaller than that of the liquid branch of the curve $\left(\frac{dp}{dv}\right)_x=0$, and a similar portion lying on the right in the diagram.

Also on the locus of the points of inflection of the isobars the given diagram can throw light. So it is evident in the first place, that between the two branches of the curve $\left(\frac{dp}{dv}\right)_x=0$ starting from the double point, both on the left and on the right a connected series of points is found where $\left(\frac{d^2v}{dx^2}\right)_p=0$. If the curve $\left(\frac{dp}{dv}\right)_x=0$ itself should possess a double point, which is the case when T has exactly the value of T_k minimum, this locus of the points of inflection of the p-lines passes through this double point, and when the curve $\left(\frac{dp}{dv}\right)_x=0$ has split up into two separate portions, as is the case for still higher value of T, then those points of the two portions where $\frac{dv}{dx}=\infty$ belong to this locus. It is also apparent from the diagram that two more series of points start from the double point, one on the right and one on the left, as locus of the points of inflection, and that these run to smaller volumes.

An isobar with somewhat larger value of p than that of the loop-shaped isobar has a tangent // to the x-axis where it passes through the curve $\left(\frac{dp}{dx}\right)_v=0$. On the right and on the left of that point it turns its concave side to the x-axis, whereas at larger distance it must again turn its convex side to it on both sides. So there start from the double point four branches on which $\left(\frac{d^2v}{dx^2}\right)_p=0$. It is also easy to see that the branch which moves to the right towards smaller volumes, must pass through that point of the curve $\left(\frac{dp}{dx}\right)_v=0$ where the tangent is // x-axis. For an isobar which passes through the curve $\left(\frac{dp}{dx}\right)_v = 0$ on the left of this point, turns its concave side to the x-axis, but when it passes for the second time through the said curve on the right of the point, its convex side. Hence an isobar where these two intersections have coincided, has its point of inflection in the point itself. If we wish to divide all the v,x-diagram into regions where $\left(\frac{d^2v}{dx^2}\right)_p$ is either positive or negative, it must be borne in mind that also the two branches of line $\left(\frac{dp}{dv}\right)_x = 0$ themselves form the boundaries for these regions, because on that line $\left(\frac{dv}{dx}\right)_p = \infty$.

In all this $\frac{d^2a}{dx^2}$ is supposed to be positive. For on the contrary the course of the line $\left(\frac{dp}{dx}\right)_v = 0$, to which we could now assign an existence on the right of the asymptote which is given by $MRT\frac{db}{dx} = \frac{da}{dx}$, would be directed to the left of this asymptote, when $\frac{d^2a}{dx^2}$ should be negative, so if $2a_{12}$ could be $> a_1 + a_2$. For as

$$\left(\frac{v}{v-b}\right)^2 = \frac{\frac{da}{dx}}{MRT\frac{db}{dx}},$$ the value of $\frac{v}{b}$ decreases only, when $\frac{da}{dx}$ increases.

If we put $a = A + 2\,Bx + Cx^2$, and so $\frac{da}{dx} = 2(B + Cx)$, it appears that with C negative x must decrease in order to make $\frac{da}{dx}$ increase.

For the points of this line p would then possess a minimum for given value of v, and so $\frac{d^2p}{dx^2}_v$ would be positive. From this follows then that the two points of intersection of this line with the curve $\left(\frac{dp}{dv}\right)_x = 0$ have interchanged rôles. The point of intersection with the smallest volume represents then a real minimum of p, and will have the same significance for the course of the p-lines as the second point of intersection has, when $\frac{d^2a}{dx^2}$ is positive. And the point of intersection with the smallest volume has now become double point. I have, however, omitted the drawing of this case 1. because most likely the case does not really occur, and 2. because the drawing may easily be found by reversing the preceding one. There are e.g. with the solution of salts in water cases which on a cursory examination present some resemblance with the assumption $\frac{d^2a}{dx^2}$ negative, but which yet are brought about by influences perfectly different from the fact of a negative value for $\frac{d^2a}{dx^2}$.

Such a diagram for the case $\frac{d^2a}{dx^2}$ negative, though, would quite fall in with the right side of fig. 1. As in the given figure T_k increases with x on the right side, and there is a maximum value of T_k on the supposition $\frac{d^2a}{dx^2}$, fig. 1 might be still extended to the right till such a maximum T_k was reached. But then we should also have to suppose that a value of x could exist or rather a mixture for which at a certain value of x the quantity $\frac{d^2a}{dx^2}$ reverses its sign.

Every region of fig. 1 of certain width which is taken parallel to the v-axis can now be cut out for $a_1 + a_2 - 2a_{12}$ positive, to denote the course of the isobars. Regions on the left side indicate the course of the isobars for mixtures for which with increasing value of b the critical temperature decreases — regions on the right side for mixtures for which with increasing value of b the critical temperature increases — the middle region with the complicated course of the isobars when there is a minimum T_k. The left region would be compressed to an exceedingly small one if we wished to exclude the case $\frac{da}{dx}$ negative or $\frac{da}{dx} = 0$. We do so when putting $a_{12} = \sqrt{a_1 a_2}$. On such a supposition a minimum T_k is still possible, but the left region must then have an exceedingly narrow width. There is, however, no reasonable ground for the supposition $a_1 a_2 = a_{12}^2$. There would be, if the quantity a for the different substances depended only on the molecular weights, and so $a = \varepsilon m^2$ held for constant value of ε. If the attraction, just as with NEWTON's attraction, is made to depend on the mass of the molecules, and so if we put $a_1 = \varepsilon_1 m_1^2$, and also $a_2 = \varepsilon_2 m_2^2$, it appears that ε_1 and ε_2 are not equal. If we now put $a_{12} = \sqrt{a_1 a_2}$, we put $a_{12} = m_1 m_2 \sqrt{\varepsilon_1 \varepsilon_2}$. What reasonable ground is there now for the sup-

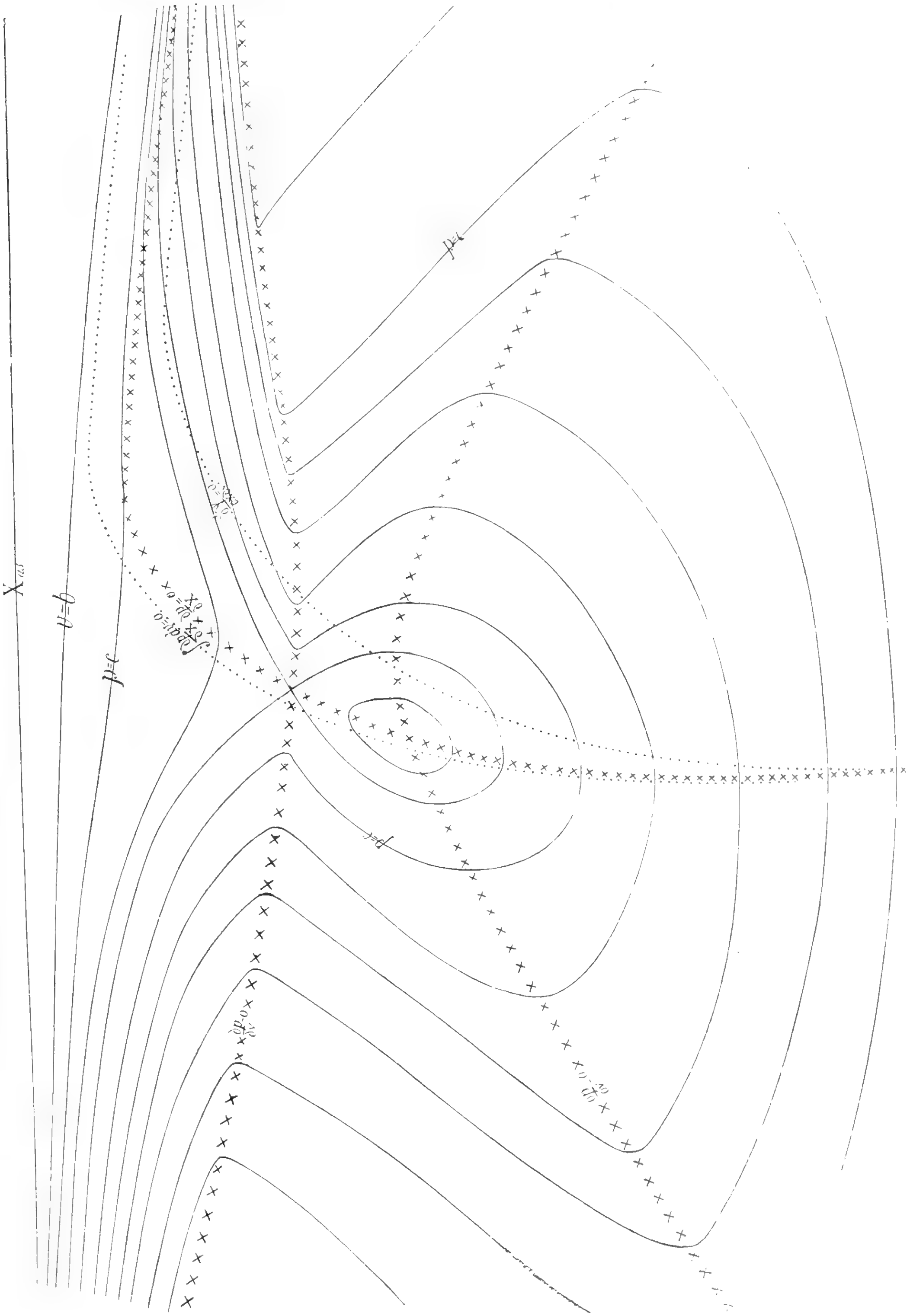
X_{a3}
$v=b$
$p=c$
$p=c$
$p=c$
$\frac{d^2\psi}{dx^2}=0$
$\frac{d^2\psi}{dx^2}=0$
$\int p\,dv=0$
$\frac{dp}{dx}=0$
$\frac{dp}{dx}=0$

Fig 1.

position that if there is a specific factor ε_1 for the mutual attraction of the molecules of the first kind of which we do not know with what property of these molecules it is in connection, and if there is also a perfectly different factor ε_2 for the mutual attraction of the second substance, we must not represent the specific factor for the attraction of the different molecules inter se by ε_{12}, but by $\sqrt{\varepsilon_1\varepsilon_2}$. It is true that this supposition renders the calculations simpler; I had already drawn attention to this in my Théorie Moléculaire (Cont. II, p. 45). But whether the calculations are somewhat more or somewhat less easy does not seem a sufficient ground, after all, to introduce a supposition which involves that naturally a great number of possible cases, among others also for the course of the spinodal line, are excluded. If we put all possibilities for the value of a_{12}, then $\frac{da}{dx}$ can also be $=0$, viz. for $\frac{x}{1-x}=\frac{a_2-a_{12}}{a_1-a_{12}}$. We need not go so far however, to give sufficient width also to the left region.

THE COURSE OF THE q-LINES.

The value of $\left(\frac{d\psi}{dx}\right)_v=q$ is found from the value of ψ:

$$q=MRTl\frac{x}{1-x}+\int_v^\infty\left(\frac{dp}{dx}\right)_v dv.$$

For $x=0$ this expression is negatively infinite, for $x=1$ it is positively infinite, so that we have $q_0=-\infty$ and $q_1=+\infty$.

But it follows also from the equation of state that for all values of x the value of $\int_v^\infty\left(\frac{dp}{dx}\right)_v dv$ is also positively infinite for the line $v=b$.

It is true that for such small volumes the equation of state $p=\frac{MRT}{v-b}-\frac{a}{v^2}$ is not accurate when b is not made to depend on v, and the quasi association in the liquid state is left out of account, and that the conclusion: $\int_v^\infty\left(\frac{dp}{dx}\right)_v dv$ is infinitely large for v equal to the limiting volume, calls for further consideration before we may accept this as an incontestable truth. But it seems to me that simple considerations lead to this conclusion. For the limiting volume p is infinitely great, and if b increases with x, $\left(\frac{dp}{dx}\right)_v$ is infinitely large of higher order, whereas $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv$ can again diminish the order of infinity by a unit, because the factor of dv has this higher order of infinity only for an infinitesimal value of dv. But still the thesis remains true that $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv$ is infinitely great for $v=b$.

So there is strong asymmetry in the shape of the q-lines. Whereas $q=-\infty$ holds for $x=0$ and every value of $v>b_1$, $q=+\infty$ holds all over the line of the limiting volumes, and for all volumes on the line $x=1$ which are larger than b_2. We derive immediately from this, that all the q-lines without exception start from the point $x=0$ and $v=b_1$. In this point the value of q is indefinite, as also follows from the value of q as it is given by the approximate equation of state, viz.:

$$q = MRT\, l \frac{x}{1-x} + MRT \frac{\frac{db}{dx}}{v-b} - \frac{\frac{dv}{dx}}{v}.$$

It also follows from the approximate equation of state that at their starting point all the q-lines touch the line $v=b$, of course with the exception of the line $q=-\infty$. For we derive from $\left(\frac{d\psi}{dx}\right)_v = q$

$$\left(\frac{d^2\psi}{dxdv}\right)\left(\frac{dv}{dx}\right)_q + \frac{d^2\psi}{dx^2} = 0$$

or

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

For $\frac{d^2\psi}{dx^2}$ the approximate equation of state yields:

$$\frac{d^2\psi}{dx^2} = \frac{MRT}{x(1-x)} + \frac{MRT\frac{d^2b}{dx^2}}{v-b} + \frac{MRT\left(\frac{db}{dx}\right)^2}{(v-b)^2} - \frac{\frac{d^2a}{dx^2}}{v}.$$

We already found the value of $-\frac{d^2\psi}{dxdv} = \left(\frac{dp}{dx}\right)$ above. For $\left(\frac{dv}{dx}\right)_q$ we find therefore:

$$\frac{dv}{dx_q}=\frac{\dfrac{MRT}{x(1-x)}+\dfrac{MRT}{v-b}\dfrac{d^2b}{dx^2}+\dfrac{MRT\left(\dfrac{db}{dx}\right)^2}{(v-b)^2}-\dfrac{\dfrac{d^2a}{dx^2}}{v}}{\dfrac{MRT}{(v-b)^2}\dfrac{db}{dx}-\dfrac{da}{dx}\dfrac{1}{v^2}}$$

If we multiply numerator and denominator by $(v-b)^2$ and if we put $v=b$, we find for the starting point of the q-lines $\left(\dfrac{dv}{dx}\right)=\dfrac{db}{dx}$ at least if we can prove that $\dfrac{(v-b)^2}{x}$ is equal to zero for $x=0$ and $v=b_1$. To show this, we put $b=b_1+\beta x+\gamma x^2$, and so $v-b=$ $=(v-b_1)-x\beta-\gamma x^2$, and then we find for $(v-b)\dfrac{v-b}{x}$ the value:

$$(v-b)\left\{\frac{v-b_1}{x}-\beta-\gamma x\right\}.$$

The term $\dfrac{v-b_1}{x}$ is indefinite, but nevertheless the given value multiplied by $v-b$ is really equal to zero. This result, too, is still to be subjected to further consideration, because it has been obtained by the aid of the equation of state, which is only known by approximation. And then I must confess that I cannot give a conclusive proof for this thesis. But I have thought that I could accept it with great certainty, because in all such cases where a whole group of curves starts from one vertex of an angle, e. g. for the lines of distillation of a ternary system, I have found this thesis confirmed that then they all touch one side of the angle. Only in very exceptional cases the thesis is not valid.

Moreover, the theses which I shall give for the further course of the q-lines, are independent of the initial direction of these lines. Only, the q-lines themselves present a more natural course when their initial direction is the indicated one than in the opposite case.

From the value given above for $\left(\dfrac{dv}{dx}\right)_q$ follows that they have a tangent // v-axis, when $\left(\dfrac{dp}{dx}\right)_v=0$, and a tangent // x-axis, when $\dfrac{d^2\psi}{dx^2}=0$. Hence they have a very simple shape in a region where the lines $\left(\dfrac{dp}{dx}\right)_v=0$ and $\dfrac{d^2\psi}{dx^2}=0$ do not occur. Starting from the point $x=0$ and $v=b_1$ they always move to the right and towards larger volume, and $\left(\frac{dv}{dx}\right)_q$ is always positive. Therefore $\left(\frac{dp}{dx}\right)_v$ and as will presently appear, $\frac{d^2\psi}{dx^2}$ are always positive in such a region. As v becomes greater the value of q approaches to $MRTl\,\frac{x}{1-x}$, and for very large value of v the q-lines may be considered as lines parallel to the v-axis, for which the distribution over the region from $x=0$ to $x=1$ is symmetrical. The lines for which q is negative, extend therefore from $x=0$ to $x=\frac{1}{2}$ and for $x=\frac{1}{2}$ the value of $q=0$. It will only appear later on that yet in their course probably two points of inflection always occur for small volumes, a fact to which my attention was first drawn by a remark of Dr. KOHNSTAMM, who had concluded to the presence of such points of inflection in the q-lines from perfectly different phenomena.

But as soon as the line $\left(\frac{dp}{dx}\right)_v=0$ is present (the case that also $\frac{d^2\psi}{dx^2}$ may be $=0$ will be discussed later on), a new particularity makes its appearance in the course of the q-lines. A q-line, viz., which cuts this locus, has a tangent // v-axis in its point of intersection, and reverses its course in so far that further it does not proceed to higher value of x, but runs back to smaller value — so that $\left(\frac{dv}{dx}\right)_q$, which is always positive in the beginning, is henceforth negative. From that point where they intersect the line $\left(\frac{dp}{dx}\right)_v=0$ and where $\left(\frac{dv}{dx}\right)_q$ may be considered negatively infinite, this quantity becomes smaller negative. Still for $v=\infty$, the q-line must again run parallel v-axis. So there must again be a point of inflection in the course of the q-line. In fig. 2 this course of the q-lines has been represented, both in the former case when they do not intersect the curve $\left(\frac{dp}{dx}\right)_v$, and when they do so. In the latter case they have already proceeded to a higher value of x in their course than that they end in. They end asymptotical to a line $x=x_c$, and at much smaller volume they also pass through a point $x=x_c$. The point at which with smaller volume they have the same value of x as that with which they end, lies on a locus which has a shape presenting great resemblance with the line $\left(\frac{dp}{dx}\right)_v=0$. The value

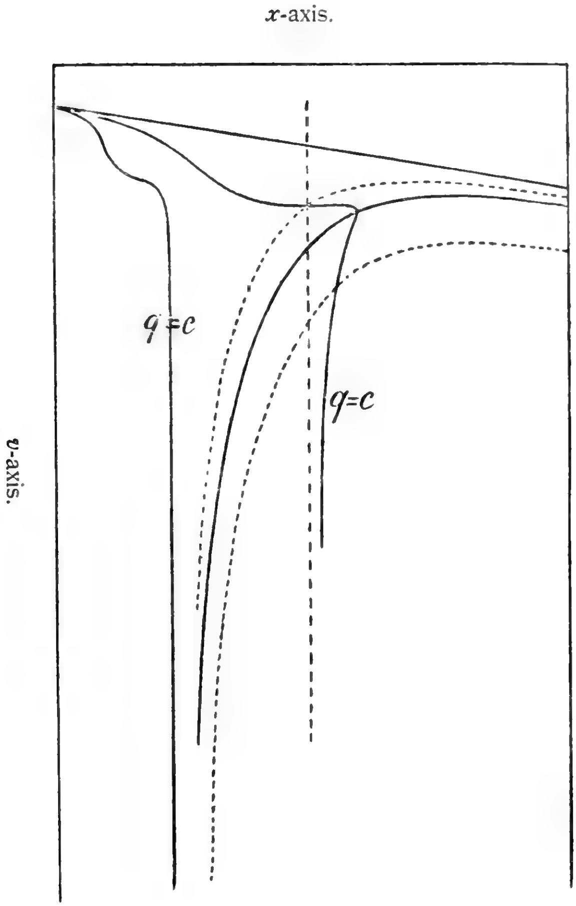

Fig. 2.

for the points of this locus may be derived in the following way.

If we write $\psi = MRT\{(1-x)\,log\,(1-x) + x\,log\,x\} + \int\limits_v^\infty p\,dv$

then $\left(\frac{d\psi}{dx}\right)_v = q = MRT\,l\,\frac{x}{1-x} + \int\limits_v^\infty \left(\frac{dp}{dx}\right)_v dv.$

At infinite volume the value of $q = MRT\,l\,\frac{x}{1-x}$ as we saw above. The locus under consideration must therefore be determined by $\int\limits_v^\infty \left(\frac{dp}{dx}\right)_v dv = 0$. Hence on the line $x =$ the final value, a point must be found such that, proceeding along that same x-line, $\int_v^\infty \left(\frac{dp}{dx}\right)_v dx = 0$.

So from this follows immediately 1. that the points of the said locus restrict themselves to those values of x in which the curve $\left(\frac{dp}{dx}\right)_v = 0$ occurs, 2. that the points must be found with smaller volumes than those of $\left(\frac{dp}{dx}\right)_v = 0$. For such points with smaller volume is viz. $\left(\frac{dp}{dx}\right)_v$ positive, and for points with greater volume negative — however when the volume may be considered as a gas volume this negative value has an exceedingly small amount. And even without drawing up the equation $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv = 0$, we conclude that the said locus has the same x-asymptote as $\left(\frac{dp}{dx}\right)_v = 0$ itself, and is further to be found at smaller volumes. Hence it will also have a point where its tangent runs // x-axis. There is even a whole series of loci to be given of more or less importance for our theory, which have a course analogous to that of $\left(\frac{dp}{dx}\right)_v = 0$ and $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv = 0$.

The latter is obtained from $\left(\frac{dp}{dx}\right)_v$ by integration with respect to v; all the differential quotients with respect to v of the same function $\left(\frac{dp}{dx}\right)_v$ put equal to 0 have an analogous course — thus $\frac{d^2p}{dxdv} = 0$ which is a locus of great importance for our theory. That it has the same x asymptote as $\left(\frac{dp}{dx}\right)_v = 0$ itself, and that all its other points are to be found at higher value of v, follows immediately from the following consideration. For a point of the line $\left(\frac{dp}{dx}\right)_{vT} = 0$ the value of $\left(\frac{dp}{dx}\right) = 0$. For points of the same x and smaller v this value is positive — but for points with larger v negative. For $v = \infty$ this negative value has, however, again returned to 0. So there must have been a maximum negative value for a certain volume larger than that for which this value $=0$. These are the points for which $\frac{d^2p}{dxdv}=0$.

For smaller value of the volume $\frac{d^2p}{dxdv}$ is therefore negative — on the other hand positive for larger volumes. The approximate equation of state yields for the loci mentioned and for following loci these equations:

$$\frac{\frac{db}{dx}}{v-b}=\frac{\frac{da}{dx}}{v} \quad \text{for} \quad \int_v^\infty \frac{dp}{dx}\,dv=0$$

$$\frac{\frac{db}{dx}}{(v-b)^2}=\frac{\frac{da}{dx}}{v^2} \quad \text{for} \quad \left(\frac{dp}{dx}\right)_v=0$$

$$\frac{\frac{db}{dx}}{(v-b)^3}=\frac{\frac{da}{dx}}{v^3} \quad \text{for} \quad \left(\frac{d^2p}{dxdv}\right)=0.$$

And so forth.

But let us now return after this digression to the description of the shape of the q-lines. Whenever a q-line passes through the locus $\int_v^\infty \left(\frac{dp}{dx}\right)dv=0$, the asymptote to which it will draw near at infinite volume is known by the value of x for that point of intersection. For the present it does, indeed, pursue its course towards higher value of x, but when its meets the locus $\left(\frac{dp}{dx}\right)_v=0$, it has the highest value of x, and a tangent // v-axis. From there it runs back to smaller value of x.

And this would conclude the discussion of the complications in the shape of the q-lines, if in many cases for values of T at which the solid state has not yet made its appearance, there did not exist another locus, which can strongly modify the shape of the q-lines, and as we shall see later on, so strongly that three-phase-pressure may be the consequence of it.

The quantities $\frac{d^2\psi}{dv^2}$ and $\frac{d^2\psi}{dx^2}$ occur in the equation of the spinodal curve in the same way. It may be already derived from this that the existence of the loci $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dx^2}=0$ will have the same significance for the determination of the course of the spinodal line.

That as yet our attention has almost exclusively been directed to $\frac{d^2\psi}{dv^2}=0$ is due to the fact that we know with certainty that a given binary mixture furnishes points for the latter locus for values of T below T_k for that mixture, whereas the conditions for the existence of a locus $\frac{d^2\psi}{dx^2}=0$ are not known — and it might be suspected that this remained confined to temperatures so low that the solid state would have set in, and so the complications which would be caused by this, could not be observed. That such a supposition is not quite unfounded may still be safely concluded from the behaviour of many mixtures, which quite answer to the considerations in which the curve $\frac{d^2\psi}{dx^2}$ is left out of account. But that the behaviour of mixtures for which more complicated phenomena occur, cannot be accounted for but by taking into consideration that $\frac{d^2\psi}{dx^2}$ can be $=0$, seems also beyond doubt to me.

The approximate equation of state gives for this quantity the following value:

$$\frac{d^2\psi}{dx^2}=\frac{MRT}{x\,(1-x)}+\frac{MRT\left(\frac{db}{dx}\right)^2}{(v-b)^2}+\frac{MRT\frac{d^2b}{dx^2}}{v-b}-\frac{\frac{d^2a}{dx^2}}{v}$$

which I shall still somewhat simplify by assuming that b depends linearly on x, and so $\frac{d^2b}{dx^2}=0$. We can easily derive from this form that if $\frac{d^2\psi}{dx^2}$ can be $=0$, this will be the case in a closed curve. At the boundaries of the v,x-diagram $\frac{d^2\psi}{dx^2}$ is certainly positive. For $x=0$ and $x=1$ even infinitely great. Also for $v=b$. And for $v=\infty$ it reduces to $\frac{MRT}{x\,(1-x)}$, the minimum value of which is equal to $4\;MRT$. That, if only T is taken low enough, it can be negative, at least if $\frac{d^2a}{dx^2}$ is positive, is also obvious. At exceedingly low value of T it can take up a pretty large part of the v,x-diagram, which must especially be sought in the region of the small volumes. With rise of temperature this locus contracts, and at a certain maximum temperature for its existence, it reduces to a single point. So it is no longer found above a certain temperature.

(To be continued).

Physics. *"On the shape of the three-phase-line solid-liquid-vapour for a binary mixture."* By Dr. Ph. Kohnstamm. (Communicated by Prof. J. D. van der Waals.)

Already for a considerable time I have been engaged in arranging Prof. Van der Waals' thermodynamic lectures, and having arrived at the discussion of the three phase line solid-liquid-vapour, and the metastable and unstable equilibria solid-fluid which are in connection with it, I have formed on some points a different opinion from that laid down in the literature known to me on this subject. It does not seem unprofitable to me to shortly discuss the points of deviation in this and the following communication.

The first concerns the shape of the three phase line solid-liquid-vapour when the solid substance is one of the components, viz. the least volatile one. We find given for this that this line must always possess a pressure maximum [1]), and that it must also possess a temperature maximum [2]) when the solid substance, — as is usual, — melts with expansion of volume. The latter remark is the generalisation of a supposition, advanced by Van der Waals [3]) with respect to the line for ether and anthraquinone. These considerations, however, hold only for definite assumptions on the extent of the difference of volatility of the two components. This appears immediately from the differential equation of the three phase line given by van der Waals [4]):

$$\frac{dp}{dT}=\frac{\eta_v-\eta_s-\dfrac{x_v}{x_l}(\eta_l-\eta_s)}{v_v-v_s-\dfrac{x_v}{x_l}(v_l-v_s)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which η, x and v denote resp. entropy, concentration and volume of the coexisting phases, the index v, l and s denoting that resp. the vapour, liquid and solid phase is meant. x_s does not occur, because we assume, that the solid phase is the first component itself so $x_s=0$. The pressure maximum will now occur in the line when the numerator, the temperature maximum when the denominator can become zero. Now $\eta_v-\eta_s>\eta_l-\eta_s$ and $v_v-v_s>v_l-v_s$: the two cases are therefore only possible when $x_v>x_l$, i.e. when the vapour is richer in the component which does not form the solid phase,

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[1]) Bakhuis Roozeboom. Die heterogenen Gleichgewichte II. p. 331.

[2]) Smits. These Proc. VIII, p. 196; Zeitsch. phys. Ch. LIV, p. 498.

[3]) These Proc. VI, p. 243.

[4]) Verslag Kon. Akademie V, p. 490.

(for in the equation is put $x_s = 0$) than the liquid. Or in other words, as we said above, the points sought can only present themselves in the three phase line with the least volatile component as solid substance[1]). However, whether those points *will* occur, depends on the value which $lim \left(\frac{x_v}{x_l}\right)_{x=0}$ will get. If this value may be put $=$ infinite, we get for $x = 0$:

$$\frac{dp}{dT} = \frac{\eta_l - \eta_s}{v_l - v_s}$$

so equal to the slope of the melting-point curve. So we must have both pressure and temperature maximum, at least when the solid substance expands on melting. This was the purport of the above cited remark of VAN DER WAALS about ether and anthraquinone; if however $\left(\frac{x_v}{x_l}\right)_{x=0}$ may not be put infinite, this conclusion is no longer valid; it then depends on the value which:

$$v_v - v_s - \frac{x_v}{x_l}(v_l - v_s)$$

assumes for $x = 0$ whether there exists a temperature maximum or not; if the difference in volatility, so $\frac{x_v}{x_l}$, should not be so large, that this expression becomes negative at the limit, the maximum does not occur, even when $v_s > v_l$.

The question whether such a maximum will occur in many systems, cannot be answered with certainty for the present. For this many data would be required, which we have not at our disposal as yet; it is, however, possible to show the probability that only in very extreme cases the volability of the components will be so diversified, that a temperature maximum is to be expected. For this maximum to be just present, viz. in the triple point of the solid component, it is evidently required that:

$$\frac{x_v}{x_l}\,\frac{v_l - v_s}{v_v - v_s} = 1.$$

Now the first datum we should want, would be the variation of volume during melting. It seems, however, that only a few data have been collected for this; I have found some in WINKELMANN's "Hand-

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[1]) If has of course been tacitly assumed here, that there is no maximum vapour pressure; in that case the points in question could be found in *both* three phase lines.

buch"[1]), and in BAKHUIS ROOZEBOOM[2]); LANDOLT's and BÖRNSTEIN's tables do not give anything on this subject. The values indicated at the places mentioned confirm that the percentage of these expansions is not very considerable, which was a priori to be expected ; they amount for the highest cases to little more than 10°/₀ and for most substances they are considerably lower. So if we take 10°/₀ as basis, we shall find for by far the majority of the cases a too great, so for our proof a too unfavourable value. If we introduce this value, we get as condition (neglecting v_l by the side of v_v):

$$\frac{x_v}{x_l}\frac{v_l}{v_v} = 10.$$

So we must now try and get a rough estimation of the relation between liquid and vapour volume in the triple point. If at the triple point the vapour tension was of the order of an atmosphere, this ratio would be about of the order of magnitude 1000. Now, however, the vapour tension is always very considerably lower ; almost for every substance the melting point lies very considerably below the boiling point. If we now assume that the triple point lies at about $^1/_2\, T_k$, we find the order of the vapour tension from the well known formula :

$$-\, l.\, nat \frac{p_c}{p_k} = f\left(\frac{T_k}{T} - 1\right).$$

With $f=7$ and $T = {}^1/_2\, T_k$ this gives $log \dfrac{p_c}{p_k} = -7$ or $p_c = \dfrac{p_k}{1000}$.
If we put p_k at 100 atms.[3]), p_c becomes of the order of 0.1 atm. So we may safely say that in general v_l/v_v will be smaller than 0.0001. For a temperature maximum it is, therefore, necessary, that at least:

$$\frac{x_v}{x_l} = 10^5 \text{ or } l.\, nat \frac{x_v}{x_l} = 11.5 .$$

Now according to a formula which has been repeatedly derived by VAN DER WAALS[4]), for low temperatures (a condition which in this case is certainly fulfilled) the equation :

$$log. \frac{x_l}{1-x_l}\,\frac{1-x_v}{x_v} = \left(\frac{f}{m} - 1\right)\frac{dT_k}{T_k\, dx} + \frac{1}{b}\frac{db}{dx},$$

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[1]) II p. 612 2nd p. 775.

[2]) l. c. I p. 89.

[3]) In the table of LANDOLT and BÖRNSTEIN only two substances occur, ammoniac and water which have a higher p_k; the majority by far is considerably lower, particularly that of the little volatile substances which we have in view.

[4]) See e.g. These Proc. VII, p. 159.

holds, or for the limit, where $\frac{1-x_v}{1-x_l}=1$.

$$log.\frac{x}{x_v}=\left(\frac{f}{m}-1\right)\frac{dT_k}{T_k\,dx}+\frac{1}{b}\frac{db}{dx}\quad . \; . \; . \; . \; . \; . \; . \qquad (2)$$

It is clear that everything will depend on the first term here, because the second would not amount to more than -1 in the utmost case, i.e. when the b of the other component would be zero. Moreover it might even be possible that the second term was positive, it would hence decrease the value of the second member.

The greatest difficulty for our calculation lies now in our ignorance of with the variability of T_k with x, or more strictly in this that for this variability not one fixed rule is to be given, because in every special case it will depend on the special properties of the mixture in question, viz. on the quantity a_{12}, a quantity which does not admit of being expressed [1]) in the characteristic quantities of the components, at least for the present. It is, therefore, certainly not permissible to try and derive results for all kinds of systems. But it is only our purpose to determine the course of T_k for those cases, in which the components differ exceedingly much in volatility, and for those cases it is perhaps not too inaccurate a supposition to assume for the present that the line which represents T_k as function of x, does not deviate too much from a straight one. [2]) On this supposition then we may write $\frac{T_{k_2}-T_{k_1}}{T_{k_1}}$ for $\frac{1}{T_k}\frac{dT_k}{dx}$. As now $\frac{f}{m}=14$, as we already supposed, $\frac{T_{k_2}-T_{k_1}}{T_{k_1}}$ must not descend considerably below

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[1]) The equation of GALITZINE-BERTHELOT $a_{12}^2=a_1\,a_2$, which I rejected as general rule already on a former occasion on account of the properties of the mixture ether-choroform (These Proc. IV, p. 159), can certainly not be accepted as such. Not only is it easy to mention other examples which are incompatible with this rule (see e.g. QUINT, Thesis for the doctorate p. 44; GERRITS, Thesis for the doctorate, p. 68); but besides, — and perhaps this must be considered as a still more serious objection — by assuming this equation we wilfully break up the unity of the isopiestic figure (v. D. WAALS, Proc. of this meeting p. 627) by pronouncing its middle region on the left of the asymptote to be impossible, whereas the left and right regions are considered as real. For if $a_{12}=\sqrt{a_1a_2}$ it is never possible that $da/dx=0$ for whatever system; and this takes exactly place in the middle region. I had overlooked this in the paper mentioned; Prof. VAN DER WAALS has since drawn my attention to it. The already mentioned system of QUINT gives an example of the occurrence of this case $\frac{da}{dx}=0$; a_{12} is there smaller than even the smallest of the two a's.

[2]) Cf. VAN DER WAALS, These Proc. VIII, p. 272.

0.9, that $log. \frac{x_v}{x_l}$ may not become smaller than the required value 11.5, or in other words, for the maximum in temperature to be reached, the critical temperature of one component must be about ten times as high as that of the other. A system, in which hydrogen occurs, will most likely show the temperature maximum when the other component has its critical point above 0° C., but already when the more volatile component is nitrogen or oxygen, we shall be more restricted in the choice of the other component. For then the latter must have its critical point at about 1000° C. resp. 1250° C. If ether were the more volatile component, this temperature would almost amount to 4500° C.

This conclusion is hardly affected when we put the temperature of the melting point not at $^1/_2$, but at $^1/_3$ of the critical temperature, as it really is for a number of substances whose critical temperature and melting temperature are known. It is true that this considerably increases the second member of equation (2), and so $\frac{x_v}{x_l}$, but in the same ratio $\frac{v_v}{v_l}$ increases too, so that the quotient remains about unchanged. This is most easily seen when the condition on which a temperature maximum occurs, is written:

$$\frac{x_l}{x_v}\frac{v_v}{v_l} < 0.1 \text{ or } log. \frac{x_l}{x_v} + log.\, v_v - log.\, v_l < log.\, 0.1.$$

Now for $log. \frac{x_l}{x_v}$ we may introduce the value from the equation[1]):

$$log. \frac{x_l}{1-x_l}\frac{1-x_v}{x_v} = \left(\frac{f}{T}\frac{dT_k}{dx} - \frac{1}{p_k}\frac{dp_k}{dx}\right),$$

and write for $log.\, v_v$:

$$log.\, v_v = log. \frac{MRT}{p_c} = log.\, MRT + f\left(\frac{T_k}{T} - 1\right) - log.\, p_k,$$

so that the condition becomes:

$$\frac{m}{f}\left\{1 + \frac{dT_k}{T_k dx}\right\} - \frac{1}{p_k}\frac{dp_k}{dx} - log.\, p_k - log.\, v_l - f + log.\, MRT < log.\, 0.1.$$

So an increase of T will only affect the first term and the term $log.\, MRT$, and the logarithmic change of the latter will certainly amount to less than the change of the former. This now increases when T becomes smaller, hence when at $T = {}^1/_2\, T_k$ the inequality

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[1]) These Proc., VII, p. 559.

is not satisfied, this will certainly not be the case for $T = {}^1/_3\, T_k$.

Still, it would be too hazardous to assert that it has now been incontestably proved that e.g. for the system ether-anthraquinone no temperature maximum *can* occur. For we have had to make use of the supposition that T_k depends linearly on x, and though this supposition may possess some degree of probability for critical temperatures that differ much, it is just with substances which — as ether and anthraquinone-lie closer together, that there is some ground for expecting a deviation from the straight line. Only very few experimental data are at our disposal. As such may e.g. be used the determinations on the increase of the plaitpoint temperature by addition of little volatile substances, made by SMITS, CENTNERSZWER and BÜCHNER. For by means of the formula given by VAN DER WAALS[1])

$$\frac{dT}{Tdx_0} = \frac{dT_k}{T_k dx} + \frac{49}{45}\left\{\frac{dT_k}{T_k dx} - \frac{1}{7}\frac{dp_k}{p_k dx}\right\}^2 \quad . \quad . \quad . \quad . \quad (3)$$

in which we need only pay regard to the principal terms (those with T_k), we may calculate the value of $\frac{dT_k}{T_k dx}$ from those directly measured. If we now calculate by the aid of the thus found value of $\frac{dT_k}{T_k dx}$ and the supposition of rectilinearity, T_{k_2}, i. e. the value of T_k for the admixed substance, we find the data collected in the following table. (P. 645).

From this appears that the values calculated in this way at least for some substances, and particularly for anthraquinone according to the determination by SMITS, are not inconsiderably lower than double the melting point temperature. It may, therefore, be considered highly probable that these lines are convex seen from below, and so the absolute value of $\frac{dT_k}{T_k dx}$ will be larger than might be expected from the supposition of rectilinearity. With our imperfect knowledge of the further course of the plaitpoint line, and hence à fortiori of the line for T_k an estimation as to this will, naturally, remain very uncertain; but yet it seems to me that something about this may be ascertained in the following way. We have on the side of the ether:

$$\left(\frac{dT_k}{T_k dx}\right)_{x=0} = \left(\frac{da}{adx} - \frac{db}{bdx}\right)_{x=0},$$

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[1]) These Proc. VII, p. 272 and 296.

Second component	First component	Observer	T_k calculated	Double the melting-point temperature
Anthraquinone	Ether	Smits	932°	1120°
”	SO_2	Centnerszwer	1032	1120
Resorcin	”	”	903	960
Camphor	”	”	790	900
Naphthaline	”	”	770	700
”	CO_2	Büchner	640	700
Paradichloro benzene	”	”	670	650
Paradibromo benzene	”	”	690	720
Bromoform	”	”	640	560
Orthochloronitro benz.	”	”	760	610

Büchner's values have been borrowed from his thesis for the doctorate (Amsterdam 1905); those of Centnerszwer from a table by van Laar (These Proc. VIII, p. 151); that of Smits has been calculated from his determination: plaitpoint at 203° and $x = 0.015$, (These Proc. VII, p. 179).

and so when introducing for a the quadratic and for b the linear function:

$$\left(\frac{dT_k}{T_k dx}\right)_{x=0} = \frac{2a_{12} - 2a_1}{a_1} - \frac{b_2 - b_1}{b_1} \quad . \; . \; . \; . \; . \quad (4)$$

Now it will not be too hazardous an estimation, when — keeping in view that the formula for ether is $C_4H_{10}O$ and for anthraquinone $C_{14}H_8O_2$ —, we put the size of the anthraquinone molecule at about two or three times that of the ether molecule; so $b_2 = 2b_1$ à $3b_1$. If we introduce this value and the value of $\frac{dT_k}{T_k dx}$, calculated by the aid of equation (3), into equation (4), we obtain a value for a_{12}. Assuming that the value of T_k for anthraquinone is $2 \times 560° = 1120°$, we can find an a_2 from the ratio of the critical temperatures of ether and anthraquinone, and the a for ether; and with these quantities we can finally calculate the $\frac{dT_k}{T_k dx}$ on the anthraquinone side from:

$$\left(\frac{dT_k}{T_k dx}\right)_{x=1} = \frac{2a_2 - 2a_{12}}{a_2} - \frac{b_1 - b_2}{b_2}.$$

Starting from $b_2 = 2b_1$ we find in this way $\left(\frac{dT_k}{T_k dx}\right)_{x=1} = 0.66$; with $b_2 = 2.5$: 0.65 and with $b_2 = 3\,b_1$: 0.64. The error which we committed in our choice of b_2, will, therefore, bring about no considerable modification in the result; it would, indeed, be considerably modified if the critical point of anthraquinone should prove to lie considerably higher than 1120°. This is not in contradiction with our former remark that it is of little importance whether the reduced temperature is $^1/_2$ or $^1/_3$ at the triple point; for this we started from the supposition of the linear dependence, whereas here we have abandoned this supposition, and calculate this dependence from the experimental data. So according to the course of reasoning followed here the a_{12} is given by the experiment, and the smaller value of m would now result in a higher value of a_2 at given b_1, b_2 and a_{12}. If our estimation may be considered as not too inaccurate, we may conclude that the deviation from rectilinearity does increase the value of $\left(\frac{dT_k}{T_k dx}\right)_{x=1}$, but by no means in the degree which would be required to reach the critical value 0.9. (The value derived from the supposition of rectilinearity is 0,58).

Though the foregoing calculations teach us hardly anything positive, they fix first of all our attention on the great desirability of more data concerning the values of the quantities a and b of very little volatile substances; for it appears again that the whole behaviour of all the systems in which such substances appear, is controlled by these quantities, and it would exactly be of great importance for the theory of mixtures, if its results could be tested by such cases where the properties of the two components differ strongly. It is true that it will not be easy to determine the critical point of such substances in the usual way, but we should have gained already much if we could obtain an estimation of the critical temperature by calculation of the a and b from the deviations from the law of BOYLE in rarefied gas state, so still some hundreds of degrees below the critical point.

And further I think that after the foregoing I may be allowed to draw this conclusion, that the appearance of a temperature maximum in the three phase line, far from being the general case, will be confined to mixtures of very exceptional nature.

Much more frequently than a temperature maximum will a pressure maximum occur. It appears from equation (1) that this will always be the case, when the expression:

$$(\eta_v - \eta_s) - \frac{x_v}{x_l}(\eta_l - \eta_s)$$

may become negative. Now it is true that we cannot properly say that $\eta_v - \eta_s$ is a heat of sublimation and $\eta_l - \eta_s$ a latent heat of melting, because the η's do not refer to the same concentration, but we may say that $\eta_v - \eta_s$ is of the order of magnitude of a heat of sublimation, $\eta_l - \eta_s$ of the order of a latent heat of melting. Or in other words $\eta_v - \eta_s$ will be about 7 or 8 times $\eta_l - \eta_s$. So in all cases where $\left(\frac{x_v}{x_l}\right)_{x=0} \leq 7$ the pressure maximum in the three phase line will also fail. Here too the necessary data are wanting to ascertain whether there are many systems for which the $\frac{x_v}{x_l}$ at the triple point will descend to this amount. For, determinations of vapour tension or direct determinations of the required ratio have been nearly always carried out at considerably higher temperature[1]), and for the calculation by the aid of the just used formula the necessary data fail here too; besides, it would be doubtful whether the formula would be accurate enough, now that we have to deal with such small amounts. But — quite apart from the existence of mixtures with minimum vapour pressure — the existence of a system like ether-chloroform[2]) where on the chloroform side x_v becomes almost equal to x_l, already proves, that such systems exist.

In any case to the scheme for the possible course of the two three phase lines in a binary system plotted by BAKHUIS ROOZEBOOM in Fig. 108 of Vol. II of his "Heterogene Gleichgewichte", must be added types VII and VIII, characterized by a succession of sections,

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[1]) Particularly when we notice that the ratio of x_v and x_l would have to be calculated from the formula:

$$\frac{1}{p}\frac{dp}{dx_v} = \frac{x_v - x_l}{x_v(1 - x_v)} \quad \text{or} \quad \frac{1}{p}\frac{dp}{dx_l} = \frac{x_v - x_l}{x_l(1 - x_l)}$$

and the value obtained will, therefore, strongly vary in consequence of a change of temperature of some ten degrees, which have generally an enormous influence per cent on the pressure in the neighbourhood of the triple point.

[2]) KOHNSTAMM and VAN DALFSEN, These Proc. IV, p. 159. BAKHUIS ROOZEBOOM (l.c. I p. 41) deems it probable that also systems of gases with water and of water with many salts will show a similar shape. However, for such systems whose three phase line for the least volatile substance shows a pressure maximum, at least at temperatures that do not lie too far from the triple point, the shape of the p, x-line will have to deviate considerably from the line drawn there in Figs. 15 and 19, because from that shape would follow $x_v = x_l$.

denoted by 1 . 7 . 4 . 5 and 1 . 7 . 8 . 5 in ROOZEBOOM's nomenclature [1]). Type VII (see Fig. 1), is therefore distinguished from III in this that section 3 disappears; our Fig. 3 (lacking with ROOZEBOOM) takes its place. Type VIII (see Fig. 2) is distinguished from type V in this that instead of section 6 the section indicated in Fig. 4 appears between 8 and 5.

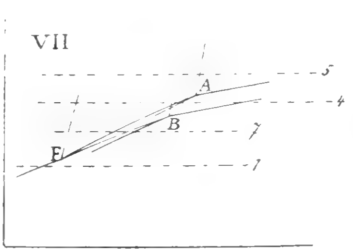

Fig. 1.

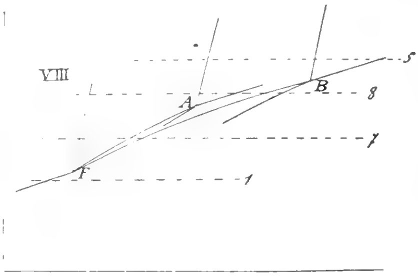

Fig. 2.

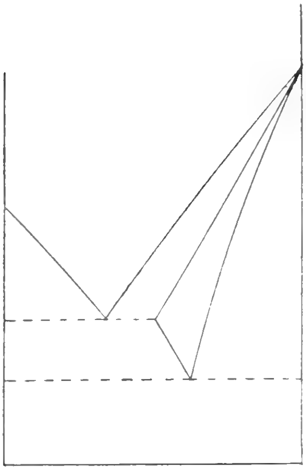

Fig. 3.

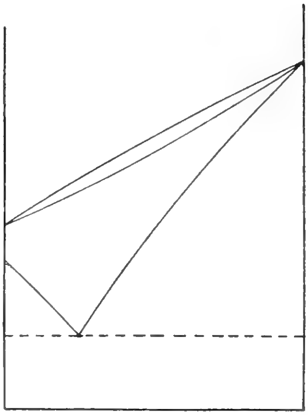

Fig. 4.

Physics. — *"On metastable and unstable equilibria solid-fluid."* By Dr. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS.)

In a preceding communication [2]) I discussed a point on which I could not agree with the existing literature on the equilibria solid-fluid. A second point which will prove to be allied to the preceding one, concerns the course of the curves which are to indicate the

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[1]) Loc. cit. p. 392.

[2]) Proceeding of this meeting, p. 639.

metastable and unstable equilibria solid-fluid in the T,x-figures drawn up by VAN DER WAALS [1]), and the v,x- and p,x-figures drawn up by SMITS [2]). VAN DER WAALS himself has already pointed out a defect in those figures [3]), viz. that the spinodal curve falls here within the connodal one, whereas in reality it falls far outside it at low temperatures; but it is not this that I have in view.

Let us first take the p,x-figures. According to them the complication which the binodal curve solid-fluid shows for temperatures below the triple-point, will disappear in this sense that at the triple point a *new complication* makes its appearance with three phase pressure, horizontal and vertical tangent, that then these two complications together give rise to the existence of a detached closed branch which contracts more and more, and at last disappears as isolated point. It is clear that in this way it is supposed that the complication can only disappear *above* the triple point, and not in the triple point itself, or in other words, that when the triple point is passed, always another three phase pressure is added to the existing one, and that these two more or less high, but always above the triple point pressure and the triple point temperature concur and disappear. Or expressed in another way still, it has been supposed in these figures that there is always found a temperature maximum in the three phase line. In the light of the considerations of our preceding communication this supposition is by no means legitimate. But apart from this there rise serious objections against these views. First of all, if these views are held, it is impossible to see what the shape of the binodal curve solid-fluid must be when the solid substance is the more volatile component. Moreover all through the succession of the p,x-figures the binodal curve solid-fluid has only one point in common with the axis $x=0$. Now it is, however, known, that for the components themselves, so for the concentrations $x=0$ and $x=1$ the p,T-diagram of fig. 1 holds (see the plate), i. e. at the triple point temperature there exists by the side of the triple point pressure C a second pressure of equilibrium solid-fluid (viz. of an unstable phase) C', and above and below the triple point temperature these exist even two such pressures, one of which indicates metastable equilibrium, the other unstable equilibrium. But then the binodal curve solid-fluid for the mixture will not have to cut the axis of the component which becomes solid, once, but three times. And finally the p,x-figures of SMITS and the T,x-figures of VAN DER WAALS

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[1]) These Proc. VIII p. 193.
[2]) These Proc. VIII p. 196.
[3]) loc. cit. p. 95.

cannot be made to harmonize with the v, x-figures plotted by the former; for in these threefold intersection of the binodal with the rim does really occur before the detachment takes place (Compare in fig. 6 of the said paper by SMITS the line fed with $f_1c_1e_1e_1'c_1'f_1'$; between this a v, x-line must necessarily be found intersecting the rim in three points). Now that attention has once been drawn to these unstable and metastable equilibria, it seems desirable to remove these discrepancies.

For this purpose the best thing is to start from the v, x-figure. The general equation of coexistence of phases in the variables v, x and T becomes in this case, if we now consider phase 2 as solid phase, 1 as fluid phase[1]):

$$(v_s - v_f)\left\{\frac{\partial^2\psi}{\partial v_f^2}dv_f + \frac{\partial^2\psi}{\partial v_f\partial x}dx_f\right\} + (x_s - x_f)\left\{\frac{\partial^2\psi}{\partial v_f\partial x_f}dv_f + \frac{\partial^2\psi}{\partial x_f^2}dx_f\right\} + $$
$$+\left(\frac{\varepsilon_{sf}}{T}\right)dT = 0,$$

so that we get for constant temperature:

$$\frac{dv}{dx} = -\frac{\dfrac{\partial^2\psi}{\partial v\partial x}(v_s - v_f) + \dfrac{\partial^2\psi}{\partial x^2}(x_s - x_f)}{\dfrac{\partial^2\psi}{\partial v^2}(v_s - v_f) + \dfrac{\partial^2\psi}{\partial v\partial x}(x_s - x_f)}.$$

In what follows we shall denote the numerator and the denominator of this fraction by N and D. The geometrical meaning of D has already been given by VAN DER WAALS in his first paper on these subjects[2]): the locus $D=0$ is the locus of the points of contact on the tangents drawn from the point for the solid substance to the isobars. It is easily shown that the locus $N=0$ is the locus obtained by putting the q-lines i.e. the lines $\frac{\partial\psi}{\partial x} = C$ in this instead of the p-lines. So a double point or an isolated point, as they are assumed by SMITS, can only occur where the loci $N=0$ and $D=0$ intersect. As in such a point, as appears from the geometric meaning, the p- and the q-lines have the same tangent, and accordingly touch, such a point must also lie on the spinodal line[3]). In perfect agreement

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[1]) Cont.. II p. 104.

[2]) These Proc. VI p. 233.

[3]) For from the equation of the spinodal curve

$$\frac{\partial^2\psi}{\partial v^2}\frac{\partial^2\psi}{\partial x^2} - \left(\frac{\partial^2\psi}{\partial x\partial v}\right)^2 = 0 \text{ or } \frac{\dfrac{\partial^2\psi}{\partial v\partial x}}{\dfrac{\partial^2\psi}{\partial v^2}} = \frac{\dfrac{\partial^2\psi}{\partial x^2}}{\dfrac{\partial^2\psi}{\partial v\partial x}}$$

with this we easily obtain for the case that x_s is not 0 or 1, the course of the loci mentioned indicated in fig. 2. The dotted line denotes the concentration of the solid phase P; the lines $A\,Q\,B$ and $C\,Q'\,D$ are the two branches of the spinodal curve, the two other lines joining A with B and C with D the branches of $\left(\frac{\partial p}{\partial v}\right)_x = 0$. When now $x_s = 0$ becomes, it is evident that at this rim the line $D = 0$ must pass through the point where $\frac{\partial^2\psi}{\partial v^2} = 0$, and this point coincides, as is known, with the spinodal curve at the rim. The conclusion seems obvious that the points Q and Q', the points of intersection of the spinodal curve and $D = 0$ have shifted towards the rim, and that, accordingly, the points of detachment and contraction from figs. 2—8 of Prof. Smits (loc. cit.) would have to lie at the rim. However, this conclusion would not be correct. For the inference that where the spinodal curve and $D = 0$ intersect, on account of the geometrical meaning of $D = 0$ and $N = 0$, the latter must also intersect, does not hold good at the rim. This is in connection with $\frac{\partial^2\psi}{\partial v^2}$ becoming zero and $\frac{\partial^2\psi}{\partial x^2}$ becoming infinite. If we introduce the value MRT/x, which the last quantity for $x = 0$ gets, then N assumes the value:

$$\frac{\partial^2\psi}{\partial v\partial x}(v_s - v_f) - x_f\frac{MRT}{x_f} = \left(\frac{\partial p}{\partial x}\right)_v (v_f - v_s) - MRT$$

and in general this expression will by no means be equal to zero in the points where $\left(\frac{\partial p}{\partial v}\right)_{x=0} = 0$, as already appears from the simple consideration that there can be no connection between $\frac{MRT}{v_f - v_s}$, a quantity which depends exclusively on the properties of the pure component and $\left(\frac{\partial p}{\partial x}\right)_v$ in the maximum and minimum points of its isotherm, because this latter quantity will also have to depend on the properties of the second component. So the points Q and Q' will certainly not lie at the rim, and in the points where $D = 0$

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follows:

$$-\left(\frac{dv}{dx}\right)_p = \frac{\left(\frac{dp}{dx}\right)_v}{\left(\frac{dp}{dv}\right)} = \frac{\frac{\partial^2\psi}{\partial v\,dx}}{\frac{\partial^2\psi}{\partial v^2}} = \frac{\frac{\partial^2\psi}{\partial x^2}}{\frac{\partial^2\psi}{\partial x\partial v}} = \frac{\left(\frac{\partial q}{\partial x}\right)_v}{\left(\frac{\partial q}{\partial v}\right)} = -\left(\frac{dv}{dx}\right)_q$$

cuts the rim the binodal curve will simply have a tangent parallel to the v-axis.

The shape which the different figures will assume, will now depend entirely on the fact whether such points Q and Q' will also exist when the solid substance is one of the components and if so, where they lie. The best and most general way of solving these questions would be a full consideration of the different forms which the q-lines may present. As however the solution of the special question we are dealing with does not call for such a discussion, I believed to be justified in preferring another briefer mode of reasoning. For this purpose I point out first of all that it is easy to see that at least in a special case such a point must exist also now. Let us imagine a plait, the plaitpoint of which has shifted so far to the side of the small volumes, that the tangent to the plait in the plaitpoint points towards the point indicating the solid state[1]). The plait touching the isobar in the plaitpoint, the plaitpoint lies evidently on the line $D=0$ in this case[2]). But the plaitpoint lies also on the spinodal line, so the point Q lies here in the plaitpoint, as neither $\frac{\partial^2 \psi}{\partial v^2}=0$, nor $\frac{\partial^2 \psi}{\partial x^2}=\infty$. We may conclude from this that in such like cases, so those cases where the plaitpoint has been displaced still somewhat further or somewhat less far to the side of the small volumes, and perhaps in general when the difference in volatility between the two components is great, a branch of $N=0$ will pass through the figure, and that it will most likely have a point of intersection with the line $D=0$. A closer investigation of this supposition can, of course, only be given by the calculation.

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[1]) The above was written before Prof. ONNES' remarkable experiment (These Proc. VIII p 459) had called attention to "barotropic" plaitpoints. Now that the investigations started by this experiment have furnished the proof that plaitpoints can exist, in which the tangent runs // x-axis, the existence of plaitpoints as assumed in the text, in which the slope of the tangent need not even be so very small, has, of course been a fortiori proved.

[2]) We may cursorily remark that it is therefore not correct to say in general that the line $D=0$ runs round the plait in the sense which VAN DER WAALS (These Proc. VIII p. 361) evidently attaches to this expression, i. e. that the point of intersection of the line $D=0$ with the binodal and spinodal curves would lie on either side of the plaitpoint. For if the plaitpoint should have moved still a little further to the side of the small volumes, the two points of intersection of $D=0$ with binodal and spinodal curves lie evidently on the vapour branch of these lines (the part of these lines between the plaitpoint and the point with the largest volume on the x-axis).

For this we shall start with the case that b increases and a decreases with increasing x, so that T_k decreases strongly, and $\left(\frac{\partial p}{\partial x}\right)_v$ is positive everywhere; and for the present we confine ourselves only to the solidification of the least volatile component, so $x_s = 0$. Let us write the value which N gets at the rim by the aid of the value derived for $\left(\frac{\partial p}{\partial x}\right)_v$ from the equation of state, in the form:

$$(v_f - v_s)\left\{\frac{MRT}{(v-b)^2}\frac{db}{dx} - \frac{{}^{da}/_{dx}}{v^2}\right\} - MRT. \quad . \quad . \quad . \quad . \quad (1)$$

It is clear that this value will become negative for $v = \infty$, on the contrary positive for $v = b$ [1]; so there will always have to be a point on the axis $x = 0$, where $N = 0$. The value which N assumes for $x = 1$, is:

$$\left(\frac{\partial p}{\partial x}\right)_v (v_f - v_s) - \frac{MRT}{1-x}$$

and this expression will, accordingly, be negative for $x = 1$ for all possible liquid volumes, and even negative infinite. From this follows that from the point of intersection of $N = 0$ with the axis $x = 0$, the locus $N = 0$ will run to smaller volumes. Now whether $N = 0$ and $D = 0$ will intersect in our figure depends on the place where $N = 0$ cuts the axis $x = 0$. In this we may distinguish three cases:

1. The point of intersection of $N = 0$ and the axis lies at smaller volume than the points where $D = 0$ cuts the axis. Then no intersection of $N = 0$ and $D = 0$ will take place; the points Q and Q' lie quite outside the axes $x = 1$ and $x = 0$;

2. The point of intersection $N = 0$ with the axis lies between the points of intersection of $D = 0$ with it. Then the point of detachment does fall inside the figure, but not the point of contraction;

3. The point of intersection of $N = 0$ and the axis lies at larger

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[1] If we should object to putting $v = b$, yet assuming that $v_f > v_s$, we shall in any case have to grant that there is nothing incompatible in the assumption that at a certain high pressure the volume in the solid state can be smaller than that in the liquid state, and that yet a great increase of pressure may be required to keep the substance in the same volume after we have replaced some of the molecules by much larger ones (so $\left(\frac{\partial p}{\partial x}\right)_v = \infty$).

[2] As said, in every point of the line $N = 0$ the q-line passing through it, is directed to the point indicating the solid substance. Every q-line for infinite volume being // v-axis, and terminating in the point $v = b$, it follows from the existence of the line $N = 0$ that every q-line cutting this locus, must at least possess one point of inflection.

volume. Then both the point of detachment and the point of contraction fall in the figure.

The consequences for the change of the v,x-projection of the binodal curve with variation of temperature will probably be clear from the figures 3—5 without further elucidation in these three cases. With regard to the frequency with which the three cases occur, it is evident that the last case will occur only rarely, with exceptionally high values of $\frac{db}{dx}$ and $-\frac{da}{dx}$, or in general of $\left(\frac{\partial p}{\partial x}\right)$. This case would be altogether impossible, if we had to take the temperature of the triple point, and the volume which the saturated vapour then has, into account, for this amounts certainly to some thousands of times b, and hence there will probably never be any question of an intersection of $N=0$ with the branch $D=0$ holding for the large volumes at the triple point temperature. But for our case we have not to reckon with this temperature, but with the highest temperature at which the binodal curve solid-fluid has still three points in common with the axis $x=0$, and this is evidently the temperature of point A in fig. 1. This, now, can probably lie very considerably above the triple point, and moreover — as we observed before — not the volume of the saturated vapour, but the much smaller one of the maximum of the isotherm must be introduced here. If we e. g. put the temperature of A so high that the maximum point of the isotherm lies at a volume $4b$, the expression will already become positive with $\frac{db}{dx}=3b_1$, or $b_2=4b_1$ and v_s near b, (da/dx is negative). So the case of 3 is, indeed, possible, but it also appears that it will occur only in exceptional cases [1]).

With none of these three cases do the T,x- and p,x-figures construed by van der Waals and Smits, agree. They agree in so far with that mentioned under 3, that the point of detachment and the point of contraction are assumed to fall within the figure. But it is at the same time clear from the vx-figures, that a complication must begin

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[1]) It appears from what has been said here that the figures 6—9 are meant quite schematically, for though we have drawn several binodals solid-fluid which hold for different temperatures, we have left the loci $N=0$ and $D=0$ unchanged. This has, of course, been done to save space, for else we could not have represented much more than one temperature in each figure without rendering the figures indistinct. But after what has been said it is clear that also the points Q and Q' move, and that it might e.g. very well happen that at lower temperatures the point Q' is not yet present in the figure, and that it makes its appearance only at higher temperatures. The following figures, too, are meant schematically, and serve only to elucidate the properties mentioned in the text.

in the p, x- and T, x-figures far below the triple point, viz. already at the temperature B of fig. 5, i. e. the temperature, at which in fig. 9 the new branch of the binodal curve (on the left side) makes its appearance in the figure. Let us first consider the p, x-lines.

At the temperature mentioned (T_1) a new branch begins to form at the same height as the spinodal line, so far below the point of the stable coexistence. In the p, x-figure the point where this appears, is, in opposition with the v, x-figure, indeed a point where the tangent is indefinite; for the equation:

$$N \, . \, dp = (x_s - x_f) \left\{ \frac{\partial^2 \psi}{\partial v_f^{\,2}} \frac{\partial^2 \psi}{\partial x_f^{\,2}} - \left(\frac{\partial^2 \psi}{\partial v_f \, \partial x_f} \right)^2 \right\} dx_f \, ,$$

holds for the former figure; the factor of dx_f is zero on the spinodal line and the factor of dp on the line $D=0$, which both pass through the point considered; so $\frac{dp}{dx}$ is there indefinite. The new branch extends more and more (fig. 6); its maximum continues to lie on the spinodal curve, and the point with the vertical tangent on the line $D=0$. When the temperature of detachment in the v, x-figure (T_2) has been reached, the old branch and the new one unite (fig. 7), and separate again as figure 8 represents. At the triple point temperature (T_3) the middle one and the topmost one of the three points of intersection with the axis coincide (in the final point of the double line vapour-liquid) (fig. 9); afterwards they exchange places. At still higher temperature the downmost point of intersection with the axis and that which has now become the middle one coincide; at this place there is again a point with indefinite tangent (T_4, the temperature A of fig. 1) (fig. 10); at still higher temperature the binodal curve solid-fluid has got quite detached from the axis, and its downmost branch forms a closed curve, which contracts more and more, and at last disappears at the temperature of the isolated point of fig. 5. Here it is evidently essential that T_4 lies above T_3, and T_3 above T_1, according to the significance which they have in fig. 1; also T_5, the point at which the detached branch disappears from the figure, must lie above T_3, the triple point, because in the triple point the binodal curve solid-liquid must still have two points in common with the rim (a little above it even three). But it is not essential that T_2 lies between T_3 and T_1; T_2 might just as well lie above T_3. Then we get the succession: fig. 6, fig. 9*a* (triple point), fig. 10*a*. If now T_2 lies below T_4, there is confluence and section, and we get after fig. 10*a* fig. 11, and then SMITS' figs. 4 and 5 (loc. cit); if T_2 lies also above T_4, first the two lowest points of intersection of the binodal curve solid-liquid with the rim join, then they are detached from the rim, and we get, therefore, in this case, but only above T_4, so above temperature A of fig. 1, the continuous line drawn by SMITS fig. 3 (loc. cit.), which then passes into figs 4 and 5 (loc. cit.).

The case mentioned under 2 that the point of contraction falls outside the figure may after all, be derived from the foregoing by putting T_5, the temperature at which the detached branch disappears from the figure, below T_4, the temperature at which it detaches itself from the rim. In our figures it has only this influence that the loop of figs. 9 and 10*a* cannot detach itself from the rim, as in fig. 10, and disappear as isolated point; but this loop contracts more and more at the rim and disappears there. In this case, too, T_2 can lie above T_3, but of course, not above T_4. If T_2 lies under T_3, we have the succession 6, 7, 8, 9 and disappearance of the loop in the rim; if T_2 lies above T_3 then: 6, 9*a*, 10*a*, 11, and disappearance of the loop in the rim.

The above case mentioned under 1, when also the point of detachment falls outside the v, x-figure, may be considered as the case that T_2 lies below T_1, and T_4 above T_5. We have then the succession, the upper portion of fig. 6 (viz. without the downmost loop), figs. 12, 8, 9, after which the loop merges in the rim. Now in all the cases mentioned, except in the second subdivision of the case under 3 (so T_2 above T_3), we meet still with two possibilities. Up to now we have assumed for those cases, that the triple point temperature is the highest temperature at which the two binodal curves intersect in the stable region, and that they have got detached above it. It is now, however, possible, that also in these cases the two binodals intersect twice at the triple point and above it. Then fig. 9*b*, is put everywhere for fig. 9, and then this is changed into fig. 11.

We get then the following summary:

Case under 1.	
Upper portion of 6, 12, 8, 9,	disappearance of the loop in the rim
,, ,, ,, 6, 12, 8, 9*b*, 11	,, ,, ,, ,, ,, ,, ,,
Case under 2.	
6, 7, 8, 9,	,, ,, ,, ,, ,, ,, ,,
6, 9*a*, 10*a*, 11	,, ,, ,, ,, ,, ,, ,,
6, 7, 8, 9*b*, 11	,, ,, ,, ,, ,, ,, ,,
Case under 3.	
6, 7, 8, 9, 10,	disappearance of the loop in the fig.
6, 9*a*, 10*a*, 11, 4 and 5 SMITS	,, ,, ,, ,, ,, ,, ,,
6, 9*a*, 10*a*, 3, 4 and 5 SMITS	,, ,, ,, ,, ,, ,, ,,
6, 7, 8, 9*b*, 11, 4 and 5 SMITS	,, ,, ,, ,, ,, ,, ,,

The greatest chance to only one intersection with the binodal curve liquid-vapour presents, of course, as is best seen from the v,x-figure, the case under 1, more particularly when in this case the line $N=0$ cuts the axis at such small volumes, that it has no longer any point in common not only with the spinodal curve, but even with the binodal curve of the transverse plait. Only with a very exceptional course of the binodal curve of the transverse plait double intersection could take place in this case. On the other hand it will be highly probable that always when the line $N=0$ cuts the binodal curve of the transverse plait (which will always have to take place in the cases under 2 and 3), also double intersection of the two binodals will be found.

This shows at the same time the connection of this investigation with that of the preceding communication. For it appears now that the shape of the p,x-lines holding for 1 with single intersection is, after all, by far the most frequently occurring, i. e. in almost all cases where no temperature maximum occurs in the three phase line; for in this case the triple point temperature is the highest temperature for which a three phase coexistence exists.

For a complete survey I have also indicated in figs 13—16, how the binodal curve for the other solid phase gets detached from the transverse plait. This is only possible in one way, because here there cannot be intersection of the lines $D=0$ and $N=0$. For $x=1$ for this binodal curve, and so the expression for T at the rim becomes :

$$\left(\frac{\partial p}{\partial x}\right)_v (v-v_s)+\frac{MRT}{x}$$

so always positive for both rims. The line $N=0$ would therefore, have to become a closed curve, which on account of the shape of the q-lines may be considered as excluded [1]).

In the T,x-lines double intersection will, of course, always occur above the triple point when the three phase line has a maximum pressure. For the rest nothing of interest is to be said of the T,x-lines; they have the same general course as the p,x-lines given here, provided the figures are made to turn 180° round the x-axis, or in other words, provided a negative T-axis is made of the p-axis. Then the points with vertical tangent lie here, of course, on the line $W_{sf}=0$, instead of on the locus $D=0$; only at the rim they coin-

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[1]) At least as long as the complications, which are in connection with the existence of a locus $\frac{d^2\psi}{dx^2}=0$, do not present themselves. (See v. D. WAALS, Proc. of this meeting p. 637). I shall perhaps revert later on to the changes which are to be made in what precedes in consequence of this.

cide. If the pressure maximum of the three phase line should be found at higher pressure than the point A of fig. 1, we must, of course, have the case mentioned under 3, i. e. the point of contraction must lie within the figure.

It has been assumed in the above that throughout the region $\left(\frac{\partial p}{\partial x}\right)_v =$ positive, and that a decreases with increasing b. The case that a increases with increasing b does not present any new points of view. If we have a system where a strongly increases, so that the critical temperature rises with b and $\left(\frac{\partial p}{\partial x}\right)_v$ is negative, the expression

$$(v - v_s)\left(\frac{\partial p}{\partial x}\right)_v + (x_s - x_f)\frac{MRT}{x_f(1-x_f)}$$

is evidently always negative for $x_s = 0$. And this is obvious, because this axis is now also that of the more volatile component; on the other hand the reversal of sign may now take place with the other axis. What happened on the left just now, will now take place on the right, and vice versa. It is only worthy of notice that now the line $N=0$, if it exists, must intersect the axis $x=1$ in two points. For the expression

$$(v - v_s)\left\{\frac{MRT}{(v-b)^2}\frac{db}{dx} - \frac{da/dx}{v^2}\right\} + MRT$$

where db/dx and da/dx are positive, becomes positive for $v=b$ and $v=\infty$. From this follows that besides the just mentioned cases, another possibility may be found, i. e. that the point of contraction does fall within the figure, but not the point of detachment. For the p,x- and T,x-figures it makes only this difference that a loop formed in the way of fig. 12, (which always disappeared in the rim in the other cases) may now also disappear like the loop of fig. 10 in a point within the figure. It is further clear, that in this case the point of contraction will much sooner fall within the figure than in the preceding case. For according to formula (1) $\frac{db}{dx}$ must have an excessively high value for the expression to be able still to become positive with a volume $v = 10b$. If, however, $da/dx = 2a_2 - 2a_{12} = 1.8\,a_2$ [1]), then:

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[1]) With the values for a and b of LANDOLT and BÖRNSTEIN's table 82 we find about 12 for the highest value of $\frac{b_2}{b_1}$, about 250 for that of $\frac{a_2}{a_1}$; if hydrogen is excluded, the values become resp. 8 and 40. So, whereas with exclusion of hydrogen, pairs with a ratio $\frac{b_2-b_1}{b_1} > 7$ cannot occur, $\frac{a_2-a_1}{a_1}$ can reach the value 39.

$$\frac{da/dx}{v^2} = 1.8\frac{a}{v^2} = 1.8\left(\frac{MRT}{v-b} - p\right)$$

and so $(v-v_s)\dfrac{da/dx}{v^2}$ becomes of the order of magnitude $1.8\{MRT - p(v-v_s)\}$. With this volume and the low temperature holding here the latter term is certainly a small fraction of MRT, also $\dfrac{MRT}{v-b}\dfrac{db}{dx}$, so that the expression becomes negative.

Nor does the case that $\left(\dfrac{\partial p}{\partial x}\right)$ may become zero in the examined region, call for a further discussion, for it does not present any new points of view. If $\left(\dfrac{\partial p}{\partial x}\right)_v$ becomes zero in consequence of $\dfrac{da}{dx}$ first being negative then positive (minimum critical temperature), we shall have on either side what in the first case took place on the left side (fig. 6—12); if da/dx is first positive then negative (minimum of vapour pressure) we have on either side what happens on the right side in figs. 13—16.

Nor does, in view of the foregoing, the occurrence of cases in which the plaitpoint curve meets the three phase line, offer any difficulty. It is only clear, that the two points where this meeting takes place, must lie below the point of detachment (double point of the binodal curve solid-fluid) both in pressure and in temperature. For when detachment has taken place, and so the binodal curve has split up into two branches, it seems no longer possible, when the v,x-figure constantly contracts and hence $(\varepsilon_{sf})_v$ has a negative value, that the three phase pressure coincides with a plaitpoint pressure [1]. But nothing indeed pleads against this conclusion. Only when we cling to the supposition that the point of detachment must always lie at the rim we are confronted by unsurmountable difficulties. For then the temperature and pressure of the point of detachment coincide with those of B (fig. 1), and this point, lying considerably below the triple point, lies certainly, at least in pressure, far below any plaitpoint.

In conclusion we may remark that the cases where x_s lies between 1 and 0, i.e. where the solid substance is a compound entirely or partially dissociated in the fluid state, may be derived in all their details from the v, x-figure (fig. 2) without any further difficulty. We get then at low temperatures SMITS' diagrams in the figures 4—7 in his

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[1] Compare the figures referring to this in VAN DER WAALS, (These Proc. VI, p. 237, VIII, p. 194 fig. (2) and SMITS (These Proc. VI, p. 491 and 495 and VIII, p. 200 (fig. 10).

paper: Contibution to the knowledge of the p, x- and the p, T-lines [1], at least when we take the maxima of pressure very much higher and the minima very much lower, so that on the left side the figure intersects itself twice. The detachment of the two binodal curves then takes place in a very intricate way by means of a series of modifications, which I shall, however, omit, with a view to the available space. So, for this I must refer to the lectures which I am arranging for publication as mentioned in the beginning of my preceding communication, though certainly some time will elapse before they see the light.

Physics. — "*Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XIII. *On the conditions for the sinking and again rising of a gas phase in the liquid phase for binary mixtures.* (continued). By Dr. W. H. KEESOM. Communication N°. 96^c from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

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

§ 6. *Conditions for the occurrence of barotropic plaitpoints for mixtures with* $M_2 = 2\,M_1$, $v_{k_1} = 8\,v_{k_2}$. Now that it had appeared in § 5 (These Proc. p. 510), that there exists a barotropic plaitpoint [2]) on the assumptions mentioned there, first of all the occurrence of barotropic plaitpoints with $M_2/M_1 = 2$, $v_{k_2}/v_{k_1} = {}^1/_8$ was subjected to a closer investigation, partly also on account of the importance of these considerations for mixtures of He and H_2 [3]). The barotropic plaitpoints given in table I respectively for the ratio of the critical

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[1]) These Proc. VIII, p. 200.

[2]) The proof that this barotropic plaitpoint really lies on the gas-liquid plait, is in connection with the discussion of the longitudinal plait. In a following Comm. by Prof. KAMERLINGH ONNES and me on this latter subject, the treatment of which was postponed for the present as stated in Comm. N°. 96^b, the proof in question will be included.

[3]) To enable us to judge in how far this last assumption is in accordance with what is known about mixtures of He and H_2, the following remark may follow here, in the name of Prof. KAMERLINGH ONNES too, (cf. Comm. N°. 96*b* § 4, Dec. '06 p. 506) on *b* (cf. VAN DER WAALS, These Proc. Jan. '07, p. 528) and *a* for helium: It proved in the preliminary experiment described in Comm. N°. 96*a* that on analysis the liquid phase contained at least (some He has evaporated from it during the drawing off of the liquid phase) about 3 % He, the gas phase at least (a very small quantity of liquid has been drawn along with the gas phase being blown off) about 21 % H_2 (estimations of the corrections which for the reasons mentioned ought to be applied to the results of the analysis make it probable that they will not considerably influence the results derived here [added in the English translation]). Let us put the density of liquid hydrogen boiling under

temperatures of the components given there are found in the way explained in § 5.

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atmospheric pressure according to DEWAR (Roy. Institution Weekly Evening Meetings), 25 March '04) at 0.070, and let us derive the coefficient of compressibility according to the principle of the corresponding states, e.g. from that of pentane at 20° C., then the density at 40 atms. is 0,072. If we calculate the increase of density in consequence of the solution of helium from VAN DER WAALS' equation of state for a binary mixture by putting $b_{M\mathrm{He}} = \frac{1}{2} b_{M\mathrm{H}_2}$ for this correction term, we get for the density of the liquid phase at the p and T mentioned if it contained 3 % He : 0.077.

The gas phase will have the same density at about the p and T mentioned (cf. Comm. N⁰. 96*a*, Nov. '06, p. 460). The theoretical density (AVOGADRO-BOYLE-GAY-LUSSAC) at $T=20°$ and $p=40$ atms. $=$ 0.0885. If we assume VAN DER WAALS' equation of state with a_x and b_x for constant x not dependent on v and T, to hold for this gas phase, it follows with the above given value of the density that $\frac{b_x}{v-b_x} - \frac{a_x}{RT}\frac{1}{v} = 0.15$.

For $a_{22} = a_{12} = 0$ with $a_{11M} = 0.00042$ (KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen), and with $v_M = 0.0021$, putting $x = 0.80$ for the gas phase, we should obtain: $b_{xM} = 0.21\ v_M = 0.00044$. We should then, if we may put $b_{12M} = \frac{1}{2}(b_{11M} + b_{22M})$, get $b_{22M} = 0.00033 = {}^3/_8\, b_{11M}$ ($b_{11M} = 0.00088$, KOHNSTAMM l. c.). If we wish to assume positive values for a_{12} and a_{22} (cf. Comm. N⁰. 96*a*, p. 460), we should have to put $b_{22M} > {}^3/_8\, b_{11M}$ for $T = 20°$; if we assumed that the gas phase contained 15% He we should derive from the above mentioned experiment for positive values of a_{11} and a_{12} : $b_{22M} > 0.31\, b_{11M}$.

These results harmonize very well with what may be derived about $b_{M\mathrm{He}}$ at 0° C.; the ratio of the refracting powers (RAYLEIGH) gives: $b_{22M} = 0.31\, b_{11M}$, while the ratio of the coefficients of viscosity and also that of the coefficients of the conduction of heat lead to a greater value for $b_{M\mathrm{He}}$ (about $^1/_2\, b_{M\mathrm{H}_2}$).

If we take $b_{22M}/b_{11M} = {}^1/_2$, we should obtain from the above given considerations (putting $a_{12M} = \sqrt{a_{11M}\, a_{22M}}$) : $a_{22M}/a_{11M} = {}^1/_{175}$, so that $T_{k\mathrm{He}} =$ about 0.35°. This renders a value for the critical temperature of He $< 0.5°$ probable.

This conclusion would not hold if b_{xM} for $x = 0.8$ were considerably greater than follows from the hypothesis that b_{xM} varies linearly with x. This however is according to the experiments of KUENEN, KEESOM and BRINKMAN on mixtures of $CH_3Cl - CO_2$ and $CO_2 - O_2$, not to be expected. The experiments of VERSCHAFFELT on mixtures of $CO_2 - H_2$ would admit the possibility, but give no indication for the probability of it. [Added in the English translation].

So though probably b_{22}/b_{11} for mixtures of He and H_2 is larger, yet we shall here retain the supposition made in § 5 on b_{22}/b_{11}, with which the calculations were started, because the accurate amount is not yet known to us, and we only wish to give here an example for discussion; moreover the course of the ψ-surface will not be considerably modified by this difference in any essential respect.

TABLE I.

Barotropic plaitpoints at $M_2/M_1 = {}^1/_2$, $v_{k_2}/v_{k_1} = {}^1/_8$.

T_{k_2}/T_{k_1}	x_{bpl}	v_{bpl}/v_{k_1}	T_{bpl}/T_{k_1}	p_{bpl}/p_{k_1}
0.0002	0.6	0.3957	1.005	4.805
0.0210	0.65	0.3481	0.934	4.772
4/121	2/3	1/3	441/484	576/121
0.0604	0.7	0.3048	0.867	4.758
0.1044	0.75	0.2636	0.800	4.780
0.1472	0.8	0.2234	0.726	4.811
0.1842	0.85	0.1833	0.638	4.800
0.2106	0.9	0.1424	0.521	4.567
0.2176	0.925	0.1212	0.444	4.202
0.2190	0.94	0.1081	0.387	3.751
0.2182	0.95	0.0991	0.343	3.282
0.2148	0.965	0.0851	0.266	2.107
0.2106	0.975	0.0752	0.204	0.687
0.2040	0.985	0.0644	0.130	— 1.927
0.1996	0.99	0.0585	0.078	— 5.191
0.1960	0.995	0.0518	0.033	— 9.723
0.1956	0.9965	0.0495	0.028	—10.326
0.1964	0.9975	0.0478	0.019	—12.086
1/4	1	1/24	0	— 27

For so far as the assumed suppositions hold, the barotropic plaitpoints given in the table have only physical significance if T_{bpl} does not become so low that solid phases make their influence felt (cf. Comm. N°. 96*b*, § 5 *b*), and if moreover the portion of the ψ-surface in the neighbourhood of the plait-point is not covered by a portion of the derived surface indicating more stable equilibria (as e. g. will be the case for negative pressures). In how far the indicated barotropic plaitpoints will belong to the gas-liquid-plait will be more fully treated in a following communication (cf. footnote 2, p. 660).

In the first place it follows from table I that with the assumed ratios of the molecular weights and of the critical volumes, barotropic plaitpoints prove only possible (quite apart from the question whether they are physically realisable, and whether they belong to the gas-liquid plait) for $T_{k_2}/T_{k_1} < \frac{1}{4}$.

The barotropic plaitpoint for the ratio $T_{k_2}/T_{k_1} = 0.0002$ is a plaitpoint for a mixture, one component of which is a gas almost without cohesion (Comm. No. 96*b* § 1). A further consideration of it would lead us again to the region of the longitudinal plait.

The conditions relating to barotropic plaitpoints for x_{bpl} near 1 furnish a contribution to the knowledge of VAN DER WAALS' ψ-surface for binary mixtures with a small proportion of one of the components [1]). We find for T_{k_2}/T_{k_1} near $^1/_4$, putting $x_{bpl} = 1 - \xi$:

$$u = - \xi^{-2/3} \left\{ 1 - \frac{1}{2} \xi^{2/3} - \frac{1}{3} \xi \ldots \right\}, \mu = - \frac{9}{7} \left\{ 1 - \frac{4}{9} \xi^{1/3} + \frac{20}{9} \xi^{2/3} - \frac{29}{9} \xi \ldots \right\}, T_{k_2}/T_{k_1} = \frac{1}{4} \left\{ 1 - \frac{7}{2} \xi^{1/3} + \frac{315}{16} \xi^{2/3} - \frac{735}{16} \xi \ldots \right\}.$$

It is seen from the series of the ratios T_{k_2}/T_{k_1} in table I, that in this a maximum and a minimum occur, respectively for about $T_{k_2}/T_{k_1} = 0.219$ and 0.196. From the formulae derived for x_{bpl} near 1, a minimum and a maximum for μ is found, and hence for T_{k_2}/T_{k_1}, respectively at $x_{bpl} = 0.9968$ and 0.969. That the latter is in reality found at $x_{bpl} = 0.94$ is due to following terms in the development.

For $T_{k_2}/T_{k_1} < 0.196$ or $0.219 < T_{k_2}/T_{k_1} < 0.25$ one barotropic plaitpoint is found, for $0.196 < T_{k_2}/T_{k_1} < 0.219$ three. In connection with Comm. No. 96 *b* § 2 (Dec. '06 p. 502, cf. also this Comm. § 1, Dec. '06, p. 508) it follows also from this that for the mixtures considered here at lower temperature the longitudinal plait makes its influence felt.

The experiment described in Comm. N°. 96*a* proved that for mixtures of He and H_2 at — 253°, i.e. about $T = 0.65\, T_{kH_2}$, a barotropic tangent chord is found on the ψ-surface. If at that temperature only *one* barotropic tangent chord occurs, this will point to this (Comm. N°. 96*b* p. 504) that for the mixtures of these substances $T_{bpls} > 0.65\, T_{kH_2}$, and therefore according to this table $T_{kHe} < 0.18\, T_{kH_2}$, while the found considerable difference in concentration between the gas and the liquid phase (see Footnote 3,

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[1]) Cf. Comm. N°. 75 (Dec. '01), N°. 79 (April '02), N°. 81 (Oct. '02), Suppl. N°. 6 (May, June '03).

p. 660) indicates, that T_{bpls} would have to lie still pretty much higher, and therefore $T_{k\mathrm{He}}$ pretty much lower (probably $<$ about 4°) [1]. Of this result we availed ourselves in the treatment of the estimation of the critical temperature of He in Comm. N°. 96*b*.

(To be continued).

Physics. — "*Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XIV. *Graphical deduction of the results of* KUENEN'S *experiments on mixtures of ethane and nitrous oxide.*" Supplement 14 to the Communications from the Physical Laboratory of Leiden. By Prof. H. KAMERLINGH ONNES and Miss T. C. JOLLES.

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

§ 1. *Introduction.* In what follows we have endeavoured to derive quantitatively by first approximation the behaviour of the mixtures of N_2O and C_2H_6 (mixtures of the II type [2]), which has become known through KUENEN'S experiments [3]), by the aid of VAN DER WAALS' free-energy surface. The ψ-surfaces construed for this purpose (see plate I) are the counterparts of those construed in Comm. N°. 59 (These Proc. Sept. 1900) and Comm. N°. 64 [4]) for the derivation of the results of KUENEN'S and HARTMAN'S experiments on mixtures of CO_2 and CH_3Cl (mixtures of the I type). In the graphical treatment [5]) of our problem we have chiefly followed the method given in Comm. N°. 59, where the critical temperature and pressure of some mixtures were borrowed from KUENEN'S determinations, and then the results of another group of experiments — those referring to the conditions of coexistence of two phases at a certain temperature — were deduced by the aid of VAN DER WAALS' theory.

KUENEN'S results for N_2O and C_2H_6 are principally laid down in

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[1]) If b_{22}/b_{11} is taken larger than $1/8$ (Cf. Footnote 3 p. 660) this supposition too makes the upmost limit for $T_{k\mathrm{He}}$ on the said supposition smaller. This is seen when we compare with table I that we obtain $T_{bpl}/T_{k_1} = 0.679$ for $b_{22}/b_{11} = 1/4$ with $T_{k_2}/T_{k_1} = 0.15$.

[2]) HARTMAN, Leiden Comm. Suppl. no. 3, p. 11.

[3]) KUENEN, Leiden Comm. no. 16, Phil. Mag. 40, p. 173, 1895, cf. also KAMERLINGH ONNES and ZAKRZEWSKI, Leiden Comm. Suppl. no. 8. (These Proc. Sept. 1904).

It is remarkable that the possibility of this case was foreseen by VAN DER WAALS, Contin. II, p. 49 [added in the English translation].

[4]) Arch. Néerl. Serie II, Tome V, p. 636.

[5]) Only graphical solutions for definite cases are here possible. (Cf. Suppl. 8, These Proc. Sept. 1904. § 1).

four figures [1]); one of them gives the critical quantities from which we shall start in our deduction, and the border curves for mixtures of different concentration; the three others, which represent the *xv*-projection of the connode with the connodal or tangent chords at the temperatures 20° C, 25° C, 26° C, show the contraction of the transverse plait with rise of temperature, and finally its splitting up into two plaits.

We have thought that we could obtain a better comparison of observation and calculation, when representing the observations by the *xv*-figures for 5° C., 20° C. and 26° C., and the *pT*-figure, instead of by the *xv*-figures at the before mentioned temperatures and the *pT*-figure.

§ 2. *Basis of the calculation. Law of the corresponding states and reduced equation of state.* We start (cf. Suppl. N°. 8, These Proc. Sept. 1904 § 1) from the supposition that the law of the corresponding states — at least within the region of the observations — holds as well for C_2H_6 and N_2O as for their mixtures. As reduced equation of state we chose equation V. s. 1 of Comm. N°. 74[2]) p. 12 For a region of reduced temperature and pressure which incloses the region which corresponds to that of the observations under investigation, this equation is as closely as possible adjusted to CO_2, which in thermical properties has much in common with N_2O, and there is no reason to suppose that this will not be the case with C_2H_6.

In the application we are, however, confronted by this difficulty, that V. s. 1 deviates most strongly from the observations on CO_2 exactly in the neighbourhood of the critical state. (Cf. Comm. N°. 74 and later KEESOM, Comm. N°. 88). If from V. s. 1 [3]) the point is derived, for which

$$\frac{\partial \mathfrak{p}}{\partial \mathfrak{v}} = 0 \text{ and } \frac{\partial^2 \mathfrak{p}}{\partial \mathfrak{v}^2} = 0 \,,$$

we find $\mathfrak{t} = 1.010595$, $\lambda\mathfrak{v} = 1.0407.10^{-3}$, $\mathfrak{p} = 1{,}06566$. KEESOM'S observations, Comm. N°. 88, give for the critical volume, when it is sought by the application of the law of the rectilinear diameter, for CO_2

$$v_k = 0.00418 \text{ and for } \lambda = \frac{p_k v_k}{T_k} = 1.0027.10^{-3}. \quad . \quad . \quad (1)$$

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[1]) Where it was necessary, KUENEN'S figures have been rectified in accordance with the results of observation given by him.

[2]) Arch. Néerl. Vol. Jubil. Bosscha. Serie II, tome 6, 1901.

[3]) In the calculations T is put 273°,04 for the freezing point of water, because V. s. 1 was calculated with this value.

We find then:

$$\mathfrak{t}_k = 1.010595 \text{ instead of } \mathfrak{t}_k = 1$$
$$\mathfrak{v}_k = 1.0379 \quad ,, \quad ,, \quad \mathfrak{v}_k = 1$$
$$\mathfrak{p}_k = 1.06566 \quad ,, \quad ,, \quad \mathfrak{p}_k = 1.$$

The isotherms from which V. s. 1 has been derived by the computation of the virial coefficients $\mathfrak{B}$, $\mathfrak{C}$ etc. (See comm. N°. 71, These Proc. June 1901), indicate therefore, by means of interpolation according to this mode of calculation, a critical state, which, drawn in the *pv*-diagram, has shifted with respect to that which was found by immediate observation; the critical temperature according to V. s. 1 is namely $\mathfrak{t}_k T_k$ when T_k is the observed critical temperature. So are also the values found for $\mathfrak{p}_{max.}$, $\mathfrak{v}_{liq.}$ and $\mathfrak{v}_{vap.}$ at $\mathfrak{t}$ by the application of MAXWELL's criterion, different from those which we should find when dividing $p_{max.}$ by p_k, $v_{liq.}$ and $v_{vap.}$ by v_k. The deviations are of the same order as the deviations of the substances inter se, when they are compared by the law of the corresponding states. At $\mathfrak{t} = 0{,}9$ they are about zero, but they increase as we approach the critical state, so that the deviations agree with a gradual transformation of the net of isotherms. The following table gives a survey of the deviations in the corresponding values.

Column *A* refers to V.s. 1 and implicitly to p_k, T_k of CO_2
,, *B* ,, ,, the observations ,, CO_2
,, *C* ,, ,, ,, ,, ,, N_2O.

A		*B*		*C*	
$\mathfrak{t}$	$\mathfrak{p}$	$\mathfrak{t}$	$\mathfrak{p}$	$\mathfrak{t}$	$\mathfrak{p}$
1.0106	1.066				
		1.	1.	1.	1.
0.975	0.826	0.975	0.845	0.975	0.854
0.950	0.695	0.950	0.709	0.950	0.720
		0.925	0.589	0.925	0.599
0.900	0.490	0.900	0.494	0.900	0.486

In the neighbourhood of the critical temperature the phenomena are governed by the difference of the temperature of observation and the critical temperature, $T - T_k$; for this reason we have chosen for the detailed model of 26° such a temperature T' for the comparison of the observations at that temperature T' with the result of computation that

$$T_k - T = \mathfrak{t}_k T_k - T'.$$

At the general survey for 26° we have applied to $\mathfrak{t} = \frac{T}{T_k}$ a correction $= \Delta\,\mathfrak{t}$, so that $\Delta\,\mathfrak{t} = 0.0106\,\theta$, when $\theta = 10(\mathfrak{t} - 0{,}9)$ for $0 < \theta < 1$, whereas $\Delta\,\mathfrak{t} = 0$ for all other values of θ. The correction $\Delta\mathfrak{t}$ to $\mathfrak{t}$ was accompanied by a correction $\Delta\mathfrak{v}$ to $\mathfrak{v}$ and $\Delta\mathfrak{p}$ to $\mathfrak{p}$, so that $\Delta\mathfrak{p} = 0.0657\,\theta$ and $\Delta\mathfrak{v} = 0.0379\,\theta$, which together represent a regular increase of the corrections from $\mathfrak{t} = 0{,}9$ to the critical state. For the detailed model of the ψ-surface for 26°, on which only the part from $x = 0{,}35$ to $x = 0{,}65$ was represented, we used everywhere the same correction viz. $\Delta\,\mathfrak{t} = 0.0106$, $\Delta\mathfrak{p} = 0{,}0657$, $\Delta\mathfrak{v} = 0{,}0379$.

§ 3. *Critical quantities for the mixtures.* KUENEN has determined the plaitpoints $T_{pl.x}, p_{plx}, v_{pl.x}$, for some mixtures with the molecular concentration x. T_{rx}, p_{rx}, v_{rx}, the critical points of contact, and T_{kx}, p_{kx}, v_{kx} the critical states of the mixtures taken as homogeneous differ so little [1]) from these values, that this difference may be disregarded for our purpose, and so they are also known for the mixtures investigated by KUENEN.

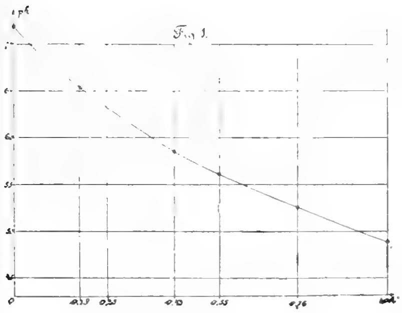

Fig. 1.

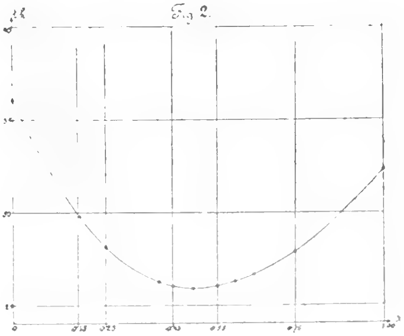

Fig. 2.

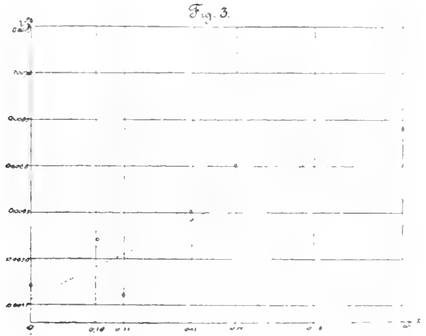

Fig. 3.

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[1]) This has been fully treated by VAN DER WAALS, Cont. II, § 11.

The critical quantities for the other mixtures were found by graphical interpolation. Fig. 1 gives p_{kx}, fig. 2 T_{kx} as function of x; in fig. 3 v_{kx} has been calculated from p_{kx} and T_{kx}, by the aid of λ (see formula (1)); the v_{kx} observed by KUENEN have been indicated there.

By carrying out the construction for the connode by the aid of the p, $\frac{\partial\psi}{\partial x}$ and $\psi - x\frac{\partial\psi}{\partial x} - v\frac{\partial\psi}{\partial v}$ curves (see Comm. N°. 59a[1])), which the models for those different temperatures yield, we may derive $v_{kx} - v_{pl.x}$, $p_{kx} - p_{pl.x}$ in first approximation (see Comm. N°. 59a). Applying these corrections we should then have to repeat the calculation from the beginning, to obtain more accurate values for v_{kx}, p_{kx}. We have confined ourselves to a first approximation in all our constructions, as also a further correction of the equation of state V.s. 1., which can cancel the deviations mentioned in § 2, has not been applied and we were the more justified in this, as these latter deviations are larger than those we have now in view.

§ 4. *Construction of the ψ-surfaces.*

From the equation of state V. s. 1 we find immediately the reduced ψ_{xT} curves, from which are then deduced the ordinary ψ-curves according to Suppl. N°. 8, § 4; or the ordinary virial coefficients, whic hare then used for the calculation of ψ according to Comm. N°. 59.

For the construction (cf. Comm. 59) use was made of:

at 5° $\psi'_5 = \psi + 0{,}10\,x + 25\,v$
,, 20° $\psi'_{20} = \psi + 0{,}10\,x + 36{,}5\,v$
,, 26° $\psi'_{26} = \psi + 0{,}24\,x + 57{,}3\,v$,

while a suitable constant was subtracted from every ψ. Here v is expressed in the theoretical normal volume, just as in the diagrams. From the ψ_{xT} curves (cf. fig. 1, pl. II) the ψ_{vT} curves (see fig. 2, pl. II) and the p_T curves were graphically derived. The models for ψ were construed on a scale 5 times larger than the diagrams on pl. II, pl. III and pl. IV.

§ 5. *Determination of the coexisting phases.*

Applied was both the construction by rolling a glass plate on the

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[1]) In giving the figure 3 in Comm. N°. 59a for this construction it was stated that this figure was very imperfect. It appears now that the loop ought to contain two cusps. We found out the error by the aid of the general properties of the substitution-curves treated by VAN DER WAALS (Comp. Proceedings of this meeting). This error shows the more how necessary it is that graphical solutions are controlled by such general properties as VAN DER WAALS is now publishing. [Added in the English translation].

model, which yields the connode and the tangent chords, and the simplified construction in the plane given in Suppl. N°. 8, § 7, to which a small correction was applied. After viz., a provisional connode, that of the mixtures taken as homogeneous, has been found by tracing curves of double contact to the ψ_{xT}-curves, and by determining conjugate points b on the gas branch at some points a on the liquid branch of that connode, so that every time $\frac{\partial\psi}{\partial x}$ is the same for the two conjugate points, the lines which join every two of these points a and b, are produced outside the provisional connode, till they cut the isobars which pass through a, in points c, which together represent the required gasbranch of the connode; c and a are then considered as conjugate points. In the ψ-surface at 5° C. the two constructions yielded fairly well corresponding results, both with regard to the chords and to the connode itself, as appears from pl. II fig. 4, where — — — — denotes the connode and the connodal tangent-chords found by rolling a glass-plate on the model, —.—.—.— those found by means of the just mentioned construction. That the simplified construction, which was more particularly plotted for equilibria far below the critical temperature (see Suppl. N°. 8, § 7) still leads to our end, is probably due to the fact, that we have here to deal with a mixture of the II type.

With the ψ-surface for 20° the slight depth of the plait rendered it necessary, to considerably diminish the longitudinal scale for the v-coordinate of the model. This compression (cf. pl. I, fig. 2) rendered the plait sufficiently clear to determine the connode and the place of the connodal tangent chords by rolling a glass plate. By means of the simplified construction the connode was still to be obtained, but the determination of the tangent-chords became uncertain.

With the ψ-surface of 26° the depth of the plait (here split into two) becomes so exceedingly slight, that it does not appear but with a computation with 7 decimals, and even then it manifests itself almost quite in the two last decimals. Hence it is not possible to model a ψ'-surface (we mean a surface derived from the ψ-surface, on which the coexisting phases are still to be found by rolling a plane), on which this plait is visible, nor is it of any avail to confine ourselves to a small part of the surface, because the curvature of the ψ_{vT}-curves is very strong exactly there where something important might be shown. The determination of the connode and the connodal tangent chords by construction according to § 8 of Comm. N°. 59a, which can always be carried out provided enough decimals are worked with, remained still uncertain up to 7 decimals, so that we have not pursued it any further. Thus the represented part of the ψ-surface for 26° from x=0.35 to x=0,65 and from v=0.0038 to v=0.0070, has been given by us chiefly to demonstrate how exceedingly small the influences must be on which a plait depends, and how much care is required to determine a plait experimentally which is not at all to be seen on the surface. The curves drawn on the surface, which relate to the plait, were found by indirect ways, partly by construction, partly by calculation. To facilitate a comparison of the models inter se the region of x and v, on which the model for 20° and that for 26° extends, has been indicated on the model for 5°, on the model for 20° that for 26°.

§ 6. *Further remarks on the different models and drawings obtained by construction.*

a. The ψ'-surface for 5°. The model, pl. I, fig. 1, and the drawings pl. II, figs. 1, 2 and 3 show curves of equal concentration, ψ'_{xT}, equal volume and equal pressure, the connode and the connodal tangent chords. As $-\dfrac{\partial\psi'}{\partial v}=p-25$, some pressures are represented by negative slopes on the stable part of the ψ'-surface, in consequence of which the character of this ψ'-surface does not in this respect immediately express that of the ψ-surface, where all the slopes are positive. A connodal tangent-chord, near the concentration with maximum pressure, almost touches the ψ_x-line. With the concentration of maximum pressure this would be just the case. Just as the connodal tangent chords the isobars are traced in the projection on the $x\,v$-plane (Pl. II, fig. 3) in full lines, the connode is denoted by —.—.—.

For the isobars [1]) we may note several peculiarities, to which VAN DER WAALS has drawn attention in his theory of ternary systems [2]). The isobar which touches the connode on the liquid and vapour side, belongs to the pressure $p=36{,}6$, which is found for the mixture which when behaving as a simple substance should have a maximum coexistence pressure. The pressure curve π determines the transition between the continuous isobars (taking the region outside the drawing into consideration) and those split up into two branches. The parts of the continuous isobars which point to P, have each a point of inflection on either side of the top. The shape of the curves $\dfrac{\partial^2\psi}{\partial v\partial x}=0$ and $\dfrac{\partial^2\psi}{\partial v^2}=0$

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[1]) Cf. the sketch by HARTMAN, Leiden Comm., Suppl n⁰. 3, pl. II, fig. 5.

[2]) These Proc. March 1902, p. 540.

is as has been indicated by VAN DER WAALS [1]). The points of intersection of these two curves are the centre Q of the isobars and the double point of the pressure curve π, P.

b. The ψ'-surface for 20°. Fig. 1, pl. III denotes the ψ_{xT}-curves and the connode. Fig 2, pl. III the ψ_{vT}-curves and the connode. Fig. 3 gives the projection on the xv-plane of the connode, of the tangent chords and of some isobars. The connode is denoted by ——.——.——. Pl. I fig. 2 gives a representation of the model.

c. The ψ'-surface for 26°. Fig. 1 pl. IV gives the ψ_{xT}-curves, fig. 2 pl. IV gives the critical states, K_1 and K_2 the isobars and the connodes for the mixtures which are taken as homogeneous, and whose gas branch as well as whose liquid branch is almost a straight line. Though in the calculations (see § 2) the plaitpoint x_{T_p} and the critical point of the homogeneous mixture x_{T_k}, have been considered as coinciding, a distance has now been given between these points which has been fixed by estimation [2]). The dotted parabola has been taken from VERSCHAFFELT's calculation, Suppl. N°. 7, p. 7, though properly speaking it holds only for the case that the maximum pressure falls in P_1 or P_2; the produced connode denotes the probable course of this part by approximation. Pl. I, fig. 3 gives a representation of the model. All this refers to a small region of x and v; fig. 3 pl. IV, however, indicates by ——.——.——. the connode according to the construction for the mixtures taken as homogeneous all over the width of the ψ'-surface. The square drawn denotes the extension of the just treated part of the ψ'-surface.

d. The contraction and the subsequent splitting up of the plait appears from fig. 4 Pl. III, where the xv-projections of the connode and some connodal tangent chords of the three models have been drawn on the same scale after the xv-figures for 5°, 20° and 26° mentioned under *a b c*.

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[1]) Prof. VAN DER WAALS was so kind as to draw our attention to a property which might also have been represented in the figure, when also the curve for $\frac{\partial^3 \psi}{\partial v^2 \partial x} = 0$ had been drawn, viz. that the minimum volume in the vapour branch, and the maximum volume in the liquid branch lie on the curve $\frac{\partial^3 \psi}{\partial v^2 \partial x} = 0$ which has a course similar to that of the curve $\frac{\partial^2 \psi}{\partial v \partial x} = 0$, more particularly it has the same asymptotes, and it deviates from it only in this, that with greater density the curve passes over larger volumes.

[2]) Here the representation of the plait must come into conflict with the theory or with the simplification introduced at the basis of the calculation. With a view to the illustration of the theory by figures the latter has been chosen.

§ 7 *Comparison of the construction with the observation.* On the whole this is very satisfactory, taking the degree of approximation into consideration.

a. In pl. II fig. 4 the diagram for the plait at 5° indicating KUENEN's observations, has been drawn in full lines. The figure contains at the same time that obtained by construction. The single observations have been denoted by ⊡ (see § 6*a*). Besides the construction with the model indicated by — — — — and by $\overline{\triangledown}$, also the simplified constructions in the plane indicated by —.—.— and by ⊙, the outermost of which refers to the less simplified construction, represent the character and also the numerical values satisfactorily.

b. In pl. III, fig. 3 the figure representing KUENEN's observations for the plait of 20°, has been indicated by — — — —. The figure contains at the same time the —.—.—., obtained by construction on the model (see § 6*b*). The correspondence at $x = 0.3$ is the worst, which is no doubt in connection with this, that here we have already got very near the critical temperature, and that strictly speaking, different values should be assigned to T'' (see § 2) for all x, and corresponding $\Delta\mathfrak{v}$ and $\Delta\mathfrak{p}$ should have been taken into consideration.

c. In pl. IV fig. 3 the figure representing KUENEN's observations, have been indicated by full lines; the figure contains also the figure derived in § 6*c* denoted by —.—.— curves.

d. Plate IV fig. 4 and 5 may serve for a comparison of KUENEN's pT-figure (fig. 4) with that derived by construction (fig. 5). In accordance with the remark on T'' in § 2, we have proceeded for 26° as follows:

For 5° and 20° the values of p and T have simply been taken from the construction with the model, mentioned under *a* and *b*. Then we marked *α*) the p's and T's, obtained by multiplying KUENEN's p_k and T_k by $\mathfrak{p}_k$ and $\mathfrak{t}_k$ (see § 2); *β*) for the different values of x the values of T'' and of θ for the temperature of 26° have been calculated, and then Δt and $\Delta\mathfrak{p}$ determined by the aid of this θ according to § 2; the values of p and T corrected in this way have been denoted by + + + and joined by .....—. ..— curves with the points mentioned under *α*). The full and the dotted curves give the corrected values. Between the parts where we started from the critical temperature, and the pT-lines derived fromthe models of 5° and 20° a space has been left open.

Pathology. — "*On the Origin of Pulmonary Anthracosis.*" By P. NIEUWENHUIJSE. (From the Pathological Institute in Utrecht). (Communicated by Prof. C. H. H. SPRONCK.)

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

As is known, von BEHRING and CALMETTE oppose the doctrine according to which the pulmonary tuberculosis among mankind proceeds in most cases from inhalation or aspiration of tuberclebacilli. They presume the tractus intestinalis to be the porte d'entrée of the virus.

In connection with this new hypothesis VANSTEENBERGHE and GRISEZ [1]) have made some experiments at the end of 1905 in CALMETTE's laboratory about the origin of lung-anthracosis.

They mixed the food of full-grown cavies with soot, Indian ink or carmine and made the animals eat a large quantity of this. After 24 hours already they found resp. black and red spots in the lungs especially in the upperlobes and along the edge of the underlobes. VANSTEENBERGHE and GRISEZ concluded from these results that the fine parts, taken up in the intestines, pass through the mesenteric glands and thoracic duct and after having reached the blood in this way, they are caught by the lungs.

According to their conclusion the carbon particles suspended in the atmosphere would not be inhaled, but swallowed, thus reaching the lungs via the intestines. The theory of the intestinal origin of the pulmonary anthracosis was propounded half a century ago by VILLARET [2]); it had however met with little success, and after the careful researches made by ARNOLD [3]) on the inhalation of fine particles it was totally forgotten.

Whereas VANSTEENBERGHE and GRISEZ tried to defend the theory of VILLARET, after having made new experiments and no less a person than VON BEHRING doubted the exactness of the generally assumed opinion, no one will be surprised that criticism soon followed.

Whilst I was working in the laboratory of Prof. SPRONCK, to whom I offer my thanks for his continual interest in this research, repeating the experiments of VANSTEENBERGHE and GRISEZ, several treatises appeared on this subject. First of all ASCHOFF [4]) advanced

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[1]) Annales de l'Institut Pasteur, 1905, p. 787.

[2]) VILLARET: Cas rare d'anthracosis, Paris, 1862, ref. in Schmidt's med. Jahrb. 1862, Bd. 116.

[3]) ARNOLD: Untersuchungen ueber Staubinhalation und Staubmetastase, Leipzig, 1885

[4]) Sitzungsber. der Gesellschaft zur Bef. der Ges. Naturwissenschaft, Marburg, 13 Juni, 1906.

the opinion that there must have been technical mistakes in the experiments of VANSTEENBERGHE and GRISEZ; some time afterwards he was enabled to convince himself of the incorrectness of their opinion by his own experiments [1]).

MIRONESCO [2]) after bringing fine particles into the stomach of rabbits, was not able to recover them in the lungs.

In August 1906 VANSTEENBERGHE and SONNEVILLE [3]) described a new series of experiments which confirmed the results of VANSTEENBERGHE and GRISEZ.

Fine particles which were brought into the mouth with a catheter were already to be recognised in the lungs after a lapse of 5 or 6 hours.

Soon afterwards the opinion of VANSTEENBERGHE and GRISEZ was opposed by two authors: SCHULZE [4]) in a temporary publication concluded that the pulmonary anthracosis could not proceed from the resorbing of fine particles from the intestines and Prof. SPRONCK communicated shortly afterwards at the 5th International Conference on Tuberculosis the results of some of the following experiments, which were adverse to the results, gained by VANSTEENBERGHE and GRISEZ.

In a more extensive treatise SCHULZE [5]) demonstrated further how substances are lightly aspirated into the lungs either by administering them with the catheter or by ordinary eating. A rabbit however, had received within two months the total quantity of 200 grams of vermillion through a gastrotomy, yet no trace of vermillion was to be found in the lungs.

On the other hand some investigators took the part of VANSTEENBERGHE and GRISEZ: PETIT [6]) brought carbon particles into the stomach of six children who were in an advanced state of tuberculosis or athrepsy and after a post-mortem examination he found pigment in the lungs in three of them and HERMANN [7]), on the authority of experiments, esteemed an intestinal origin of the lung-anthracosis possible, but compared with the inhalation-anthracosis of very inferior significance.

Afterwards the results of VANSTEENBERGHE and GRISEZ were empha-

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[1]) BRAUER's Beiträge zur Klinik der Tuberculose, 1906, Bd VI, Heft 2.

[2]) Compt. rend. de la Soc. de Biol. 1906, T. 61, N⁰. 27.

[3]) Presse médicale, 11 Août 1906.

[4]) Münchener Med. Wochenschr. 1906, N⁰ 35.

[5]) Zeitschrift für Tuberculose, October 1906.

[6]) Presse médicale, 13 Octobre 1906.

[7]) Bulletin de l'Académie royale de médecine de Belgique, Séance du 27 Octobre 1906. La Semaine médicale, 1906, N⁰ 44.

tically contradicted from various sides. (Cohn[1]), Remlinger[2]), Basset[3]), Küss et Lobstein[4]), Beitzke[5])).

Some of the above mentioned considered the normal anthracosis in test-animals as a source of mistakes, which Vansteenberghe and Grisez had not taken into account whereas others described the aspiration also as a source, which might give rise to wrong conclusions.

Meanwhile Vansteenberghe and Grisez, supported by Calmette[6]) maintained their opinion. They explain the negative results of their opponents in the following manner: some allowed too much time to pass between the introducing of carbon particles into the stomach and the killing of the test-animals, because after 48 hours the pigment would have almost completely disappeared from the lungs; others used rabbits or too young cavies as test-animals, in which the fine particles are almost wholly retained by the mesenteric glands.

With a view to this last remark I wish to publish the following experiments, because I have taken into account the age of test-animals as well as the time which passed between the introduction of the fine particles and the killing of the animals.

To me it also appeared that the physiological anthracosis is a factor which must be considered, for among all my test-animals, cavies as well as rabbits, black pigment was found in the lungs.

Among some animals this spontaneous anthracosis was rather decided, with others very minute. As a rule there was much less pigment in the lungs of my rabbits than in those of the cavies.

The physiological anthracosis impedes as a matter of course the experimenting with black substances. Besides carmine, vermillion and ultramarine, I have also used Indian ink and soot, because after microscopic investigation it appeared that the first mentioned matter, even after being intensively rubbed in a mortar, was not as fine as the particles of carbon of the last mentioned.

In order to control the experiments of Vansteenberghe and Grisez

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[1]) Berliner Klin. Wochenschr. 1906, N⁰ 44 und 45.

[2]) La Semaine médicale, 1906, N⁰ 45.

[3]) La Semaine médicale, 1906, N⁰ 47.

[4]) Bulletin médical du 21 Novembre 1906.
La Semaine médicale, 1906, N⁰ 48.

[5]) Virchow's Archiv, Bd. 187, Heft 1.

[6]) Compt. rend. des séances de l'Académie de Sciences, T. 143. p. 866.
Compt. rend. de la Soc. de Biol. T. 61, p. 548.
La Semaine médicale, 1906, N⁰. 50.

the test-animals were killed already 5—48 hours after administering the forementioned substances.

Some cavies (experiment n°. 1—5) had eaten bread, mixed with soot, Indian ink or carmine. After the dissection of the animals, the lungs showed only the ordinary physiological anthracosis, but carmine was to be seen neither in the lungs nor in the bronchial glands.

One of these animals (experiment n°. 4) had evidently aspirated soot, for in many bronchi and corresponding alveolars, foodparticles and soot were distinctly seen in large quantities.

Also after introducing various matters with the catheter into the stomach of rabbits (experiment n°. 6—10), aspiration was observed once (experiment n°. 10), whereas among other animals only the normal pigmentation was present.

In order to prevent aspiration with certainty, tracheotomy was performed with three rabbits and after that a suspension of carmine was brought into the stomach with the catheter (experiment n°. 11—13); for the same purpose among some cavies I injected coloured particles into the distal part of the oesophagus which was cut through and then bound up (experiment n°. 14—18). After dissecting no traces of coloured particles were to be found neither in the lungs nor in the bronchial glands.

Further with different cavies the fine particles were directly brought into the intestines after laparotomy (experiment n°. 19—35). Neither was then any of the coloured matter to be found in the lung-tissue nor in the bronchial glands, whereas everywhere else nothing was to be seen except normal anthracosis in varying intensity.

Among some experiments I noticed that coloured particles which were injected directly into the intestines, were later on to be found also in the stomach, in the oesophagus and in the pharynx, sometimes in large quantities (experiment n°. 21, 22, 29 and 30). In the phlegm of the trachea the coloured particles could be distinctly seen sometimes with the use of the microscope (experiment n°. 21 and 29), whilst once (experiment n°. 29) the easily recognisable ultramarin-grains were to be seen even in the phlegm of the chief bronchi. It is quite probable that the animals in agony had aspirated these substances from the pharynx, for, according to NENNIGER [1]) e. g. bacteria too are often aspirated from the pharynx in agony.

The question is now, how came the matter from the pharynx into the intestines. Was it by a motion of the fine particles in a

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[1]) Zeitschr. f. Hygiene u. Infectionskrankheiten, Bd. 38.

proximal direction, as e. g. GRÜTZNER[1]) describes this for fine particles in the intestines and as KAST[2]) has also shown for the oesophagus, or, had the animals eaten their own faeces?[3])

In order to solve this question, four cavies were carefully wrapped in a bandage, after ultramarine had been brought into the intestines so that eating the faeces was quite impossible (experiment n°. 32—35). It now appeared that the ultramarine had come some way proximal from the place of injection, but in the oesophagus, in the pharynx and in the chief bronchi no ultramarine was discernible.

From this I suppose that the ultramarine had simply come into the pharynx owing to the eating of faeces and not through a proximal motion of the fine particles[4]).

From my experiments I conclude that the pulmonary anthracosis does not originate through taking up fine particles from the intestines. It may be acceptable à priori, that fine particles *can* be taken up in the intestinal mucous membrane and *can* get into the lungs along ductus thoracicus and right heart, but this phenomenon is with regard to the pulmonary anthracosis of not so much importance, as VANSTEENBERGHE and GRISEZ have supposed. Evidently these investigators have given sufficient attention neither to the physiological anthracosis of the test-animals, nor to the aspiration of the coloured particles which cannot be quite prevented, not even, as is mentioned above, by direct injecting the matters into the intestines.

If the physiological anthracosis originated by taking up carbon particles from the intestines, not only the mesenterial glands but also the marrow and the milt had to contain much carbon pigment, because firstly it cannot be understood how carbon parts should pass the mesenterial glands without leaving distinct traces of their passing behind them and on the other hand there is no possible reason why the carbon particles to a great extent should not pass through the capillaries of the lungs and deposit in the marrow and the milt.

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[1]) Archiv. f. d. Ges. Physiol. (Pflüger). Bd. 71.

[2]) Berliner Klin. Wochenschr. 1906, N° 28.

[3]) When starving cavies and rabbits usually eat their own faeces, it also often occurs when they have sufficient food.

SWIRSKI: Archiv f. exper. Path. und Pharm. 1902, Bd. 48.

[4]) UFFENHEIMER, after injecting a suspension of prodigiosusbacilli into the rectum of rabbits, noticed a motion of the bacilli in a proximal direction; they ascended up to the pharynx and from thence they were sometimes aspirated into the lungs. Deutsche Med. Wochenschr. 1906, N°. 46.

Description of the Experiments.

1. Cavy 650 grams.

First 24 hours without food, then for 24 hours exclusively dough and soot, then killed.

Results: Macroscop. intestines much soot, lungs grey with small black spots, especially in the upper lobes, bronchial glands distinctly pigmented.

Microscop. In the interstitial spaces of the lung-tissue are many cells with black pigment especially under the pleura. A very small quantity of it is also found in the alveolars and in the bronchi. The bronchial glands contain a great many cells with black pigment.

2. Cavy 200 grams.

For 48 hours exclusively dough and soot, then killed.

Results: Macroscop. intestines much soot, lungs and bronchial glands pale; microscop. lungs and bronchial glands few cells with black pigment.

3. Cavy 760 grams.

First 24 hours without food, then 5 ccm. of Indian ink in dough, killed after 24 hours.

Results: as in experiment 1.

4. Cavy 350 grams.

First 24 hours without food, then for 48 hours exclusively dough and soot, then killed.

Results: Macroscop. intestines much soot, lungs many black spots and points, bronchial glands pale; microscop. there are foodparticles mixed with soot in many bronchi and alveolars. For a part the soot has already been enclosed in cells, many cells have already penetrated into the interstitial spaces. No pigment is to be seen in the bronchial glands (so in this experiment the coal was aspirated during life; not in agony).

5. Cavy 400 grams.

First 24 hours without food, then 0,5 grams of carmine in dough; killed after 48 hours.

Results: Except in the intestines no carmine can be found.

6. Rabbit 1.75 K.G.

For three days 100 mgr. of soot is brought into the stomach by means of a catheter; killed after 24 hours.

Results: Macroscop. lungs and bronchial glands pale; microscop. few cells with black pigment are to be seen in the interstitial spaces of the pulmonary tissue.

7. Rabbit 2 K.G.

For three days totally 2,9 grams of soot is brought into the stomach with the catheter; killed after 24 hours.

Results: as in experiment 6.

8. Rabbit 2 K.G.

A suspension of 2 grams of carmine in water is brought into the stomach with a catheter; killed after 48 hours.

Results: Except in the intestines, carmine is not to be found.

9. Rabbit 2.75 K.G.

50 grams of charcoalpowder, suspended in water, is brought into the stomach with the catheter; killed after 24 hours.

Results: as in experiment 6.

10. Rabbit 3 K.G.

A suspension of 40 grams of charcoalpowder is brought into the stomach with the catheter; killed after 24 hours.

Results: Macroscop. lungs show black spots especially after dissecting them; the bronchial glands are faintly pigmented; microscop. fine carbon particles and also coarser carbon pieces can be seen in many alveolars. Carbon can be shown neither in the larger bronchi, nor in the trachea; the bronchial glands show some pigment-cells.

The presence of the coarser carbon parts in the alveolars made the diagnose "aspiration" very easy.

11. Rabbit 5 K.G.

After tracheotomy 9 grams of carmine is brought into the stomach with the catheter. About 18 hours afterwards the animal chokes, as phlegm has gathered in the canule.

12. Rabbit 4.25 K.G.

After tracheotomy 8 grams of carmine is brought into the stomach with the catheter; the animal is killed after 24 hours.

13. Rabbit 3.5 K.G.

After tracheotomy 8 grams of carmine is brought into the stomach with the catheter.

Killed after 48 hours.

Results of the experiments 11, 12 and 13: Except in the intestines I could find nowhere carmine in the body at the microscopical investigation; in the lungs and bronchial glands black pigment is present.

14. Cavy 400 grams.

The oesophagus was freeprepared and cut through. Through the lower part 5 gram of vermillion was brought into the stomach. Then the lower part of the oesophagus was bound up whereas the upper part was fastened with its opening in the wound of the skin.

Killed after 5 hours.

15. Cavy 720 grams.

10 grams of vermillion were injected as in experiment 14.

Killed after 6 hours.

16. Cavy 720 grams.

7 ccm. of a suspension of vermillion in gum arabic was injected as in experiment 14.

Killed after 5 hours.

17. Cavy 400 grams.

2 grams of carmine were injected as in experiment 14.

Killed after 5 hours.

18. Cavy 860 grams.

4 grams of carmine were injected as in experiment 14; killed after 6 hours.

19. Cavy 790 grams.

After laparotomy 4 grams of vermillion (in suspension) were brought into a twist of the intestines; killed after 18 hours.

20. Cavy 620 grams.

6 ccm. suspension of vermillion in gum arabic was brought into the small intestin as in experiment 19; killed after 19 hours.

21. Cavy 750 grams.

10 ccm. suspension of vermillion in gum arabic was brought into the small intestin as in exp. 19; killed with chloroform after 18 hours.

22. Cavy 610 grams.

5 ccm. suspension of vermillion in gum arabic was brought into the colon as in exp. 19; killed after 18 hours, by abruptly decapitating in order to prevent vomiting in agony.

Results of the experiments 14—22: In the lung-tissue and in the bronchial glands no vermillion resp. carmine was to be found.

At experiment 21 the vermillion could also be shown in the stomach, in the oesophagus and in the pharynx while some grains could be shown in the phlegm of the trachea. At experiment 22 vermillion could also be found in the stomach, oesophagus and pharynx whereas in the trachea no vermillion was to be seen. (At the experiment 19 and 20 stomach, pharynx etc. were not investigated).

23. Cavy 700 grams.

After laparotomy 5 ccm. of Indian ink is brought into the small intestines.

Killed after 18 hours.

Results: as in experiment 1.

24. Cavy 880 grams.

After laparotomy 5cm. of Indian ink is brought into the coecum.

Killed after 18 hours.

Results as in experiment 1 (the pigmentation is somewhat less intensive).

25. Cavy 750 grams.

After laparotomy 5ccm. of Indian ink is brought into the small intestines.

Killed after 18 hours.

Results: macroscop. Lungs and bronchial glands pale microscop. few pigmentcells.

26. Cavy 700 grams.

After laparotomy 5ccm. of Indian ink is brought into the coecum.

Killed after 18 hours.

Results as in experiment 1. (here the pigmentation is more intensive.)

27. Cavy 730 grams.

After laparotomy 5ccm. of Indian ink is brought into the small intestine.

Killed after 18 hours.

Results as in experiment 25; one of the mesenteric glands contains carbon parts which are also to be seen microscopically.

28. Cavy 750 grams.

After laparotomy 5 ccm. of Indian ink is brought into the colon at 20 cm. distance of the anus.

Killed after 18 hours.

Results as in experiment 1.

29. Cavy 650 grams.

After laparotomy 4 ccm. of a suspension of ultramarine in 0.9 % NaCl is brought into the small intestines.

Killed with chloroform after 18 hours.

Results: The ultramarine is in the intestines, in the stomach, in the oesophagus and in the pharynx, while some grains can be traced in the phlegm of the trachea, and in that of the chief bronchi.

The pulmonary tissue and the bronchial glands are free of ultramarine.

30. Cavy 850 grams.

After laparotomy 4 ccm. of a suspension of ultramarine in 0.9 % NaCl is brought into the small intestine.

Killed after 17 hours with chloroform.

Results: as in experiment 29; in the phlegm of the trachea and in that of the bronchi however no ultramarine was to be found.

31. Cavy 820 grams.

4 ccm. of ultramarine is administered as in experiment 30.

Killed after $16^1/_2$ hours.

Results: No ultramarine can be found, except in the intestines.

32. Cavy 360 grams.

4 ccm. of ultramarine is brought into the intestines as in experiment 30.

After this the animal is carefully wrapped up so that it can get no faeces into its mouth and cannot lick itself.

After 6 hours the animal is decapitated abruptly in order to prevent vomiting in agony.

Results: the ultramarine is in the small and in the large intestines, also somewhat proximal from the place of injection.

In the stomach, in the oesophagus, in the pharynx and in the phlegm of the chief bronchi no ultramarine can be traced.

33. Cavy 750 grams.

Treated as in experiment 32.

Killed after 16 hours.

Results: as in experiment 32; here some grains of ultramarine are in the stomach.

34. Cavy 475 grams.

Treated as in experiment 32.

Killed after 12 hours.

Results: as in experiment 32.

35. Cavy 540 grams.

Treated as in experiment 32.

Killed after 6 hours.

Results: as in experiment 32.

(March 28, 1907).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday March 30, 1907.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 30 Maart 1907, Dl. XV).

CONTENTS.

Meteorology. — *"The treatment of wind-observations."* By Dr. J. P. van der Stok.

(Communicated in the meeting of February 23, 1907).

1. When working out wind-observations we directly meet with the difficulty that a method holding generally, in which the characteristics of a wind distribution come to the fore in condensed form, does not exist. The discussion held for many a year concerning the desirability or not of an application of Lambert's formula, i. e. of the calculation of the vectorial mean of velocity or force has not led to a definite result and the consequence is that for regions where trade- and monsoon winds prevail the calculation of this mean can be applied, not for higher latitudes, so that here we have to judge by extensive tables of frequencies of direction and mean velocities, independent of direction.

When working out the wind-observations made at Batavia I did not hesitate to make an extensive use of this formula; the same method has been followed in the atlas for the East Indian Archipelago: but in order to give at least a notion of the value of the velocities annulling each other here I have added to the resulting movement (called by Hann *windpath*) a so-called factor of stability. If namely the wind were perfectly stable, the vectorial mean would be equal to the mean independent of the direction and the stability would amount to 100 %, which percentage becomes smaller and smaller according to the direction of the wind becoming more variable. So here attention is drawn to the fact, that a part of the observations is eliminated, but it is not indicated what character this vanishing part has which becomes chief in our regions.

In the climatological atlas lately published of British India the same method is followed: in the "Klima Tabeller for Norge" Mohn gives but the above mentioned tables without calculation of the vectorial mean, which is, indeed, of slight importance for this climate.

The same uncertainty is found in the graphical representation of a wind distribution by so-called windroses; almost everyone who has been occupied in arranging books of prints has projected windroses of his own; some of those roses, as e. g. in the "Vierteljahrskarte für die Nordsee und Ostsee" published by the "Deutsche Seewarte", show only the frequencies of direction without velocities; in others, as e. g. those shown in the above atlas of the East Indies, each direction is taken into account with the velocity belonging to it as weight, so that mean velocities are represented. All these roses furnish discontinuous quantities and change their aspect according to their boundaries being taken differently.

In BUCHAN's general meteorological atlas no roses are projected, only arrows indicating the most frequent direction without heeding the force, and in the "Segelhandbuch für den Atlantischen Ozean" published by the "Deutsche Seewarte" for higher latitudes where the wind is variable the use of wind-observations is entirely done away with and arrows have been drawn in accordance with the course of the mean isobars on account of the law of BUYS BALLOT, where a constant angle of 68° between gradient and direction of wind has been assumed.

This short survey of the manner in which in the most recent standard works this problem has been treated may show that indeed there is as yet no question about a satisfactory solution, as has already been observed.

The aim of this communication is to hit upon a general method of operation and representation of an arbitrary wind distribution in which to the variable part also justice is done, whilst the graphical representation has a continuous course and shows at a glance the five characteristic quantities which mark each wind distribution and which may be, therefore, called the *wind-constants.*

The method proposed here is founded on the basis of the calculus of probability, but it is important to notice that it is not at all bound to it; at the bottom it is the same which is generally applied in the treatment of directed quantities: distribution of masses and forces in mechanics, the theory of elasticity, the law of radiation and the theory of errors in a plane.

2. A wind-observation can be represented by a point in a plane such that the distance to an assumed origin is a measure for the velocity of the wind (or force) and that the angle made by the radius vector with the Y (North) axis counted from N. to E. indicates the direction. If in this way all observations, N in number, are drawn and if we think that to each point an equal mass is connected, then in general the centre of gravity will not coincide with the origin selected; its situation may be determined by the quantities R_0 and α. The distribution of the masses around the centre of gravity, is then characterized by the lengths M and M' of the two principal axes of inertia and the angle β enclosed by the axes M and Y.

As is known the five constants by which such a system is characterized can be calculated according to this purely mechanic notion by determining the moments M_x and M_y with respect to the axes and the moments of inertia M_x^2 and M_y^2 and M_{xy}, which furnish the five equations necessary for the calculation of the unknown quantities.

We arrive at quite the same equations when the distribution of the winds according to direction and velocity is regarded as a system of accidental, directed quantities in a plane. The centre of gravity then represents according to size and direction the constant part of the wind which is supposed to be connected with all observations and of which, therefore, the probability is equal to unity; the axes of inertia become principal axes of probability and the lengths M and M' are replaced by the reciprocal lengths h and h', so that

$$h^2 = \frac{1}{2M^2} \quad , \quad h'^2 = \frac{1}{2M'^2} \quad . \ . \ . \ . \ . \ . \ . \quad (1)$$

The sum of the masses is put equal to unity and for the probability that an observation lies between the limits R and $R+dR$ of velocity and θ and $\theta + d\theta$ as far as direction is concerned the expression holds

$$\frac{hh'}{\pi} e^{-f(R.\theta)} R\,dR\,d\theta, \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

where:

$$f(R,\theta) = h^2 [R \cos(\theta-\beta) - R_0 \cos(\alpha-\beta)]^2 + h^{12} [R \sin(\theta-\beta) - R_0 \sin(\alpha-\beta)]^2 . (3)$$

In the language of the theory of errors (R_0,α) would be the so-called constant error, M and M' the greatest and smallest projections of the mean errors. As observations of wind agree still less than other meteorological quantities with the opinion held in the theory of errors, where the constant part is regarded as the end of the operation and the variable quantities as deviations, it is desirable when applying the calculus of probability to quantities of this kind to be entirely free of the terminology used in the theory of errors, but which would be here without meaning and which would give rise to misunderstanding.

The treatment must also differ somewhat from that of erroneous quantities, it being if not impossible at least impractical to correct all the observations for the constant part.

3. As examples of treatment two series of observations have been selected from the treated material.

a. Observations of wind performed at Bergen (Norway) during 20 years, 1885—1904, three times daily at 8 A.M, 2 P.M. and 8 P.M. The velocity (or force) of the wind is expressed in the so-called half scale of BEAUFORT (1—6) (Jahrbuch des Norwegischen Meteorol. Instituts, Christiania).

b. Observations of wind performed at Falmouth (Channel) during 17 years, 1874—1886 and 1900—1903; the observations made in the years 1887—1899 are published in such a way as to be useless for this investigation.

Observations have been used, made daily six times: at noon, 4 P.M., 8 P.M., midnight, 4 A.M. and 8 A.M.; the velocity of wind is expressed in English (statute) miles an hour (Hourly readings obtained from the selfrecording instruments etc. London).

With respect to the force of the wind estimated at Bergen is to be noticed that in this communication these scale-values are regarded not as forces but as velocities, although in reality they are neither one nor the other. According to a recent extensive investigation [1]) the ratio of the Beaufort values to corresponding velocities can be indicated by the following numbers

BEAUFORT	velocity meters a second	ratio	BEAUFORT	velocity meters a second	ratio
0	1.34	—	6	10.95	1.83
1	2.24	2.24	7	13.41	1.92
2	3.58	1.79	8	16.09	2.01
3	4.92	1.64	9	19.67	2.19
4	6.71	1.68	10	23.69	2.34
5	8.72	1.74			

As the various velocities do not appear in an equal number the total mean out of these ratios would not give a fit factor of reduction for mean BEAUFORT-values; so a certain weight must be assigned to each separate ratio. For this the frequencies have been used of the 36000 wind-velocities observed at Falmouth calculated for a whole year; in this way has been found for the reduction-factor 1.83; the English measure, miles an hour, can be reduced to m. a. s. and BEAUFORT scale-values by means of multiplication respectively by

0.447 and 0.244.

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[1]) The BEAUFORT scale of windforce.

Report of the Director of the Meteor. Office upon an Inquiry into the Relation between the Estimates of Windforce according to Admiral BEAUFORT's Scale and the velocities recorded by Anemometers. London, 1906.

4. The calculation of the five charateristic constants of a wind distribution amounts in one respect to the integration of (2), in another respect to the means applied in this integration to a given set of observations.

The integration of (2) takes place by the introduction of rectangular coordinates :

$$x = R \sin \theta \quad , \quad y = R \cos \theta ,$$

where the element $R dR d\theta$ is replaced by the element $dx dy$, whilst the limits which were ∞ and 0 for R, 2π and 0 for θ, now become ∞ and $-\infty$.

Then the expression (2) under the sign of the integral is multiplied successively by

$$x, \; y, \; x^2, \; y^2 \text{ and } xy .$$

If we then put :

$$\begin{aligned} R_0 \cos (\alpha - \beta) &= a, & x &= x' \sin \beta + y' \cos \beta , \\ R_0 \sin (\alpha - \beta) &= b, & y &= x' \cos \beta - y' \sin \beta , \end{aligned}$$

the variables x' and y' can be separated and the integration can be done; in this way we find for the determination of the five quantities to be obtained the five equations :

$$\left. \begin{aligned} M_x &= a \cos \beta - b \sin \beta , \quad M_y = a \sin \beta + b \cos \beta \\ M_x^2 &= \frac{\cos^2 \beta}{2h^2} + \frac{\sin^2 \beta}{2h'^2} + a^2 \cos^2 \beta + b^2 \sin^2 \beta - ab \sin 2\beta \\ M_y^2 &= \frac{\sin^2 \beta}{2h^2} + \frac{\cos^2 \beta}{2h'^2} + a^2 \sin^2 \beta + b^2 \cos^2 \beta + ab \sin 2\beta \\ 2M_{xy} &= \left(\frac{1}{2h^2} - \frac{1}{2h'^2} \right) \sin 2\beta + (a^2 - b^2) \sin 2\beta + ab \cos 2\beta \end{aligned} \right\} , \qquad (3)$$

out of which, on account of (1)

$$\left. \begin{aligned} M_x &= R_0 \cos \alpha , \quad M_y = R_0 \sin \alpha \\ M_x^2 + M_y^2 - [(M_x)^2 + (M_y)^2] &= M^2 + M'^2 \\ M_x^2 - M_y^2 - [(M_x)^2 - (M_y)^2] &= (M^2 - M'^2) \cos 2\beta \\ 2M_{xy} - 2M_x M_y &= (M^2 - M'^2) \sin 2\beta \end{aligned} \right\} \; . \; . \qquad (4)$$

TABLE I. Frequencies of the wind.

Bergen. June.

In half Beaufort scale-values.

	0	1	2	3	4	5	Sum
C	261	—	—	—	—	—	261
N		59	30	29	5	2	125
NNE		6	6	1	—	—	13
NE		6	2	—	—	—	8
ENE		3	2	—	—	—	5
E		13	—	—	—	—	13
ESE		4	1	—	—	—	5
SE		24	3	1	—	—	28
SSE		40	16	3	—	—	59
S		115	54	22	6	—	197
SSW		56	39	15	4	—	114
SW		25	10	2	2	—	39
WSW		9	2	—	—	—	11
W		98	26	5	—	—	129
WNW		99	24	1	—	—	124
NW		190	51	6	—	—	247
NNW		246	118	46	12	—	422
Sum	261	993	384	131	29	2	1800

5. In order to apply the formulae (4) to a given set of observations we must compose for each period, e.g. each month, in the first place a table of frequency of direction and velocity, which can be easily done. In Table I such a composition has been given as an example.

Further out of this table have been calculated the products of these frequencies f with the scale-values R, the latter counted double, so that the products have been expressed in the ordinary Beaufort scale; finally these products have been once again multiplied by the corresponding scale-values (fR^2); in this simple way we find the sums.

TABLE II.

	$f\,R$	$f\,R^2$		$f\,R$	$f\,R^2$
N	472	2280	S	626	1500
NNE	42	156	SSW	390	1644
NE	20	56	SW	118	460
ENE	14	44	WSW	26	68
E	26	52	W	330	988
ESE	12	32	WNW	300	816
SE	66	180	NW	620	1792
SSE	162	524	NNW	1336	5296
			Som	4560	16888

The sums fR, multiplied respectively by $\cos\theta$ and $\sin\theta$ and divided by 1800, immediately furnish the quantities M_x and M_y; the sums fR^2 must be multiplied successively by $\cos^2\theta$, $\sin^2\theta$ and $\sin\theta\cos\theta$.

It is easier to multiply the latter sums by $\cos 2\theta$ and $\sin 2\theta$; if the total mean is S, we find:

$$M_x^2 = fR^2 \cos^2\theta = \tfrac{1}{2}\,S + \tfrac{1}{2}\,fR^2 \cos 2\theta$$
$$M_y^2 = fR^2 \sin^2\theta = \tfrac{1}{2}\,S - \tfrac{1}{2}\,fR^2 \cos 2\theta$$
$$2M_{xy} = fR^2 \sin 2\theta.$$

So the whole operation greatly resembles the calculation of FOURIER terms; indeed, also by the way of operation indicated here an analysis of the movement of the air is obtained.

In the Tables III and IV we find the values of the wind-constants calculated in this way; besides the five characteristic quantities we find still given as quantities practically serviceable for various ends:

$e = \dfrac{\sqrt{M^2 - M'^2}}{M}$, the excentricity of the ellipse of which M and M' represent the half principal axes,

(R_0' and α') the resultants of the squares of the velocities giving an image of the mean flux of energy,

V the mean velocity independent of the direction,

$\bar{V}^2$ the mean square of the velocity independent of the direction, i. e. a measure for the total energy; this quantity is according to (4) analogous to the square of the mean error, not corrected for the constant part, in the theory of errors,

N the number of used observations.

TABLE III^a Constants of the wind.
Bergen 1885—1904.
In BEAUFORT scale-values.

	R_0	α	M	M'	β	e
January	1.84	179°	3.39	1.65	174°	0.873
February	1.51	180	3.10	1.59	172	0.858
March	1.16	183	3.25	1.60	171	0.872
April	0.40	235	2.88	1.47	169	0.859
May	0.68	284	2.84	1.37	169	0.879
June	1.07	302	2.61	1.19	171	0.891
July	0.93	276	2.64	1.22	168	0.885
August	0.73	251	2.86	1.22	168	0.904
September	0 97	212	2 88	1.38	174	0.876
October	1.10	182	2.94	1.52	171	0.857
November	1.51	179	3 10	1.48	171	0.880
December	1.78	179	3 14	1 57	174	0 866
Year	0.85	203	2.97	1.44	171	0.875

TABLE III^b Constants of the wind.
Bergen 1885—1904.
In BEAUFORT scale-values.

	R'_0	α'	$\overline{V}$	$\overline{V^2}$	N
January	10.56	182°	3.31	17.63	1860
February	8.09	184	2.90	14.44	1695
March	5.96	186	3.06	14.48	1860
April	1.62	224	2.64	10.61	1800
May	2.62	281	2.59	10.39	1860
June	3.78	305	2.53	9.38	1800
July	3.19	272	2 58	9.32	1860
August	2.79	243	2.63	10.18	1860
September	4.30	215	2.67	11.14	1800
October	5.13	185	2 76	12.19	1860
November	7.77	182	2.91	14.09	1800
December	9.30	183	3.06	15.50	1860
Year	4.42	200	2.80	12.45	21915

TABLE IV^a^. Constants of the wind.

Falmouth. 1874—1886, 1900—1903.

In Eng. miles an hour.

	R_0	α	M	M'	β	e
January	5.23	211°	15.20	13.93	73°	0.400
February	5.33	209	14.08	13.25	164	0.339
March	3.56	255	15.02	13.26	67	0.470
April	0.85	215	13.70	12.21	72	0.454
May	2.34	255	12 02	11.52	40	0.286
June	4.60	255	11.19	10.07	158	0.436
July	6.46	254	10.39	8.92	155	0.507
August	5.79	245	10.48	9.76	82	0.363
September	3.77	229	11.05	10.67	164	0.260
October	3.56	239	13.51	13.03	81	0.266
November	4.57	248	13.75	13.03	23	0.318
December	5.69	243	13.69	12.98	22	0.318
Year	4.14	239	12.60	12.43	96	0.166

TABLE IV^b^. Constants of the wind.

Falmouth.

	R'_0	α'	$\overline{V}$	$\overline{V^2}$	N
January	146.0	205°	18.4	452.5	2821
February	159.9	203	16.9	402.1	2675
March	88.8	241	17.5	414.2	2930
April	23.0	178	15.7	337.4	2879
May	54.1	241	14.4	282.5	3140
June	92.4	252	13.7	247.8	3015
July	122.2	252	12.9	228.5	3060
August	122.0	242	13.0	238.7	3154
September	83.7	224	13.1	250.3	3047
October	78.5	223	16.4	370.0	3154
November	114.2	237	16.6	379.7	3053
December	148.6	233	16.6	388.4	2888
Year	98.2	229	15.4	330.4	35816

A closer discussion of the results arrived at in this way may for shortness' sake be left out; however, the observation is not superfluous that the two examples represent two types, a reason why they were chosen. At Bergen the ellipse of the variable winds is very constant of shape and the excentricity is very great; at Falmouth the difference between M and M' is always very slight and the differences found there are evidently to be regarded rather as accidental arithmetical results than as facts, the angle β being subject to great and irregular oscillations; evidently the ellipse approaches a circle, so that in form (2) we may put $h = h'$. This leading to a considerable simplification of the formula, these observations at Falmouth are eminently fit for comparison of the results of calculation and observation, whilst also the fact that here real velocities have been observed with well-verified instruments, makes this series very favourable.

6. The expression (2) shows: the probability that an observation lies between the limits R and $R + dR$, θ and $\theta + d\theta$; the same expression without the element $RdRd\theta$ indicates: the specific probability of a wind (R,θ) i.e. the probability with respect to the unity of surface when one imagines this surface to be small. If we put for simplification:

$$h'^2 + h^2 = 2p, \quad h'^2 - h^2 = 2q, \quad R_6^2\,(p - q\,cos\,2\,(\alpha - \beta)) = \mu$$

$$(p - q\,cos\,2\,(\theta - \beta)) = \nu, \quad s^2 = R_0^2\,(p^2 + q^2 - 2pq\,cos\,2\,(\alpha - \beta))$$

$$s\,cos\,(\theta - \varphi) = \lambda \qquad tang\,\varphi = \frac{p\,sin\,\alpha + q\,sin\,(\alpha - 2\,\beta)}{p\,cos\,\alpha - q\,cos\,(\alpha - 2\,\beta)},$$

then (2) takes the form:

$$\frac{\sqrt{p^2 - q^2}}{\pi}\,e^{-R^2\nu + 2R\lambda - \mu}\,RdRd\theta. \quad \ldots\ldots \quad (5)$$

If here we put:

$$R^2\nu - 2R\lambda + \mu = c \quad , \quad \ldots\ldots\ldots \quad (6)$$

then it follows out of the above formulated definition that the specific probability of all observations lying on the circumference of the excentric ellipse (6) is the same and equal to:

$$\frac{\sqrt{p^2 - q^2}}{\pi}\,e^{-c}\,.$$

The probability that the velocity of the wind does not surpass the value R_c expressed by (6) in function of θ, in other words the number of observations which are to lie within the area of the ellipse, is found by integrating (5), first with respect to R between the limits R_c and 0, then with respect to θ between 2π and 0.

For the simple case $R_0 = 0$, so also $\mu = 0$ and $\lambda = 0$, the first integration gives immediately

$$\frac{\sqrt{p^2-q^2}}{\pi} \cdot \frac{1-e^{-c}}{2v}$$

and as

$$\frac{\sqrt{p^2-q^2}}{2\pi} \int\limits_0^{2\pi} \frac{d\theta}{v} = 1,$$

the probability to be found becomes simply:

$$1-e^{-c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and the number of observations lying inside the circumference of the ellipse (6):

$$N\,(1-e^{-c}).$$

This amount remaining the same whether we regard the ellipse (6) from the excentric origin or from the centre, i.e. for $R_0 = 0$, if with the integration the limits are changed correspondingly, the expression (7) must also be accurate when R_0 is not equal to zero and must thus hold in general.

Indeed, an other simplification, namely $q = 0$ (which is applicable to the results for Falmouth) leads to a set of definite integrals, which can be evaluated and which confirm this conclusion.

Amongst the series of ellipses represented by (6) two are remarkable; if we assign to c the value 0.5, then on account of (1) the half axes of the ellipse become equal to the greatest and smallest projections M and M' of the mean velocities, so that the ellipse (6) then represents what we might call the *specific* or *typical windellipse*, thus a kind of windrose, in which the characteristic qualities of the wind-distribution under consideration immediately become conspicuous.

The radius vector R_m drawn to an arbitrary point in the circumference is given in the direction determined by that choice by the equation:

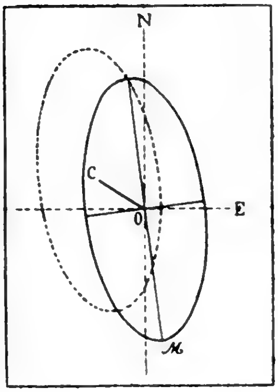
$$2\,R^2_m\,v - 4\,R_m\,\lambda + 2\,\mu - 1 = 0.$$

The probability that a velocity does not surpass this value is:

$$1 - e^{-1/2} = 0.39347.$$

So among a thousand observations there will be 393 lying inside this typical ellipse whilst the specific probability of each of the velocities R_m is:

$$0.6065 \frac{\sqrt{p^2-q^2}}{\pi}.$$



In the given diagram such a typical windellipse is represented for Bergen in the month of June by the dotted line; the vector OC represents here the constant part (R_0, α), the half axes are equal to M and M', and the angle $NOM = \beta$; one millimeter corresponds to $^3/_{20}$ BEAUFORT scale-value or to $^3/_{20} \times 1.83 = 0.275$ meter a second.

If necessary this diagram might be amplified with two circles, one of a radius

$$\sqrt{M^2 + M'^2},$$

representing the mean monthly wind velocity corrected for the constant part, the other described with radius

$$\sqrt{M^2 + M'^2 + (M_x)^2 + (M_y)^2},$$

which is according to (4) a measure for the mean total velocity, corresponding to the square root of the quantity V^2 of the tables III and IV.

An other remarkable ellipse which might be called the *probable windellipse* is obtained by requiring half of the observations to lie within its dominion; we have then to determine c in such a way that

$$1 - e^{-c} = {}^1/_2 \quad , \quad c = 0.6932,$$

so that the axes of this ellipse are

$$\sqrt{2c} = \sqrt{2} \times 0.8326 = 1.177$$

times longer than those of the typical windellipse; the number 0.8326 is a quantity known in the theory of errors in the plane.

7. The frequency of the windvelocities, setting aside the direction, cannot be represented in a finite form; we can arrive at a form serviceable for comparison with the observation by writing (5) thus:

$$\frac{\sqrt{p^2-q^2}}{\pi} e^{-\mu} \cdot e^{-pR^2} \cdot e^{-R^2(\zeta-p)+2R\lambda} R\, dR\, d\theta, \quad . \quad . \quad . \quad (8)$$

by developing the last exponential factor and then by expressing the powers and products of cosines in cosines of multiples.

It is clear that when integrating (8) with respect to θ from 2π to 0 only those terms are left which are independent of θ and which appear with the common factor 2π.

The expression to be found for the probability that a velocity lies between the limits R and $R+dR$ then becomes:

$$2\sqrt{p^2-q^2}\,.\,e^{-\mu}\,.\,e^{-pR^2}(1+a_1R^2+a_2R^4\ \ldots)\,R\,dR\,, \quad \ldots \quad (9)$$

where:

$$a_1 = s^2,$$

$$a_2 = q_2/2^2 \quad + qs^2/2!\ \cos 2\,(\varphi-\beta) + s^4/(2!)^2,$$

$$a_3 = q^2s^2/2^2 + qs^4/3!\ \cos 2\,(\varphi-\beta) + s^6/(3!)^2.$$

For Falmouth, where as was noticed above q can be put equal to nought these coefficients become simply:

$$a_n = {s^{2n}} \Big/ \left(\frac{n!}{2}\right)^2,$$

and farther

$$s = pR_0\ ,\ \mu = pR_0^2\ ,\ \nu = p\ ,\ \varphi = \alpha\ ,\ \lambda = pR_0 \cos(\theta-\alpha). \quad (10)$$

In practice it will frequently be only necessary to calculate a few of these coefficients; if we put:

$$q/p = \varepsilon,$$

the integration of (9) between the limits m and 0 leads to the expression:

$$\left.\begin{array}{l}\sqrt{1-\varepsilon^2}\,e^{-\mu}\times \\ (1-e^{-pm^2})\,.\left(1+\dfrac{a_1}{p}+\dfrac{2!a_2}{p^2}+\dfrac{3!a_3}{p^3}+\ldots\right) \\ -\dfrac{pm^2e^{-pm^2}}{1!}\left(\dfrac{a_1}{p}+\dfrac{2!a_2}{p^2}+\ldots\ldots\ldots\right) \\ -\dfrac{p^2m^4e^{-pm^2}}{2!}\left(\dfrac{2!a_2}{p^2}+\ldots\ldots\ldots\ldots\right)\end{array}\right\}\,. \quad (11)$$

As for $m=\infty$ this expression must become equal to unity, we have:

$$1+\frac{a_1}{p}+\frac{2!a_2}{p^2}\ \ldots\ldots = \frac{e^{\mu}}{\sqrt{1-\varepsilon^2}},$$

or, for the case $q=0$, (11) becomes:

$$\left.\begin{array}{l} 1-e^{-pm^2} \\[4pt] -\dfrac{pm^2e^{-pm^2}}{1!}\,(1-e^{-\mu}) \\[4pt] -\dfrac{p^2m^4e^{-pm^2}}{2!}\left(1-e^{-\mu}-\dfrac{a_1}{p}\,e^{-\mu}\right) \text{ etc.} \end{array}\right\}, \quad . \quad . \quad . \quad . \qquad (12)$$

from which is immediately evident that in many cases the three first terms are sufficient, so that then the calculation of the coefficients can be entirely avoided, or at most only a_1 must be taken into account; for generally μ is small, so that already

$$1-e^{-\mu}$$

will be a small quantity. If q is not small the calculation becomes rather tedious.

8. To find expressions for the quantities $\overline{V}$ and $\overline{V^2}$, the mean velocity and the mean square of the velocity independent of the sign, we have to multiply (9) successively by R and R^2 and to integrate between the limits ∞ and 0 which, with the well known fundamental equation, leads to the expressions:

$$\left.\begin{array}{ll} 1 & = A\left(1+\dfrac{2a_1}{2p}+\dfrac{2.4a_2}{(2p)^2}+\dfrac{2.4.6a_3}{(2p)^3}+\ldots\right) \\[8pt] \overline{V} & = \dfrac{A}{2}\sqrt{\dfrac{\pi}{p}}\left(1+\dfrac{3a_1}{2p}+\dfrac{3.5a_2}{(2p)^2}+\dfrac{3.5.7.a_3}{(2p)^3}+\ldots\right) \\[8pt] \overline{V^2} & = \dfrac{2A}{2p}\left(1+\dfrac{4a_1}{2p}+\dfrac{4.6a_2}{(2p)^2}+\dfrac{4.6.8a_3}{(2p)^3}+\ldots\right) \end{array}\right\} . \qquad (13)$$

$$A = \sqrt{1-\varepsilon^2\,e^{-\mu}}.$$

9. For the calculation of the frequency of the directions independent of the velocity we have first to integrate (5) with respect to R between the limits ∞ and 0 and then with respect to θ between the desired limits θ; the mean velocity as function of the direction is found by the application of the same operation to (5) after multiplication by R. It is then easy to give to a frequency-formula found in this way the form of a FOURIER series. For brevity we treat here only the case that $q=0$ and the angle-limits are π to 0.

By putting

$$R=\varrho+\frac{\lambda}{\nu}$$

we get (5) reduced to the form:

$$\frac{\sqrt{p^2-q^2}}{\pi} e^{-\mu+\lambda^2/\nu} \int_{-\lambda/\nu}^{\infty} e^{-\nu\varrho^2} \left(\varrho + \frac{\lambda}{v} \right) d\varrho \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

If $q = 0$, so that the formulae (10) hold good, we then find for the desired frequencies in the two easterly quadrants

$$\tfrac{1}{2} + \frac{1}{\sqrt{\pi}} \int^{R_0 \sqrt{p}\, \sin \alpha} e^{-t^2} dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

From this formula it is evident in what way and in what degree the asymmetry of the distribution is dependent of R_0, a and p.

10. The application of the given criteria has been made for Falmouth and the four seasons:

Winter: December, January, February, number 8384,
$p = 0.00258$, $q = 0.00004$
$R_0 = 5.22$, $a = 222°8'$

Spring: March, April, May, number 8949,
$p = 0.00298$, $q = 0.00028$
$R_0 = 2.21$, $a = 250°25'$

Summer; June, July, August, number 9229,
$p = 0.00485$, $q = 0.00029$
$R_0 = 5.60$, $a = 251°22'$

Autumn: September, October, November, number 9254,
$p = 0.00313$, $q = 0.00004$
$R_0 = 3.80$, $a = 239°16'$

For each series the number of observations is reduced to 10.000 and everywhere we have put $q = 0$, the calculated values are accordingly accurate as far as the fourth decimal.

In Table V we have compared the observed frequencies of wind-velocities independent of direction with those calculated according to formula (12), from which it is evident that the differences have a clearly systematic course. Just as is the case with all series of errors the number of the observed small velocities is larger than would agree with the normal distribution. The differences together amount in summer to about $10^0/_0$, in winter to $15^0/_0$.

In the calculation of the frequencies of the directions independent of the velocity, the observations regarded as calms — and to these are reckoned in the English records all velocities less than 4 miles an hour — have been distributed proportionally to the frequencies of direction; furtheron the frequencies North and South are assigned for one half to the eastern and western quadrants.

As is evident from the following table also in this comparison systematic differences appear; in all seasons the observed frequencies in the western quadrant are greater than the calculated ones, so that an increase of the constant part R_0 to which this uneven distribution can be attributed, would improve the correspondence.

TABLE VI.

Frequencies of winddirections at Falmouth

for 10.000 observations.

		Observed	Calculated	Difference
Winter	E. quadr.	3709	4006	— 297
	W. "	6291	5994	+ 297
Spring	E. quadr.	4037	4351	— 214
	W. "	5963	5649	+ 214
Summer	E. quadr.	2619	3009	— 390
	W. "	7381	6991	+ 390
Autumn	E. quadr.	3453	3980	— 527
	W. "	6547	6020	+ 527

TABLE V. Frequencies of windvelocities at Falmouth.
For 10.000 observations.

	WINTER			SPRING			SUMMER			AUTUMN		
Miles an hour	Observ.	Calculat.	Difference	Observ.	Calculat.	Difference	Observ.	Calculat.	Difference	Observ.	Calculat.	Difference
0 4^5	760	477	+ 283	756	569	+ 187	945	810	+ 135	936	588	+ 348
4^5— 9^5	1871	1482	+ 389	2073	1759	+ 314	2610	2336	+ 274	2126	1779	+ 377
9^5—14^5	1853	2026	— 173	2120	2279	— 159	2538	2728	— 190	2144	2304	— 160
14^5—19^5	1701	2030	— 329	1875	2120	— 245	1868	2133	— 265	1818	2110	— 292
19^5—24^5	1466	1650	— 184	1355	1558	— 203	1164	1225	— 61	1281	1564	— 283
24^5—29^5	967	1125	— 158	917	939	— 22	544	534	+ 10	792	920	— 128
29^5—34^5	680	656	+ 24	493	473	+ 20	224	178	+ 46	459	464	— 5
34^5—39^5	369	331	+ 38	250	201	+ 49	80	45	+ 35	258	179	+ 79
39^5—44^5	199	144	+ 55	114	72	+ 42	20	9	+ 11	116	66	+ 50
44^5—49^5	94	55	+ 39	31	22	+ 9	6	2	+ 4	37	20	+ 17
49^5—54^5	32	18	+ 14	15	6	+ 9	0	—	—	23	5	+ 18
54^5—59^5	8	5	+ 3	1	2	— 1	1	—	+ 1	10	1	+ 9
59^5—	—	1	— 1	—	—	—	—	—		—	—	—

Chemistry. — "*On the anisotropous liquid phases of the butyric ester of dihydrocholesterol, and on the question as to the necessary presence of an ethylene double bond for the occurrence of these phenomena*". By Dr. F. M. Jaeger. (Communicated by Prof. A. P. N. Franchimont).

(Communicated in the meeting of February 23, 1907).

§ 1. In order to explain the behaviour of substances which are wont to exhibit double-refracting liquid phases, some investigators have started the hypothesis that, in this kind of organic substances, it might be a question of systems formed of two components, and of equilibrium phenomena between tautomeric and isomeric modifications, which would be converted into each other with finite velocity.

Although it is difficult to understand how such a supposition, which is easy to propound, but very difficult to prove, could explain the numerous well ascertained facts of the *regular* optical anisotropism of these phases, it might explain, however, at least to some extent, the peculiar irreversible transitions of phases, which I found more particularly with the esters of cholesterol and α-phytosterol, and also the hindrance phenomena noticed on that occasion [1]).

Such a supposition, however, is perhaps of some importance for the interpretation of the brilliant colour phenomena which accompany the phase-transitions in the cholesterol esters. For a mixture, or an emulsion of substances, whose indices of refraction differ very little, but whose dispersions differ much, might, like Christhiansen's monochromes, cause a similar display of colours.

§ 2. There is more than one cause for tautomerism (or isomerism) in the case of these cholesterol esters, for all the esters, as well as cholesterol itself, possess an asymmetric carbon atom, and in solution they all polarise to the left.

Consequently, a racemisation during the esterification is by no means excluded, and we might, therefore, have a mixture of the optical antipodes. Cholesterol, moreover, possesses an ethylene double bond, so that we may also expect an isomerism in the sense of fumaric and maleic acids.

§ 3. As many other compounds (in fact most organic substances which are wont to exhibit these phenomena of doubly refracting

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[1]) F. M. Jaeger, These Proc. 1906 p. 472 and 483 (29 December).

liquid phases) possess such ethylene double bonds, one might indeed imagine that the presence thereof in the molecule is of great importance for the occurrence of the said phenomena, if not the *conditio sine qua non,* as the structure of the azoxy-compounds is not yet firmly established and because it may be assumed that they contain, perhaps, similar double bonds between N and O.

Moreover, the cholesterol esters all contain *three* liquid phases, so that this peculiar complication might perhaps also be connected with the possibility of very intricated isomerism-phenomena of those substances.

§ 4. In order to answer these questions, I asked Prof. Dr. C. **Neuberg** of *Berlin* to furnish me with a specimen of his synthetic *Dihydrocholesterol,* to which request this savant most willingly acceded.

I wish to thank Prof. **Neuberg** once more for his kindness.

In this *Dihydrocholesterol* the ethylene double bond has disappeared owing to the addition of two atoms of hydrogen, and the malenoid and fumaroid isomerism is therefore, à priori excluded.

§ 5. I have prepared from this alcohol the acetic and the normal butyric esters, by means of the pure acid-anhydrides, and have examined the same as to their phase transitions. The acetic ester will be described elsewhere later on; here the butyric ester only will be discussed.

As a highly important result I may mention that the colour phenomena on melting and the occurrence of three liquid modifications in the normal butyrate remain unaltered as before, but that the irreversibility of the phase-transitions is shown in a manner just the reverse as in the case of most of the cholesterol esters, e.g. the laurate.

Whereas of the two doubly-refracting liquid phases of the last named substance, one is always passed over *on cooling,* whilst both are found *on melting* the solid substance, this is just the reverse in the case of the dihydrocholesterol-n-butyrate.

6. The solid phase S consists of an aggregate of very thin, colourless, and clear transparent laminae in which the plane of polarisation makes an obtuse angle with the sides of demarcation and exhibit in convergent polarised light a hyperbole with very strong colour dispersion $\varrho > v$.

On heating, this phase S passes into a doubly-refracting liquid B, consisting of very small, feebly doubly-refracting individuals, which in turn passes at a higher temperature into the isotropous fusion L.

Of colour phenomena during one of these transitions, absolutely *nothing* is noticed.

If, however, we start from the phase L and allow the same to cool, we first notice the doubly-refracting phase B, which on further cooling, amid violent sudden currents of the mass, passes into a much more strongly doubly-refracting liquid A, which on continued cooling crystallises suddenly, also amid very violent currents, to an aggregate of flat needles, glittering in vivid interference colours. These in turn, rapidly assume a spherolite structure so that the solid phase S itself appears to be also *dimorphous* and *monotropous,* as the flat needles are *not* reobtained on warming the spherolitic mass. The transformation of A into these needles, during cooling, is accompanied with the most vivid display of colours. Under the microscope these may be recognised by the dark-green colour of the background of the field of vision; with the naked eye, however, with incident light, that colour-display commences with a brilliant violet gradually turning into blue and finally into a radiating green when the mass crystallises. I have never noticed red or yellow colours with incident light. These phenomena return in the same order when the experiment is repeated.

That the phase A really exhibits the behaviour of a stable phase

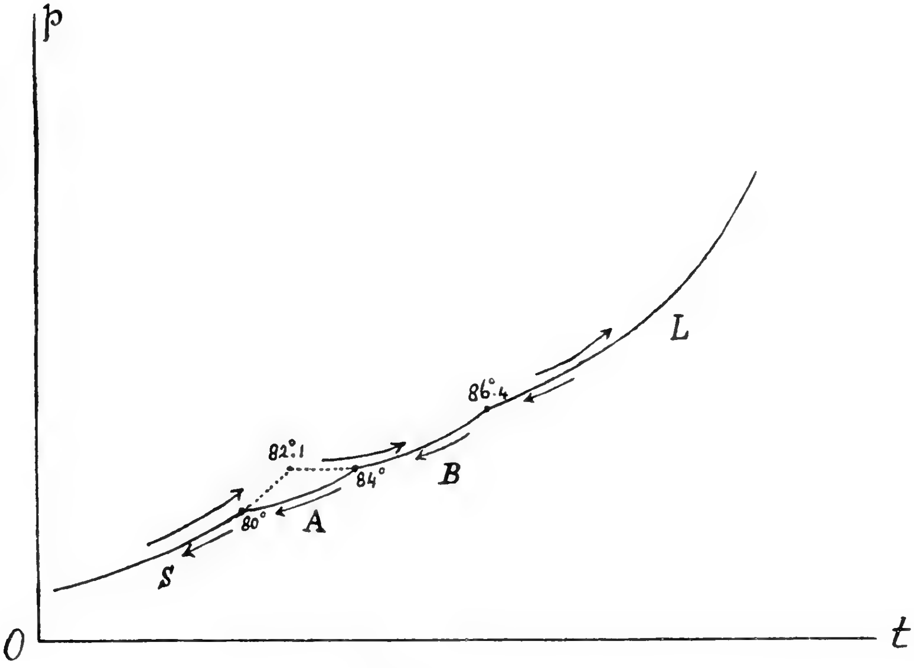


Fig. 1.
Schematic p-t-diagram for Dihydro-cholesterol-n-butyrate.

is also shown by the fact that, the colour having become blue or green on cooling, turns again violet on warming, so long as the solid phase S has not yet been attained. The phase is, therefore, realisable at a change of temperature in *two* directions.

§ 7. As I had but very little of the substance at my disposal, the thermometric determinations could only be studied in capillary tubes with the aid of a magnifying glass.

At 82.°1 the phase S melts to a doubly-refracting phase B which becomes clear at 86.°4 and passes into L. On cooling this isotropous fusion, it first passes properly into B at 86°.4, but at 84° into the more strongly doubly-refracting phase A, which may be undercooled many tens of degrees, and with retention of its violet colour, before passing into the solid phase S.

Want of material prevented my determining the true solidifying point of S by inoculation; I estimate it at about 80°.

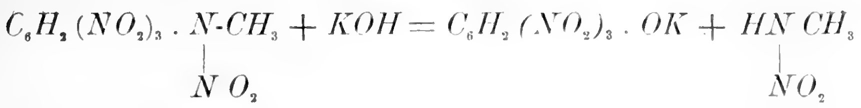
Thus the positive proof has been given that the remarkable colour phenomena accompanying the melting the cholesterol esters *cannot* be attributed to the presence of an ethylene double bound; also that an eventual presence of fumaroid and maleinoid isomers cannot be considered as the cause of the occurrence of the *three* liquids.

Zaandam, 15 Febr. 1907.

Chemistry. — *"On the action of bases, ammonia and amines on s. trinitrophenyl-methylnitramine."* By Prof. P. van Romburgh and Dr. A. D. Maurenbrecher.

(Communicated in the meeting of February 23, 1907).

s.-Trinitrophenyl-methylnitramine, as has been known for a long time, is decomposed at the ordinary temperature by ammonia in alcoholic solution, or on warming, by an aqueous solution of potassium hydroxide, or carbonate, in the first case with formation of picramide, in the second (with evolution of monomethylamine) of picric acid. One of us who formerly studied the reaction with bases concluded, from the occurrence of the amine and the formation of nitric acid which was also observed, that the methylnitramine which might be expected according to the equation :



$$C_6H_2(NO_2)_3 \,.\, \underset{\overset{|}{NO_2}}{N}\text{-}CH_3 + KOH = C_6H_2(NO_2)_3 \,.\, OK + H\underset{\overset{|}{NO_2}}{N}\,CH_3$$

might have become decomposed [1]).

From the reaction of methylamine on tetranitrophenyl-methylnitramine and on trinitromethylamidomethylnitramidobenzene he afterwards concluded [2]) that, probably, there had been formed methylnitramine, meanwhile discovered by Franchimont and Klobbie [3]).

The amount of amine formed by the decomposition of trinitrophenyl-methylnitramine by alkalis is considerably smaller than might be expected from theory; the possibility, therefore, exists that the reaction proceeds indeed mainly in the above indicated sense.

We have, therefore, taken up the problem again in the hope that by suitable modifications in the reaction, we might get at a process for the preparation of methylnitramine which would have the advantage of yielding this costly substance from a cheap, easily accessible material. We were not disappointed in our expectations.

If trinitrophenyl-methylnitramine, which is the final product of the nitration of dimethylaniline and melts at 127°, is boiled with a 10 % solution of potassium carbonate a brownish-red solution is obtained, which on cooling gives an abundant deposit of potassium picrate. If after filtration the liquid is acidified with sulphuric acid and again filtered off from the picric acid precipitated and then agitated with ether, the latter yields on evaporation crystals, which after purification, melt at 38°, and are identical with methylnitramine, as was proved by comparing the compound with a specimen kindly presented to us by Prof. Franchimont. The yield, however, was very small.

If the finely powdered nitramine, m. p. 127°, is treated with 20 % methylalcoholic ammonia this becomes intensely red, the mass gets warm and after a few hours the reaction is complete, and a large amount of picramide has formed which is removed by filtration. The alcoholic solution is distilled in vacuo, the residue treated with dilute sulphuric acid and, after removal of a yellowish byeproduct by filtration, the liquid is agitated with ether. On evaporation of the ether, crystals of methylnitramine were obtained. In this reaction also, the yield was not large, amounting to only 15 % of the theoretical quantity. With ethyl-alcoholic ammonia a similar result was obtained, whereas an experiment in which ammonia was passed into a solution

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[1]) Rec. d. Trav. chim. d. Pays-Bas, II. (1883) p. 115.

[2]) Ib. VIII (1889) p. 281.

[3]) Ib. VII (1888) p. 354.

of the nitramine in benzene gave results which were still less favourable.

One of us had noticed previously that among the aromatic amines which generally react on an alcoholic solution of the nitramine quite as readily as on picryl chloride, *p*-toluidine in particular gives a beautifully crystallised *p*-toluylpicramide m. p. 166° [1]) whilst the alcoholic solution contains only comparatively few, not very dark coloured byeproducts. In an experiment in which 35 grams of the nitramine were heated on the waterbath with an equal weight of *p*-toluidine and 100 c.c. of 96 °/₀ alcohol, a fairly violent reaction set in after some time. The heating was continued for 5 hours and, after the picramide derivative had been removed by filtration, the alcohol was distilled off and the residue extracted with dilute sulphuric acid. The liquid filtered off from the toluidine sulphate was shaken with ether. On evaporation of the ether a still yellow coloured liquid product was left which on being inoculated with a crystal of methylnitramine became crystalline and after having stood for some time over sulphuric acid weighed 7 grams. On pressing between filter paper light yellow crystals were obtained which after being sublimed in vacuo (a treatment which methylnitramine stands very well) melted at 38°. On mixing the same with a preparation consisting of pure nitramine the melting point was not affected.

p-Toluidine appears, therefore, to be a suitable means for readily procuring in a short time methylnitramine from *s*-trinitrophenylnitramine.

We are continuing our investigations with different amines and also with other nitrated aromatic nitramines, and will state the results more elaborately in the "Recueil".

Org. Chem. Lab. of the University *Utrecht.*

Physics. — "*Wave-lengths of formerly observed emission and absorption bands in the infra-red spectrum.*" By Prof. W. H. Julius.

If in the infra-red spectrum, as formed by means of a rock-salt prism, the positions of emission or absorption bands have been carefully determined, the corresponding wave-lengths still are uncertain by an amount which, in a considerable part of the spectrum, is greater than the probable error of those determinations, because the

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[1]) We now obtained this substance in two modifications, one coloured dark red and the other orange.

dispersion curve of rock-salt is not yet known with sufficient exactness.

Mr. W. J. H. MOLL [1]) has lately compared with each other the dispersion curves that have been calculated according to KETTELER's formula with two sets of constants, one given by RUBENS [2]), the other by LANGLEY [3]). LANGLEY's results held for a temperature of 20°; the numbers given by RUBENS were corrected by Mr. MOLL so as to apply to the same temperature. While coinciding in the visible spectrum, the two dispersion curves appeared to diverge very sensibly in the entire infra-red region, the wave-lengths corresponding to given indices of refraction being smaller with RUBENS' than with LANGLEY's constants. At $\lambda = 1,5\,\mu$ e. g. the difference amounts to $0,028\,\mu$; it increases unto $0,062\,\mu$ (at $\lambda = 3\,\mu$) and then decreases to $0.032\,\mu$ (at $\lambda = 8,5\,\mu$). If, on the other hand, the indices of refraction, which according to LANGLEY's and according to RUBENS' formula belong to rays of given wave-lengths, be compared with each other, the difference appears to be rather constant between $\lambda = 4\,\mu$ and $\lambda = 8,3\,\mu$, namely 1,5 units of the 4th decimal of the index, and to increase from 0 to 1.5 similar units in the region between $0.6\,\mu$ and $4\,\mu$.

The apparatus, nowadays available for the investigation of the infra-red, admit of determining the position of sharp maxima or minima of radiation with an accuracy, going a good deal farther than 1,5 units of the 4th decimal of the index.

When between 1887 and 1891 I investigated several infra-red emission and absorption spectra, our knowledge of the dispersion of rock-salt was restrained to the outcome of LANGLEY's first determinations [4]), which extended only as far as $5,3\,\mu$. As a great part of my work bore upon longer waves, I published my results in the form given by direct observation, viz, as galvanometer deflections and corresponding angles of minimum deviation, reduced to the temperature 10°. The refracting angle of the prism being also recorded, the indices of refraction of rock-salt for waves, corresponding to the observed maxima, were thus implicitly given.

In order to obtain a rough estimate of the wave-lengths, I had extended LANGLEY's dispersion curve in a straight line, though under strict reservation. The wave-lengths as read on this lengthened

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[1]) W. J. H. MOLL, Onderzoek van ultra-roode spectra. Dissertation, Utrecht, 1907.

[2]) H. RUBENS, Wied. Ann. 60, 724; 61, 224; 1897. Cf. also KAYSER, Handbuch der Spectroscopie I, 371, 1900.

[3]) S. P. LANGLEY, Ann. Astroph. Obs of the Smiths. Inst. I, 1900.

[4]) S. P. LANGLEY, Phil. Mag., Aug. 1886.

curve, to which I myself assigned little weight [1]), have found their way to some text-books [2]), where they unfortunately appear as the results of my investigation, with the incidental remark that they are incorrect, as founded on a false extrapolation. It is clear, however, that this incorrectness has nothing to do with the accuracy with which the position of the bands in the prismatic spectrum has been determined. Now I have reason to believe, that the spectrometric and heat-measuring apparatus used in that research were not less valid than those employed by many later observers of infra-red spectra (DONATH, PUCCIANTI, IKLÉ, COBLENTZ, NICHOLS, RUBENS and ASCHKINASS and others), so that the results still retain their value as a first contribution to our knowledge of the examined spectra.

I therefore thought it suitable to republish the principal results obtained at that time [3]), but now to mention the indices of refraction for the maxima of emission and absorption, as following directly from my observations, and to add the wave-lengths, as derived from the more recent dispersion curves of RUBENS and of LANGLEY.

The positions in the infra-red were determined in my work with respect to the place of the *D*-lines of a BUNSEN flame coloured with chloride of sodium. But the latter were too faint to be observed with the bolometer; and the transition from the visual observation of the *D*-lines to the bolometric observation of infra-red radiations caused an uncertainty in the determination of the relative positions, which was still increased through the necessity of displacing the bolometer along the optical axis of the rock-salt lens according to its different focus for visible and invisible rays. It was chiefly in the part of

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[1]) Cf. „Bolometrisch onderzoek van absorptie-spectra", Verhandelingen der Kon. Akad. v. W. te Amsterdam, Vol I, N⁰. 1, p. 8 (1892), or the German translation in: Verhandl. des Vereins zur Beförderung des Gewerbfleisses, 1893, p. 235, where I have clearly stated that I considered the extrapolation of LANGLEY's dispersion curve as quite uncertain, and that in the tables the direct data of observation (angles of minimum deviation) were given, because I did not like to have my results inseparably connected with a possible incorrectness of the dispersion curve. The passage in question seems not to have been noticed by W. W. COBLENTZ, for in his excellent work "Investigations of Infra-red Spectra", published by the Carnegie Inst. of Washington, 1905, he says on p. 135, after alluding to LANGLEY's extrapolation of the dispersion curve in a straight line: "JULIUS, with apparently less hesitation, has applied this extrapolation to his work".

[2]) WINKELMANN, Handbuch der Physik; KAYSER, Handbuch der Spectroscopie; CHWOLSON, Lehrbuch der Physik.

[3]) Recherches bolométriques dans le spectre infra-rouge. Arch. neérl. **22**, p. 310—383 (1888).

Die Licht- und Wärmestrahlung verbrannter Gase, Berlin, Simion. 1890.

Bolometrisch onderzoek van absorptiespectra, l. c.

the investigation, described on p. 69 of "Die Licht und Wärmestrahlung verbrannter Gase" that many pains were taken to reduce this source of error. There the CO_2-maximum of the BUNSEN flame was found at minimum deviation 38°54′20″, the refracting angle of the prism being 59°53′20″ and the temperature 10°. From this follows $n = 1,52103$. Had the temperature been 20°, then the deviation would have been found smaller by 1′50″, giving for the index of refraction: $n = 1.52069$.

If we suppose this value to be exact, then the angles of minimum deviation given in my first paper in Arch. néerl. 22, and on pages 47—68 of "Die Licht- und Wärmestrahlung" are too small by nearly 3′, owing to an instrumental error. In "Bolometrisch onderzoek van absorptiespectra" the deviation of the CO_2-maximum has been found 38°52′40″ instead of 38°54′20″; 1′ of this difference results from the fact that the refracting angle of the prism, then in use, was smaller than that of the other one by 1′; only the remaining 40″ were owing to an instrumental error.

I have now applied the corrections resulting from this re-examination, and calculated the indices of refraction for 20°, the temperature to which the dispersion curves as compared by Mr. MOLL also refer. In finding the wave-lengths corresponding to the indices, advantage has been taken of elaborate tables, prepared by Dr. MOLL for a research of his own, and which he was kind enough to put at my disposal.

Emission-spectrum of:	Indices of refraction for the maxima (Temp. 20)		Wave-lengths according to the dispersion curve of RUBENS	of LANGLEY	Intensity [1]
BUNSEN-flame	1.5268		1.905	1.953	0.5
	1.5247	H_2O	2.769	2.831	3—5
	1.52069	CO_2	4.410	4.462	10
Flame of carbon monoxyde or of cyanogen	1.52445	CO_2	2.883	2.947	1
	1.52069	CO_2	4.410	4.462	10
Hydrogen flame	1.5247	H_2O	2.77	2.83	10
	1.5176		5.41	5.46	2
Luminous gasflame. . .	1.5270	C	1.84	1.89	[2]
	1.5247	H_2O	2.77	2.83	[2]
	1.5207	CO_2	4.41	4.46	[2]
Hydrog. burning in chlor.	1.5226	HCl	3.68	3.74	
Flame of sulfur	1.5093	SO_2	7.49	7.52	
Flame of carb. disulphide	1.5247		2.77	2.83	1
	1.5207	CO_2	4.41	4.46	10
	1.5125	COS(?)	6.76	6.80	3—0 [2]
	1.5093	SO_2	7.49	7.52	2—3 [2]
Absorption-spectrum of:					
C (diamond)	1.5238		3.18	3.24	
	1.5202		4.58	4.63	10
	1.5183		5.20	5.25	
	1.5088 etc. [3]		7.59	7.62	10
H_2O	1.5287		1.41	1.43	1
	1.5265		2.01	2.06	1
	1.5236		3.25	3.31	9 s
	1.5194		4.85	4.90	
	1.5146		6.24	6.28	

[1] In each spectrum the intensity of the highest maximum is indicated by 10. The letter s following an intensity figure means, that the band is rather sharp.

[2] The relative intensity of these bands varies much with the place in the flame.

[3] The addition "etc." behind an index of refraction indicates, that the band marks the beginning of an extensive region of strong absorption.

Absorption-spectrum of:	Indices of refraction for the maxima (Temp. 20°)	Wave-lenghts according to the dispersion curve		Intensity
		of RUBENS	of LANGLEY	
CS_2	1.5203	4.55	4.60	6 s
	1.5129	6.67	6.71	10
$S_2 Cl_2$	1.5219	3.96	4.02	1
	1.5163	5.78	5.82	1
	1.5090	7.55	7.58	7 s
	1.5049	8.36	8.39	1
	1.5020	8.90	8.93	1
	1.4992	9.41	9.44	8 s
	1.4942	10.28	10.31	10
PCl_3	1.5221	3.88	3.94	0.5
	1.5082	7.72	7.75	10 s
	1.5030	8.73	8.76	0.5
	1.4944	10.25	10.28	10
$Si Cl_4$	1.5172	5.53	5.57	6 s
	1.5154	6.03	6.07	1
	1.5058	8.19	8.22	10 s
	1.5014	9.02	9.05	10
	1.4974	9.73	9.76	10
$Si HCl_3$	1.5234	3.34	3.40	0.5
	1.5173	5.50	5.54	1 s
	1.5058	8.19	8.22	2
	1.5014	9.02	9.05	10
	1.4974	9.73	9.76	3
$C Cl_4$	1.5137	6.47	6.51	9 s
	1.5058	8.19	8.22	10 s
	1.4942	10.28	10.31	5 s
$C H Cl_3$	1.5234	3.34	3.40	3
	1.5131	6.62	6.66	3 s
	1.5115	6.99	7.03	4
	1.5058	8.19	8.22	10
	1.4980	9.62	9.65	7

Absorption-spectrum of:	Indices of refraction for the maxima (Temp. 20°)	Wave-lengths according to the dispersion curve		Intensity
		of RUBENS	of LANGLEY	
CH Br$_3$	1 5235	3.30	3.36	3 s
	1.5207	4.40	4.45	3 s
	1.5164	5.76	5.80	4 s
	1 5116	6.97	7 01	3
	1.5083	8.19	8.22	7 s
	1.5024	8.83	8.86	10
	1.4992	9.41	9.44	6
C$_6$H$_6$	1.5259	2.25	2.31	1
	1.5236	3 25	3.31	4 s
	1.5211	4.26	4.31	1
	1.5173	5.50	5.54	6 s
	1.5128	6 69	6.73	10 s
	1.5107	7.18	7.21	3 s
	1.5088	7.59	7.62	1
	1.5060	8.15	8.18	2
	1.5039	8.56	8.59	7
(C$_3$H$_7$)$_2$	1.5259	2.25	2.31	2
	1.5230	3.51	3.57	7 s
	1.5154	6.03	6.07	1
	1.5118	6.93	6.96	10 s[1]
	1.5097	7.40	7.43	6
	1 5068	7.99	8.02	4
	1 5032	8.69	8.72	6 s
	1.4980	9.63	9.66	5
	1.4942	10.28	10.31	5
CH$_3$ OH	1.5259	2.25	2.31	1
	1.5229	3.56	3.62	10
	1 5194	4 85	4.90	2 s
	1.5145 etc.	6.27	6.31	10
C$_2$H$_5$ OH	1.5259	2.25	2.31	1
	1 5229	3.56	3.62	10
	1.5183	5 20	5.25	2 s
	1.5154	6.03	6.07	2
	1.5126 etc.	6.74	6.78	10

[1]) Sharply limited only toward the smaller wave-lengths.

Absorption-spectrum of:	Indices of refraction for the maxima (Temp. 20°)	Wave-lengths according to the dispersion curve		Intensity
		of RUBENS	of LANGLEY	
C_3H_7OH	1.5230	3.51	3.57	10
	1.5152	6.09	6.13	3
	1.5126 etc.	6.74	6.78	10
C_4H_9OH (normal). . . .	1.5230	3.51	3.57	10
	1.5162	5.81	5.85	3
	1.5126 etc.	6.74	6.78	10
C_4H_9OH (iso).	1.5230	3.51	3 57	10
	1.5192	4.92	4.97	1
	1.5154	6.03	6.07	2
	1.5126 etc.	6 74	6.78	10
$C_5H_{11}OH$.	1.5230	3.51	3.57	10
	1.5192	4.92	4.97	1
	1.5154	6.03	6.07	3
	1.5126 etc.	6.74	6.78	10
$(C_2H_5)_2O$.	1.5327	0.95$_3$	0.95$_8$	1
	1.5293	1.30	1.32	1
	1.5259	2.25	2.31	2
	1.5230	3.51	3.57	8 s
	1.5183	5.20	5.25	3 s
	1.5164	5.76	5.80	1
	1.5116	6.97	7.01	10
	1.5099	7.35	7.39	4
	1.5078	7.80	7.83	4 s
	1.5045 etc.	8.44	8.47	10
C_2H_5SH	1.5256	2.38	2.44	1
	1.5230	3.51	3.57	5
	1.5221	3.88	3.94	3
	1.5183	5.20	5.25	1
	1.5162	5.81	5.85	1
	1.5115	6.99	7.03	10
	1.5074	7.88	7.91	10
	1.5001	9.25	9.28	8
	1.4936	10.39	10.42	9

Physics. — "*A hypothesis relating to the origin of* Röntgen-*rays.*"

By Prof. C. H. Wind.

W. Wien[1]) has measured the energy of Röntgen-rays, converted into heat in a bolometer or in a thermo-element, and has compared it with that of the cathode-rays, likewise converted — with exception of the small fraction transformed in energy of R.-rays — into heat in the anti-cathode. He finds for the proportion of the total quantities of energy of the two kinds of rays

$$\frac{E_r}{E_k} = 2{,}18 \ . \ 10^{-3} \ ^{2)}.$$

Supposing that the R.-rays are the radiation of energy, emitted by cathode-ray electrons being brought to rest, and that this stoppage may be considered as a continually decreasing motion, he proceeds with the aid of the theory of M. Abraham to deduce the duration of the stoppage and from it the thickness of the R-waves. For the latter he finds

$$\lambda = 1{,}15 \ . \ 10^{-10} \text{ cm}.$$

Results of the same order of magnitude have afterwards been attained by Edna Carter[3]) in an investigation, also made at the laboratory directed by Wien.

These results do not very well agree with the values, derived by Haga and myself for the wave-length of R.-rays from diffraction-experiments:

$$\lambda = 270 \text{ to } 12 \ . \ 10^{-10} \text{ cm} \ ^{4)}$$

and

$$\lambda = 160 \ , \ 120 \ , \ 50 \ . \ 10^{-10} \text{ cm.} \ ^{5)}$$

If the R.-rays have to be considered as disturbances in ether of the single pulse character assumed by Wien in accordance with the current conception, the same numbers must be divided by $\frac{3.7}{1\frac{1}{2}}$ or $2\frac{1}{2}$ [6]) in order to represent the corresponding values of the thickness of the pulse-waves, which consequently become

$$\beta_1 = 110 \quad \text{to} \quad 5 \ . \ 10^{-10} \text{ cm},$$
$$\beta_2 = \ 64, \ 48, \ 20 \ . \ 10^{-10} \text{ cm}.$$

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[1]) W. Wien. Wüllners Festschrift, Leipzig, 1905; Ann. d. Ph. 18, p. 991, 1905.

[2]) L. c. p. 996. The number is doubled here, on account of the remark made regarding it on page 1000.

[3]) E. Carter. Ann. d. Ph. 21, p. 955, 1906.

[4]) H. Haga and C. H. Wind. These Proc. I. p. 426.

[5]) Id. Ibid. V. p. 254.

[6]) C. H. Wind. Physik. Zschr. 2, p. 96. Fussnote 2), 1901.

Wien's experiments would have led to results more in keeping with the diffraction experiments, if the values found for the energy of the R.-rays had been 20 to 100 times smaller. The difference is too great to ascribe it to errors of observation. We must rather think of fundamental errors in the method of observation or of a viciousness in our conceptions concerning the mechanism of the phenomena.

As for the method of observation **Wien** himself pointed out[1]) the possibility that the quantity of heat, generated in the bolometer or in the thermo-element, should not be to its full amount converted energy of R.-rays, but partly also — perhaps even for the greater part — converted atom-energy, liberated by a, say, catalytic action of the R.-rays.

J. D. v. d. **Waals** Jr. [2]) suggests the additional idea that the electrons are not generally stopped at once by a simple uniform decrease of velocity, but will mostly, by their interacting with the particles of the anti-cathode, before being brought to rest move for some time amidst the latter in rapidly changing directions with great velocities, sending out a new R.-pulse at every change of motion. Starting from this idea we could, indeed, expect from each electron a much greater contribution to the energy of radiation than in the theory accepted by **Wien** and find the results of **Wien**'s energy-measurements in better agreement with those of the diffraction-experiments.

Nevertheless it seems to me that by the side of this another idea deserves our attention, which might be more in keeping with the properties of cathode-rays as far as known. It would be this, *that not simply the cathode-ray electrons, but in combination with these the atoms of the anti-cathode are the principal centres of emission of R.-rays.*

It should be imagined, that the electrons, arriving at the anticathode with their immense velocities, are not, generally, thrown into an other direction by the atoms, but will for the greater part pass straight through them, and even, in doing so, will mostly not suffer any persisting decrease of velocity. This idea is by no means a new one. It has been worked out by **Lenard** [3]), who sees in it the best explanation for the laws of absorption of the cathode-rays. In very few cases only it will happen that an electron, when piercing an atom, gets imprisoned

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[1]) W. **Wien**. Drudes Ann. d. Ph. 18, p. 1005, 1905; cf. also E. **Carter**. Ann. d. Ph. 21, p. 957, 1906.

[2]) J. D. v. d. **Waals** Jr. Ann. d. Ph. 22. p. 603. 1907.

[3]) P. **Lenard**. Drudes Ann. d. Ph. 12, p. 734, 1903.

or changes its direction considerably [1]) in a centre of exceedingly strong electromagnetic action; in the great majority of cases it will, by the abundance of vacant space in the interior of the atom [2]), fly across it without experiencing a considerable decrease of velocity.

In this way the greater part of the electrons will pierce thousands or tens of thousands of atoms before being stopped, and we find easily explained the great penetrating power of the cathode-rays, which may still in appreciable quantity pass through a layer of aluminium 10 μ [3]) thick or a layer of atmospheric air, some cm thick [4]).

If we consider the values given by the diffraction-experiments for the order of magnitude of the thickness of R.-waves as correct, it follows from WIEN's experiments — apart from a possible catalytic action of the R.-rays — that the radiation of the cathode-ray corpuscles, by the simple fact of their stoppage, could account only for something like $\frac{1}{20}$ or $\frac{1}{100}$ of the whole energy of the R.-rays. Consequently for by far the greater part this energy must, if LENARD's views may be accepted, have a different origin. What this can be, is obvious. The atoms namely will by no means remain undisturbed during the sudden passage of an electron. Themselves probably consisting of negative and positive corpuscles, they will see their electromagnetic fields during the passage altogether altered and at the same time will no doubt send out a pulse or wave of disturbance [5]) into the surrounding ether. About the character or shape of these pulses, which moreover may vary from one case to an other, we can, without making any more definite assumptions as to the structure of the atom, say little; but there is one important point, in which all these pulses will be to a certain degree similar, viz. their *duration*.

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[1]) Together with the expulsion of electrons originally belonging to the atom, which will often occur at the same time, these changes of direction could very well account for the diffusion of the cathode-rays according to LENARD.

[2]) LENARD calculates (Drudes Ann. d. Ph. 12, p. 739, 1903) that only 10^{-9} of the volume of an atom is occupied by the "dynamids", of which he considers it to consist.

[3]) LENARD. Wied. Ann. 51, p. 233, 1894.

[4]) Id., Ibid., p. 252.

[5]) LENARD expresses himself ("Ueber Kathodenstrahlen", Nobel-vorlesung, p. 37, Leipzig 1906) as follows: "Das durchquerende Strahlenquant" — the electron — "wird vermöge der abstossenden Kräfte, welche es auf die anderen, dem Atom eigenen, negativen Quanten ausübt, eine gewaltige Störung innerhalb des Atoms hervorbringen können", and then continues thus: "und als Folge dieser Störung kann ein dem Atom gehöriges Quant aus ihm hinausgeschleudert werden (sekundäre Kathodenstrahlung)"; but he does not speak of a radiation emitted by the atom.

The latter will be, if a represents the diameter of an atom and v the velocity of the electron, which is piercing it, something like (rather smaller than) $\frac{a}{v}$, causing the wave emitted to be of a thickness of something like (rather smaller than) $c\,\frac{a}{v}$, c being the velocity of light in ether. By putting $a = 10^{-8}$ and $v = 10^{10}$, we get by this way for $c\,\frac{a}{v}$ 3.10^{-8}, a number which only slightly exceeds the order of magnitude of the values of β (p. 714), derived from diffraction experiments. It might therefore be possible, *that the waves of disturbance in question should be identical with the Röntgen rays.*

As by this theory a single electron would disturb some thousands or tens of thousands of atoms, every atom, being traversed by an electron, need only send out something like $\frac{1}{100}$ of the quantity of energy emitted by an electron itself in its total stoppage, in order to account for the relatively large amount of energy found by WIEN in the R-rays. That such proportions should exist, seems to me not impossible at all.

The views presented here as to the origin of the R.-rays bestow a new and great importance on the "wave-length" of these rays, as they intimately connect this measurable quantity with the dimensions of the atoms. Whether there really exists such a close connection, could perhaps be experimentally put to the test by diffraction experiments with anticathodes made from different materials. More generally it might be expected that experiments of this kind would throw some new light upon the structure of atoms, and also of molecules or molecule aggregates. In such experiments it would certainly have a peculiar interest to use crystals as anticathodes, as perhaps the regular structure of these bodies could manifest itself both in rather sharply defined wave-lengths of the R.-rays emitted by them as in a polarisation of these rays.

The question, whether R.-rays should or should not be expected to show total or partial polarisation, may be treated on the basis of the above hypothesis, as soon as this be supplemented by definite suppositions about the structure of the atom.

The relation that, according to our views, should have to exist between the wave-length of R.-rays and the velocity of the cathode-rays, is of course liable to rather direct experimental verification.

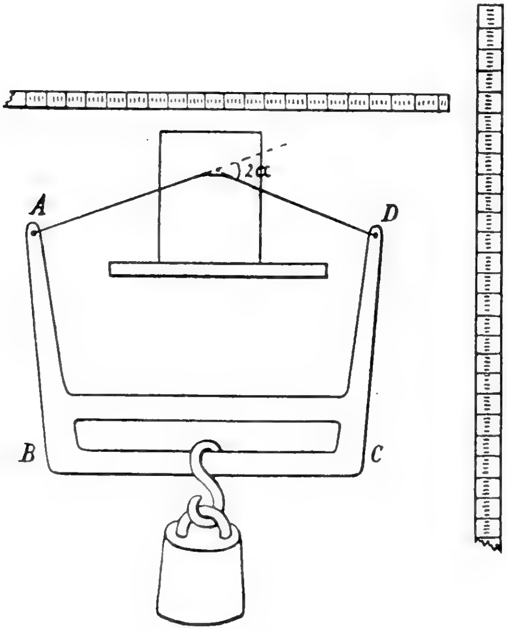
Two further questions connected with those views and perhaps liable also to be answered by way of experiment, are these:

1. whether the air molecules on the outside of the aluminium window of LENARD emit R.-rays in appreciable quantity;
2. whether the γ-rays of a radio-active substance, except by the substance itself, are to a considerable extent emitted also by the atoms of air in its neighbourhood on their being pierced by the electrons constituting the β-rays.

Physics. — *"On the motion of a metal wire through a piece of ice."* By Dr. J. H. MEERBURG. (Communicated by Prof. H. A. LORENTZ).

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

During the last and the preceding winter I made some measurements with a purpose of testing the formulae, expressing the velocity of descent of a metal wire through a block of ice, which Mr. L. S. ORNSTEIN had derived from the theory of regelation [1].



In my experiments the metal wire was fastened at both ends to

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[1] L. S. ORNSTEIN. These Proc. VIII, p. 653.

the legs A and D of an iron frame, which, in order to secure greater rigidity, had been cut from an iron plate. In the first measurements the downward displacements of the wire were observed by means of a small reading telescope, turning round a horizontal and a vertical axis, and were determined on a measuring rod, mounted at the side of the frame. The breadth of the ice-block was also read on a horizontal measuring rod. In the later experiments a cathetometer was used, placed at my disposal by the professors of the Technical University at Delft. I wish to express here my sincere thanks to these gentlemen, especially to Prof. DE HAAS. The fall of the wire was always derived from the change in the difference of level between the top of the wire and the upper edge of a small bubble, existing somewhere in the interior of the ice. Every ten minutes or, when the descent was quicker, every five minutes, the difference of level was measured in order to ascertain whether the fall was regular. Each experiment lasted 20 to 40 minutes.

The ice used was artificial commercial ice. From a larger block a clear smaller one was sawn out, in which some bubbles should be present to serve as marks. The faces were melted flat by pressing them against a metal plate, so that errors, caused by irregular refraction, were avoided.

Heat conduction along the wire was prevented by hanging small pieces of ice on the wire on both sides of the block. Still small grooves were occasionally formed when the descent was slow.

The experiments were made with wires of steel, german silver and silver. The thickness of the wires was measured by means of caliber compasses, giving results accurate to 0.01 mm. The thickness was 0.5, 0.4 and 0.3 mm. Deviations from these numbers, amounting to some hundredths of a millimetre, were occasionally found.

For the case, realised in my experiments, in which the two straight ends of the wire make a certain angle 2α with each other, formula (IIIa) of Mr. ORNSTEIN's paper [1]) holds:

$$v = \frac{2\alpha CP}{d_1 \sin \alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which v represents the velocity of descent of the wire, P the total weight and d the breadth of the ice-block. C is a constant. The value of this constant I calculated by formula (1) from the values of v, found in my experiments.

The results are summarised in the following table:

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[1]) l. c.

	P (in grammes).	C	average of C.
Steel wire.		Diameter 0.5 mM.	
	455	0.0162	
	755	0.0151	0.017
	1255	0.0172	
	2160	0.0185	
	2205	0.0169	
	5160	0.019	
		diameter 0.4 mM.	
	455	0.030	0.029
	755	0.029	
	1255	0.029	
		diameter 0.3 mM.	
	755	0.043	0.0425
	1255	0.042	
German silver.		diameter 0.5 mM.	
	755	0.0134	0.014
	1255	0.0119	
	2150	0.0143	
	5160	0.0172	
		diameter 0.4 mM.	
	755	0.0196	0.022
	1255	0.0204	
	2150	0.0208	
	5160	0.0255	
		diameter 0.3 mM.	
	555	0.0306	0.035
	755	0.0348	
	855	0.0393	
Silver wire.		diameter 0.5 mM.	
	755	0.0207	0.023
	1255	0.0255	
		diameter 0.4 mM.	
	536	0.0367	0.039
	755	0.0384	
	1036	0.0392	
	1255	0.0404	
		diameter 0.3 mM.	
	555	0.0347	0.041
	755	0.0467	

The quantity C is not expressed here in C.G.S. units, since the dimensions have been taken in millimetres, the velocities in millimetres per minute and the forces in grammes. In order to reduce them to C.G.S. units, the value of C has to be multiplied by 170×10^{-9}.

The values given in the table are averages of several measurements. In order to show the deviations of different measurements, made with the same weight, I give here an arbitrarily chosen set of separate measurements.

German silver wire, diameter 0.4 mm.

Number of the experiment	P	v	d_1	$2a$	C	averages.
8	1036	1.017	39.0	42°	0.0368	0.0392
10	1036	1.11	37.4	42°	0.0393	
14	1036	1.27	35.4	37°	0.0411	
17	1036	1.73	29.3	30°	0.0393	
87	1255	0.99	52.3	50°	0.0401	0.0404
112	1255	1.09	51.27	53°	0.043	
115	1255	0.756	66.46	53°	0.0387	

The value of C is calculated by Mr. ORNSTEIN in formula (I) of his paper. He finds

$$C = -\frac{\left(\frac{dt}{dp}\right)_0 \left[k_2 \frac{k_1 - {}^d/_R\,(k_1 - k_2)}{k_2 + {}^d/_R\,(k_1 - k_2)} + k_3\right]}{\pi R^2 W S_i} \quad . \quad . \quad . \quad (2)$$

Here k_1, k_2 and k_3 are the coefficients of heat conductivity respectively of the wire, of water and the ice, $\left(\frac{dt}{dp}\right)_0$ is the rise of the melting temperature by pressure, measured at the melting temperature, W is the latent heat of melting ice, S_i the specific gravity of ice, R the radius of the wire and d the thickness of the layer of water. Now the value of C cannot be calculated by this formula, since the quantity d is unknown. But besides the equation (I) Mr. ORNSTEIN gives in his formula (II^c) an expression, found by a hydrodynamical reasoning, in which the quantity d likewise occurs. This relation is [1]:

$$v = \frac{S_w}{S_i}\,\frac{2aP}{12\,\pi\,\mu\,d_1\,\sin a}\left(\frac{d}{R}\right)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

---

[1] In Mr. ORNSTEIN's paper this formula is given without the factor $\frac{S_w}{S_i}$ since this latter has no perceptible influence.

Here S_w is the specific gravity of water at 0°, μ the viscosity coefficient. By equalising (1) and (3) we find:

$$C = \frac{S_w}{S_i} \cdot \frac{1}{12\,\pi\,\mu} \left(\frac{d}{R}\right)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

and we should now have to eliminate $\frac{d}{R}$ between (2) and (4). In order to perform this elimination we simplify (2). We consider the form in (2) between the brackets [ ] and keep in mind that $\frac{d}{R}$ is very small, that k_1 is very much greater than k_2 and that k_3 may be neglected with respect to the first term (which amounts to neglecting the conduction of heat through the ice).

We may then write:

$$k_2 \frac{k_1 - {}^d/_R\,(k_1 - k_2)}{k_2 + {}^d/_R\,(k_1 - k_2)} = k_2 \frac{k_1}{k_2 + {}^d/_R\,k_1} = \frac{k_1}{1 + {}^d/_R\,\frac{k_1}{k_2}}.$$

Then we have

$$C = -\frac{\left(\frac{dt}{dp}\right)_0 \dfrac{k_1}{1 + {}^d/_R\,\frac{k_1}{k_2}}}{\pi\,R^2\,W S_i}$$

If we put

$$\left(\frac{dt}{dp}\right)_0 = -\,7.4 \times 10^{-9},\ S_i = 0.9167,\ W = 79.2,$$

C becomes

$$C = 3.3 \times 10^{-11} \times \frac{1}{R^2} \frac{k_1}{1 + {}^d/_R\,\frac{k_1}{k_2}}.$$

In (4) we substitute

$$S_w = 1,\ S_i = 0.9167,\ \mu = 0.0181,$$

then

$$C = 1.600 \left(\frac{d}{R}\right)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

Equalising the two values of C we have:

$$\left(\frac{d}{R}\right)^3 = 2.0 \times 10^{-11}\,\frac{1}{R^2}\,\frac{k_1}{1 + \frac{d\,k_1}{R\,k_2}}$$

or

$$\left(\frac{d}{R}\right)^3 + \left(\frac{d}{R}\right)^4 \frac{k_1}{k_2} = 2.0 \times 10^{-11}\,\frac{k_1}{R^2}.$$

From this equation $\frac{d}{R}$ can easily be found by a tentative method, when k_1, k_2 and R are given. In the different cases we find (in CGS-units),

Steel wire $k_1 = 0.166$ $k_2 = 0.0015$ $R = 0.025$ $\frac{d}{R} = 0.00166$

$k_1 = 0.166$ $k_2 = 0.0015$ $R = 0.020$ $\frac{d}{R} = 0.00190$

$k_1 = 0.166$ $k_2 = 0.0015$ $R = 0.015$ $\frac{d}{R} = 0.00229$

German silver wire $k_1 = 0\ 070$ $k_2 = 0.0015$ $R = 0.025$ $\frac{d}{R} = 0.00128$

$k_1 = 0.070$ $k_2 = 0.0015$ $R = 0.020$ $\frac{d}{R} = 0.00149$

$k_1 = 0.070$ $k_2 = 0.0015$ $R = 0.015$ $\frac{d}{R} = 0.00179$

Silver wire $k_1 = 1.50$ $k_2 = 0.0015$ $R = 0.025$ $\frac{d}{R} = 0.00239$

$k_1 = 1.50$ $k_2 = 0.0015$ $R = 0.020$ $\frac{d}{R} = 0.00279$

$k_1 = 1\ 50$ $k_2 = 0.0015$ $R = 0.015$ $\frac{d}{R} = 0.00318$

C is then found by substitution in (5). These values are given below, together with the values found by experiment, but now expressed in CGS-units.

		Calculated	*Found*
Steel wire	$R = 0.025$	73×10^{-10}	29×10^{-10}
	$R = 0.020$	110×10^{-10}	49×10^{-10}
	$R = 0.015$	192×10^{-10}	72×10^{-10}
German silver wire	$R = 0.025$	34×10^{-10}	24×10^{-10}
	$R = 0,020$	53×10^{-10}	37×10^{-10}
	$R = 0.015$	91×10^{-10}	59×10^{-10}
Silver wire	$R = 0.025$	218×10^{-10}	46×10^{-10}
	$R = 0.020$	347×10^{-10}	66×10^{-10}
	$R = 0.015$	519×10^{-10}	70×10^{-10}

The agreement must be called bad for the silver wire, satisfactory for the german silver wire. It may be called satisfactory, since different circumstances may be mentioned which make us expect a too small value. Leaving aside the great uncertainty in the values of the heat conductivities of metals, to which we cannot here ascribe the bad agreement, since we do not know in which direction this will influence the result[1]), the following causes may be mentioned.

1. The roughness of the wires. Already Mr. ORNSTEIN pointed this out. If the wire is not entirely smooth, the hydrodynamical deductions are uncertain and hence also formula (3). In order to ascertain the influence of this roughness I made some experiments with a steel wire that had for a moment been scoured with fine sand-paper in the direction of its length. Macroscopically no result of this manipulation could be discovered on the wire. Yet the effect proved considerable, for the following results were found:

	P	C	
steel wire, diameter 0,5 m.M.	455	0,009	average 0.011 m.M.
	1255	0,011	
	2205	0,014	
steel wire, diameter 0,3 m.M.	1255	0,028	

So we find a diminution of about 40 °/₀ in the value of C. After having observed this influence I tried to obtain smooth wires, but unsuccessfully; all the wires that were used in the experiments showed under the microscope numberless grooves in the direction of their length and of a breadth that might be estimated at somewhat less than 0.01 mm.

Since it is easily deduced from the calculated values of $\frac{d}{R}$ that the thickness of the layer of water increases with the size of the radius of the wire and since the influence of the roughness of the wire will be smaller with a greater thickness of this layer of water, I have still made some measurements with a thicker steel wire of 0,87 mm. diameter and heavier weights. The result was:

P	C		C (in C.G.S. units)
25200	0,00803	0,0081	13.8×10^{-10}
25200	0,00822		
5200	0,00667		11.3×10^{-10}

while calculation gives

$$k_1 = 0{,}166, \quad k_2 = 0{,}0015, \quad R = 0{,}0435 \quad \frac{d}{R} = 0{,}00120 \quad C = 27.7 \times 10^{-10}$$

The agreement is now better indeed; the value found is half the calculated one, while with the thinner steel wires it was slightly more than a third.

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[1] The values given by F. KOHLRAUSCH (Lehrbuch der praktischen Physik 10 Auflage 1905), steel $k = 0.06$ to 0.12 and silver $k = 1.01$, would give a much better agreement.

2. In the deduction of formula (1) it was assumed that within the layer of water the relation

$$\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}=0.$$

holds. This relation, however, holds for a body at rest. Here, on the other hand, we have to deal with a streaming liquid, in which case the following formula holds:

$$\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}=\frac{\varrho S_w}{k_2}\left(u\frac{\partial t}{\partial x}+v\frac{\partial t}{\partial y}\right).$$

Here ϱ is the specific heat of the liquid, u and v the velocity components in the X- and Y-directions. If we use this formula we take into account that the heat, conducted through the wire, does not entirely serve for melting the ice, but that it is partly conveyed upwards again by the streaming liquid. This also must result in a diminution of the velocity of descent. Prof. LORENTZ informed me, however, that it can be shown that this influence must be regarded as a quantity of the second order, so that the differences cannot be explained in this way.

3. If the temperature in the interior of the block of ice is not exactly 0°, but lower, the velocity of descent will also become smaller. But I observed no phenomena which point to a lower temperature in the interior. Blocks of ice that had been kept for 24 hours in a space above 0° gave the same results as blocks that had just been received. Moreover the wires as a rule went down at a distance of only a few millimetres from one of the faces of the block, and in some experiments they even came out of the block by melting of that face. Yet in the last moment, before the wire came out, no acceleration of the descent was observed.

Nor does theory support such an explanation. Prof. LORENTZ informed me that when the surface of a ball of ice of 3 centimeters diameter and at a temperature of — 2°, is raised to 0° and kept at this temperature, it may be shown that in less than an hour the temperature at the centre has risen to — 0.01°.

4. Another important influence on the velocity of descent is found in the fact that it is possible that not all the ice, melting at the lower side of the wire, freezes again exactly at the upper side, but that this water perhaps flows off laterally. It is clear that this must have a great influence since then the heat, necessary for the melting, is furnished by conduction through the ice. Already J. THOMSON

BOTTOMLEY [1]) showed that the lateral flow of water causes a great retardation.

The experiments now showed that this lateral flow really exists. For even when the ice was perfectly clear, in the places where the wire had passed through it various small bubbles were observed. Consequently not all the ice had been re-formed which had been there.

In this respect I also mention a curious change, found in the values of C: these values rise with the weight. This is very conspicuous with the silver and german silver wires, but also with the steel wires it exists, especially with the thick one of 0.87 mm.

Accordingly it was often seen that the bubbles on the path of the wire were more numerous with small than with heavy weights. This became particularly clear in experiments in which, during one descent, first a heavy and then a small weight was used, With the smaller weight more water flows off laterally.

I still made several experiments in which the wire was pulled upwards through the ice, hoping to prevent this lateral flow. The result was not the expected one, for bubbles also appeared and the values, found for C, were even somewhat smaller than in the former case. In regard to this question it would be desirable to investigate the descent of a whole body, e.g. of an iron ball, through perfectly clear ice.

In my opinion this lateral flow is the chief reason why theory and observation disagree. It also explains why with the silver wires larger differences were found than with the german silver and the steel wires. For if the heat is only partly furnished by the freezing process above the wire and if the rest has to be furnished by conduction through the ice, it seems to be of little consequence whether the wire be a good conductor of heat.

5. Ice is a crystalline substance. This also may have its effect. Perhaps the melting point is not the same at the different faces of the crystals which the wire touches. Though this influence may exist, we cannot say in which direction it would modify the result.

In order to find out whether such an influence makes itself felt, I made the wire pass several times through the same block of ice in three mutually perpendicular directions. But no perceptible difference was found.

As the general result of the experiments I think we may state, that they indicate that the regelation theory will be found capable of explaining the phenomena not only qualitatively but also quantitatively.

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[1]) Pogg. Ann. 148, p. 492, 1871.

Physics. — *"Contribution to the theory of binary mixtures, II"*, by Prof. J. D. VAN DER WAALS. (Continued, see p. 621).

Not to suspend too long the description of the course of the q-lines in the case that the locus $\frac{d^2\psi}{dx^2}=0$ exists, we shall postpone the determination of the temperature at which this locus has disappeared, and the inquiry into the value of x and v for the point at which it disappears — and proceed to indicate the modification in the course of the q-lines which is the consequence of its existence.

From the value of $\frac{dv}{dx_q}=-\frac{\frac{d^2\psi}{dx^2}}{\frac{d^2\psi}{dxdv}}$ follows that when a q-line passes through the curve $\frac{d^2\psi}{dx^2}=0$, it has a direction parallel to the

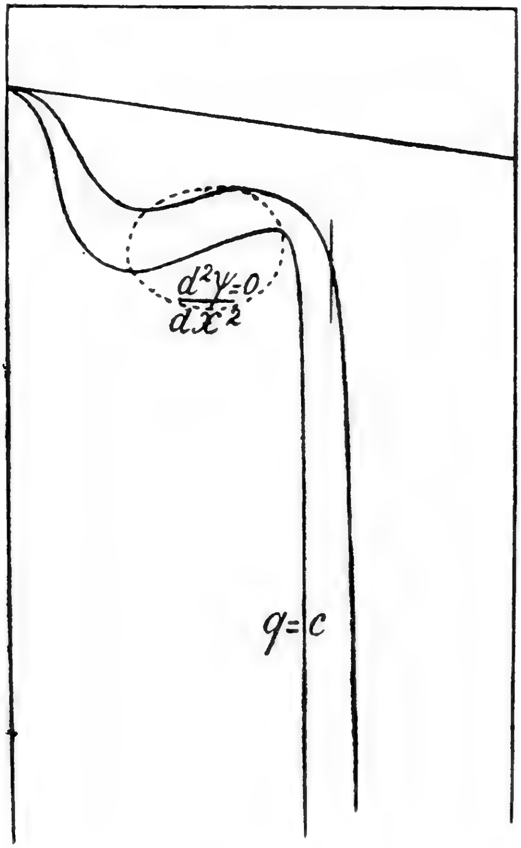

Fig. 3.

x-axis in such a point of intersection. So a q-line meeting $\frac{d^2\psi}{dx^2}=0$, will be twice directed parallel to the x-axis, and have a shape as represented in fig. 3 — at least as long as the curve $\frac{d^2\psi}{dxdv}=\left(\frac{dp}{dx}\right)_v=0$ does not occur. Such a shape may, therefore, be found for the q-lines, in the case that the second component has a higher value of b, and lower value of T_k —, and such a shape will certainly present itself in the case mentioned when the temperature is low enough.

Then there is a group of q-lines, for which maximum volume, and minimum volume is found. The outmost line on one side of this group of q-lines, viz. that for which q possesses the highest value, is that for which maximum and minimum volume have coincided, and which touches the curve $\frac{d^2\psi}{dx^2}=0$ in the point, in which this curve itself has the smallest volume. The other outmost line of this group of q-lines, viz. that for which q possesses the smallest value, is that for which again maximum and minimum volume have coincided, and which also touches the curve $\frac{d^2\psi}{dx^2}=0$, but in that point in which this curve itself has its largest volume. So for these two points of contact the equation $\frac{d^3\psi}{dx^3}=0$ holds. These two points of contact are, therefore, found by examining where the curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^3\psi}{dx^3}=0$ intersect. This last locus appears to be independent of the temperature, as we may put $\frac{d^3a}{dx^3}$ equal to 0. We find from the equation on p. 638

$$\frac{d^3\psi}{dx^3}=MRT\left\{-\frac{1-2x}{x^2(1-x)^2}+2\frac{\left(\frac{db}{dx}\right)^3}{(v-b)^3}+\frac{\frac{d^2b}{dx^2}}{(v-b)^2}\right\}=0.$$

If we neglect $\frac{d^2b}{dx^2}$, we find from $\frac{d^3\psi}{dx^3}=0$

$$\frac{\frac{db}{dx}}{v-b}=\sqrt[3]{\frac{1-2x}{2\,x^2\,(1-x)^2}}.$$

The locus $\frac{d^3\psi}{dx^3}=0$ occurs, therefore, only in the left side of the figure or for values of x below $\frac{1}{2}$. The line $x={}^1/_2$ is an asymptote for this curve, and only at infinite volume this value of x is reached.

And as for $x=0$ also $v-b$ must be $=0$, the curve $\frac{d^3\psi}{dx^3}=0$ starts from the same point from which all the q-lines start. If $\frac{d^2b}{dx^2}$ should not be equal to 0, we have ground for putting this quantity positive (Cont. II, p. 21), and we arrive at the same result for the initial point and the final point of the curve $\frac{d^3\psi}{dx^3}=0$.

So the points of the curve $\frac{d^2\psi}{dx^2}=0$, where tangents may be drawn to it parallel to the x-axis, lie certainly at values of x smaller than $\frac{1}{2}$, and accordingly the two outer ones of the group of the q-lines with maximum and minimum volume have their horizontal tangents also in the left side of the figure. The q-line with the highest value of q at lower value of x than that with the lowest value. This is represented in fig. 4.

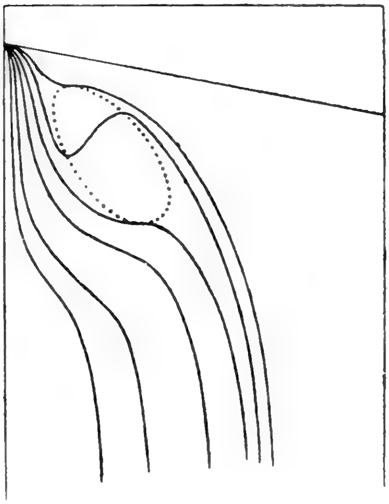

Fig. 4.

We notice at the same time that the points in which a q-line touches the curve $\frac{d^2\psi}{dx^2}=0$, are points of inflection for such a q-line, just as this is the case with the p-lines when a p-line touches the curve $\frac{d^2\psi}{dv^2}$. From

$$q=\left(\frac{d\psi}{dx}\right)_v$$

follows :

$$\frac{d^2\psi}{dxdv}\left(\frac{dv}{dx}\right)_q+\frac{d^2\psi}{dx^2}=0,$$

and

$$\frac{d^2\psi}{dxdv}\,\frac{d^2v}{dx^2}_q+\left\{\frac{d^3\psi}{dxdv^2}\left(\frac{dv}{dx}\right)_q^2+2\,\frac{d^3\psi}{dx^2dv}\left(\frac{dv}{dx}\right)_q+\frac{d^3\psi}{dx^3}\right\}=0.$$

In the points mentioned $\left(\frac{dv}{dx}\right)_q=0$, because $\frac{d^2\psi}{dx^2}=0$, and at the same time $\frac{d^3\psi}{dx^3}=0$. Hence $\left(\frac{d^2v}{dx^2}\right)_q=0$, which appears also immediately from the figure.

Within the curve $\frac{d^2\psi}{dx^2}=0$ every q-line that intersects it, has also a point of inflection, because the latter must pass from minimum volume to maximum volume in its course. So there is a continuous series of points in which q-lines possess points of inflection between the two points in which horizontal tangents may be drawn to $\frac{d^2\psi}{dx^2}=0$. But there is also a continuous series of points in which the q-lines must possess points of inflection on the left of the curve $\frac{d^2\psi}{dx^2}=0$, so with smaller value of x. For every q-line has its convex side turned to the x-axis just after it has left the starting point. If it is to enter the curve $\frac{d^2\psi}{dx^2}=0$ in horizontal direction and to pass then to smaller volume, it must turn its concave side to the x-axis in that point, and so it must have previously possessed a point of inflection. Most probably the last-mentioned branch is somewhere continuously joined to the first mentioned one. If so, there is a closed curve in which $\frac{d^2v}{dx^2}_q=0$ — and then it may be expected that this closed curve contracts with rise of T, and has disappeared above a certain temperature. But these and other particulars may be left to a later investigation.

We have now described the shape of the q-lines, 1. in the case that neither $\frac{d^2\psi}{dx^2}$, nor $\frac{d^2\psi}{dxdv}$ is equal to 0, 2. in the case that the curve $\frac{d^2\psi}{dxdv}=0$ exists, 3. in the case that the curve $\frac{d^2\psi}{dx^2}=0$ is found. It remains to examine the course of the q-lines when both curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dxdv}=0$ exist.

For the occurrence of the $\frac{d^2\psi}{dx^2}=0$ it is only required that $\frac{d^2a}{dx^2}$ be positive, as we shall always suppose, and that T is below the value of the temperature at which the curve $\frac{d^2\psi}{dx^2}=0$ has contracted to a single point. It may, therefore, occur with every binary system, without our having to pay attention to the choice of the components.

But the occurrence of the curve $\frac{d^2\psi}{dxdv}=\left(\frac{dp}{dx}\right)_v=0$ is not always possible, as we already showed in the discussion of the shape of the isobars. If we consult fig. 1 (These Proc. IX p. 630) it appears that the curve $\left(\frac{dp}{dx}\right)_v=0$ does not exist throughout the whole width of the diagram of isobars.

With mixtures for which the course of the isobars is, as is the case in the left side of the figure, the line $\left(\frac{dp}{dx}\right)_v=0$ does not exist at all. Only with mixtures for which the course of the isobars is represented by the middle part of fig. 1 it exists and if the asymptote is found, it can occur with all kinds of volumes. Also with mixtures for which the course of the isobars is represented by the right part of fig. 1, it exists, but then only at very small volumes, and it possesses only the branch which approaches the line $v=b$ asymptotically.

Let us now consider a mixture such that the curve $\left(\frac{dp}{dx}\right)_v=0$ is really present at such a temperature that also the curve $\frac{d^2\psi}{dx^2}=0$ exists; then we have still to distinguish between two cases, i. e. 1. when the two loci mentioned do not intersect, and 2. when they do intersect. If they do not intersect, and the curve $\left(\frac{dp}{dx}\right)_v=0$ lies on the right of $\frac{d^2\psi}{dx^2}=0$, then the q-line, after having had its maximum and minimum volume, will intersect the line $\left(\frac{dp}{dx}\right)_v=0$, in that point of intersection will have a tangent // v-axis; it will further run back to smaller volume, just as this is the case with one of the q-lines drawn in fig. 2. This may e.g. occur for mixtures corresponding to the left region of the diagram of isobars, when this region is so wide that also the asymptote and a further part of the curve $\left(\frac{dp}{dx}\right)_v=0$ is found. If with non-intersection the relative position of the two curves $\frac{d^2\psi}{dx^2}=0$ and $\left(\frac{dp}{dx}\right)_v=0$ are reversed, this can probably not occur but for mixtures which correspond to a region of the diagram of isobars which has been chosen far on the right side. The course of the q-lines which then pass through the curve $\frac{d^2\psi}{dx^2}=0$, is represented in fig. 5. But when the two

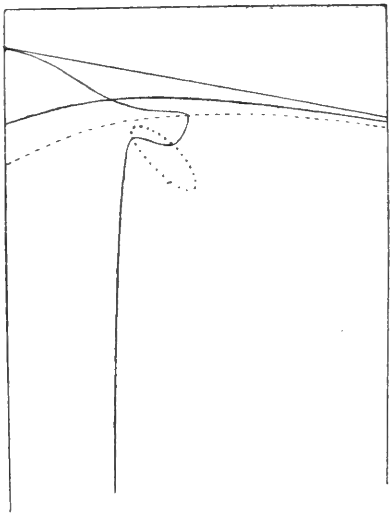

Fig. 5.

curves $\frac{d^2\psi}{dx^2} = 0$ and $\left(\frac{dp}{dx}\right)_v = 0$ intersect, which then necessarily takes place in 2 points, the shape of the q-lines is much more intricate. Then numerator and denominator are equal to zero in $\left(\frac{dv}{dx}\right)_q = \frac{\frac{d^2\psi}{dx^2}}{\left(\frac{dp}{dx}\right)_v}$, and $\left(\frac{dv}{dx}\right)_q$ is not to be determined from this equation. Then $\left(\frac{dv}{dx}\right)_q$ must be determined from :

$$\left(\frac{d^3\psi}{dxdv^2}\right)\left(\frac{dv}{dx}\right)_q^2 + 2\left(\frac{d^3\psi}{dx^2dv}\right)\left(\frac{dv}{dx}\right)_q + \left(\frac{d^3\psi}{dx^3}\right) = 0.$$

In the discussion of the shape of the p-lines we came across an analogous case when the curves $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dxdv} = 0$ intersect; and there we found that the two points of intersection had a different character. For one point of intersection the p-line has two different real directions, depending on the sign of $\frac{d^3\psi}{dv^3}\frac{d^3\psi}{dvdx^2} - \left(\frac{d^3\psi}{dxdv^2}\right)^2$. If this expression was negative, the loop-isobar passed through that point of intersection. In the same way, when from the above quadratic equation for $\left(\frac{dv}{dx}\right)_q$ we write the condition on which the roots are real, we find the condition :

$$\left[\frac{d^3\psi}{dx^3}\frac{d^3\psi}{dxdv^2} - \left(\frac{d^3\psi}{dx^2dv}\right)^2\right] \text{negative;}$$

which may be immediately found from the condition for the loop of the *loop-isobar*, as requirement for the loop of the *loop-q-line*, when we interchange x and v.

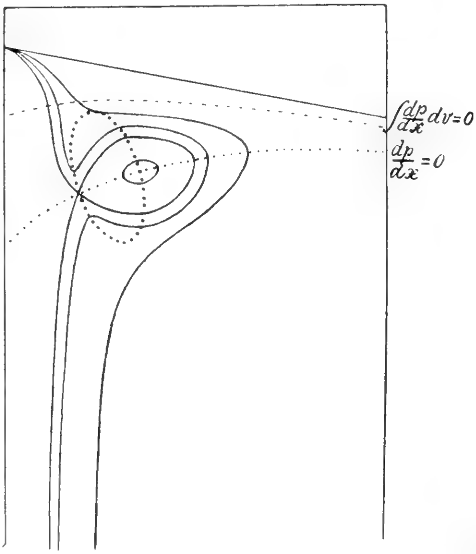

Fig. 6.

The q-line which passes through the first point where the above condition is negative, has, therefore, a real double point, and runs round the other point of intersection before passing through this double point for the second time. In Fig. 6 the dotted closed curve $\frac{d^2\psi}{dx^2}=0$ has been traced, and also the dotted curve $\left(\frac{dp}{dx}\right)=-\left(\frac{d^2\psi}{dvdx}\right)=0$. The point of intersection lying on the left, is the double point. According to what was stated before, $\frac{d^3\psi}{dx^3}$ is negative in this point, and the quantity $\frac{d^3\psi}{dxdv^2}$ is positive, which is also to be deduced from what was mentioned previously about the sign of $\frac{d^2p}{dxdv}=-\frac{d^3\psi}{dxdv^2}$. So the criterion by which the reality of the two directions of $\left(\frac{dv}{dx}\right)_q$ is tested is satisfied in that point of intersection. In the second point of intersection $\frac{d^3\psi}{dx^3}$ is positive, and $\frac{d^3\psi}{dxdv^3}$ is also positive. It is true that it does not follow from this that $\frac{d^3\psi}{dx^2}\frac{d^3\psi}{dxdv^2}>\left(\frac{d^3\psi}{dvdx^2}\right)^2$ — but 1 it appears in the drawing of the loop-q-line that there is no other possibility but that it runs round the second point of intersection, and 2 it appears, that just as we have mentioned in the analogous case for the shape of the p-lines (Footnote p. 626), only when the two points of intersection coincide, so when the two curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dxdv}=0$ touch, the quantity $\frac{d^3\psi}{dx^3}\frac{d^3\psi}{dxdv^2}-\left(\frac{d^3\psi}{dvdx^2}\right)^2$ is equal to 0. In the case that $\frac{d^2\psi}{dx^2}=0$ has greater dimensions, so at lower temperature, the loop-q-line will, of course, extend still much more to the right, and the higher q-lines must be strongly compressed at the point where the curve $\left(\frac{dp}{dx}\right)_v=0$ cuts the second axis (the line $x=1$).

This loop-q-line determines the course of all the other q-lines. Thus in fig. 6 a somewhat higher q-line passes through $\frac{d^2\psi}{dx^2}=0$, in vertical direction just above the double point, rises then till it passes through this curve for the second time, reaches its highest point, after which it meets the curve $\left(\frac{dp}{dx}\right)_v = 0$ in vertical direction, and then pursues its course downward after having been directed horizontally twice more.

It must then again approach asymptotically that value of x, at which it intersected the line $\int \frac{dp}{dx}\, dv = 0$ shortly after the beginning of its course. This line has also been drawn in fig. 6. It is evident that it may not intersect the curve $\frac{d^2\psi}{dx^2} = 0$. In fig. 6 it has, accordingly, remained restricted to smaller volumes than those of the curve $\frac{d^2\psi}{dx^2} = 0$. For the assumption of intersection involves that a q-line could meet the locus $\int \frac{dp}{dx}\, dv = 0$ several times. As $q = MRT\, l \frac{x}{1-x}$ in such a meeting point, it follows from this that only one value of x can belong to given q. It deserves notice that in this way without any calculation we can state this thesis: "The curves $\frac{d^2\psi}{dx^2} = 0$ and $\int \frac{dp}{dx}\, dv = 0$ can never intersect." According to the equation of state it would run like this: "The equations:

$$MRT \left\{ \frac{1}{x\,(1-x)} + \frac{\left(\frac{db}{dx}\right)^2}{(v-b)^2} \right\} = \frac{\frac{d^2a}{dx^2}}{v} \text{ and } \frac{MRT \frac{db}{dx}}{v-b} = \frac{\frac{da}{dx}}{v}$$

can have no solution in common. Indeed, if v from the second equation is expressed in x and T, and if this value is substituted in the first equation, we get the following quadratic equation in MRT:

$$(MRT)^2 \left\{ \frac{1}{x\,(1-x)} + \frac{1}{b^2}\left(\frac{db}{dx}\right)^2 + \frac{1}{b}\frac{db}{dx}\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}} \right\} -$$

$$- 2\,(MRT) \left\{ \frac{1}{b^2}\frac{db}{dx}\frac{da}{dx} - \frac{1}{b}\,\frac{1}{2}\,\frac{d^2a}{dx^2} \right\} + \frac{1}{b^2}\left(\frac{da}{da}\right)^2 = 0.$$

A value of MRT, which must necessarily be positive to have significance, requires $\frac{1}{b^2}\frac{db}{dx}\frac{da}{dx} > \frac{1}{2b}\frac{d^2a}{dx^2}$. From the foregoing remarks it is sufficiently clear that $\frac{da}{dx}$ must be positive to render the locus $\int\frac{dp}{dx}\,dv = 0$ possible, and that $\frac{d^2a}{dx^2}$ must be positive to render $\frac{d^2\psi}{dx^2} = 0$ possible. The roots of the given quadratic equation, however, are then imaginary, the square of $\frac{1}{b^2}\frac{db}{dx}\frac{da}{dx} - \frac{1}{2b}\frac{d^2a}{dx^2}$ being necessarily smaller than the square of $\frac{1}{b^2}\frac{db}{dx}\frac{da}{dx}$, and the square of this being smaller than the product of $\frac{1}{b^2}\left(\frac{da}{dx}\right)^2$ and the factor of (MRT).

But let us return to the description of the course of the remaining q-lines. There is, of course, a highest q-line, which only touches the locus $\frac{d^2\psi}{dx^2} = 0$, directed horizontally in that point of contact, and for which also $\frac{d^3\psi}{dx^3} = 0$ in that point. There is also a q-line which touches the locus $\frac{d^2\psi}{dx^2} = 0$ in its downmost point, and which as a rule will be another than that which touches it in its highest point. The q-lines of higher degree than the higher of these two have again the simple course which we have traced in fig. 2 (p. 635) for that q-line which intersects the locus $\left(\frac{dp}{dx}\right)_v = 0$. Only through their considerable widening all of them will more or less evince the influence of the existence of the above described complication. The q-lines of lower degree than the loop-q-line have split up into two parts, one part lying on the left which shows the normal course of a q-line which cuts $\left(\frac{dp}{dv}\right)_v = 0$; and a detached closed part which remains enclosed within the loop. Such a closed part runs round the second point of intersection which $\left(\frac{dp}{dx}\right)_v = 0$ and $\frac{d^2\psi}{dx^2} = 0$ have in common, passes in its lowest and highest point through $\frac{d^2\psi}{dx^2} = 0$, and through $\left(\frac{dp}{dx}\right)_v = 0$ in the point lying most to the right and most to the left. With continued decrease of the degree of q this detached part contracts, and disappears as isolated point. This takes place before q has descended to negative infinite, so that q-lines of very low degree have entirely resumed the simple course which such lines have when only the curve $\left(\frac{dp}{dx}\right)_v = 0$ exists.

Also in this general case for the course of the q-lines we can form an opinion about the locus of the points of inflection of these curves, so of the points in which $\left(\frac{d^2v}{dx^2}\right)_q = 0$. We already mentioned above that when the line $\left(\frac{dp}{dx}\right)_v = 0$ exists at a certain distance from it there must be points of inflection on the q-lines at larger volume. If also the asymptote of $\left(\frac{dp}{dx}\right)_v = 0$ should exist, also this series ot points of inflection of the q-lines has evidently the same asymptote. In fig. 6 this asymptote lies outside the figure, and so it is not represented — but the remaining part is represented, modified, however, in its shape by the existence of the double point. The said series of points of inflection is now sooner to be considered as consisting of two series which meet in the double point, and which have, therefore, got into the immediate neighbourhood of the line $\left(\frac{dp}{dx}\right)_v = 0$ there. So there comes a series from the left, which as it approaches the double point, draws nearer to $\left(\frac{dp}{dx}\right)_v = 0$, and from the double point there goes a series to the right, which first remains within the space in which $\frac{d^2\psi}{dx^2} = 0$ is found, and which passes through the lowest point of this curve, but then moves further to the side of the second component at larger volume than that of the curve $\left(\frac{dp}{dx}\right)_v = 0$. The double point of the q-loop-line is, therefore, also double point for the locus of the points of inflection of the q-lines, and the continuation of the two branches which we mentioned above, must be found above the curve $\left(\frac{dp}{dx}\right)_v = 0$. Accordingly, we have there a right branch, which runs within $\frac{d^2\psi}{dx^2} = 0$, and passes through the highest point of this curve, and a left branch which from the double point runs to the left of the loop-q-line, and probably merges into the preceding branch. If this is the case the outmost q-lines on the two sides, both that lying very low and that lying very high, have no points of inflection.

THE SPINODAL CURVE AND THE PLAITPOINTS.

The spinodal curve is the locus of the points in which a p- and a q-line meet. In these points $\frac{dv}{dx_p} = \frac{dv}{dx_q}$ and so $-\frac{\frac{d^2\psi}{dxdv}}{\frac{d^2\psi}{dv^2}} = -\frac{\frac{d^2\psi}{dx^2}}{\frac{d^2\psi}{dxdv}}$ or $\frac{d^2\psi}{dv^2}\frac{d^2\psi}{dx^2} = \left(\frac{d^2\psi}{dxdx}\right)^2$. In order to judge about the existence of such points of contact, we shall have to trace the p and the q lines together. As appears from fig. 1 p. 630 the shape of the p-lines is very different according as a region is chosen lying on the left side, or in the middle or on the right side; but the course of the q-lines in the different regions is in so far independent of the choice of the regions that $q_{-\infty}$ always represents the series of the possible volumes of the first component, and $q_{+\infty}$ the series of the possible volumes of the second component, and also the line of the limiting volumes. As the shape of the p-lines can be so very different we shall not be able to represent the shape of the spinodal line by a single figure. Besides the course of the p-lines depends on the existence or non-existence of the curve $-\frac{dp}{dv} = \frac{d^2\psi}{dv^2} = 0$, and the course of the q-lines on the existence or non-existence of the curve $\frac{d^2\psi}{dx^2} = 0$, and besides, and this holds for both, on the existence of the curve $\frac{d^2\psi}{dxdv} = 0$. Hence if for all possible cases we would illustrate the course of the spinodal curve in details by figures, this examination would become too lengthy. We shall, therefore, have to restrict ourselves, and try to discuss at least the main points.

Let us for this purpose choose in the first place a region from the left side of the general p-figure, and let us think the temperature so low, so below $(T_k)_2$, that there are still two isolated branches for the curve $\frac{dp}{dv} = 0$ all over the width of the region.

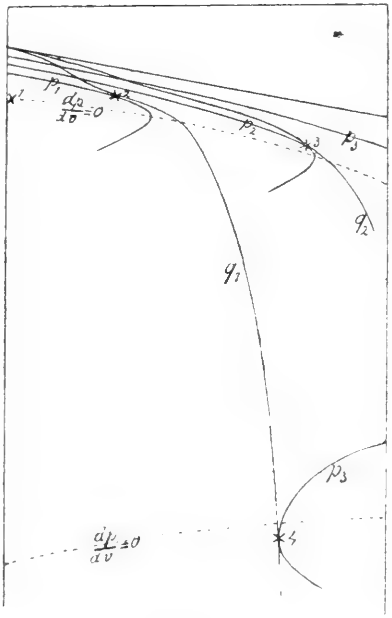

Fig. 7.

In fig. 7 T is thought higher than the temperature at which $\frac{d^2\psi}{dx^2}=0$ vanishes, and in fig. 8 below this temperature. In fig. 7 all the q-lines have the very simple course which we previously indicated for them, and the p-lines the well-known course, with which $\left(\frac{dv}{dx}\right)_p$ is positive on the liquid side of $\frac{dp}{dv}=0$, and on the vapour side of $\frac{dp}{dv}=0$, negative between the two branches of this curve, the transition of $\left(\frac{dv}{dx}\right)_p$ from positive to negative taking place through infinitely large. The isobars p_1, p_2 and p_3 have been indicated in the figure, in which $p_1 < p_2 < p_3$. Also a few q-lines, $q_1 < q_2$ and the points of contact of p_1 to q_1 and of p_3 to q_2. Also on the vapour side a point of contact of p_3 to q_1. It is clear 1st that every q-line yields two points for the spinodal curve, and 2nd that these points of contact lie outside the region in which $\frac{dp}{dv}$ is positive. On the other hand we see that the distance from the spinodal curve to the curve $\frac{dp}{dv}=0$ can be nowhere very large. Only by drawing very accurately it can be made evident that on the vapour side the spinodal curve has always a somewhat larger volume than the vapour branch of the curve $\frac{dp}{dv}=0$. In the four points, in which $\frac{dp}{dv}=0$ intersects the sides, indeed, the spinodal line coincides with this curve.

Fig. 7*b* has been drawn to give an insight into the circumstances at the plaitpoint. At $T > (T_k)_x$ the two branches of the curve $\frac{dp}{dv}=0$ have united at that value of x, for which $T=(T_k)_x$. One of the p-lines, namely that of the value $p=(p_k)'_x$, touches in the point at which the two branches have joined at a volume $v = (v_k)_x$, and has a point of inflection there. Two parts of q-lines have been drawn as touching the p-line. The two points of contact (1) and (2) are points of the spinodal curve, and lie again outside the curve $\frac{dp}{dv} = 0$. For a higher p-line these points will come closer together. And the place where they coincide is the plaitpoint. As in point (1) $\left(\frac{d^2v}{dx^2}\right)_p > \left(\frac{d^2v}{dx^2}\right)_q$ and reversely in point(2) $\left(\frac{d^2v}{dx^2}\right)_q > \left(\frac{d^2v}{dx^2}\right)_p$, $\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$ when (1) and (2) have coincided, and this may be considered as the criterion for the plaitpoint so that in such a point the two equations:

$$\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$$

and

$$\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q.$$

hold.

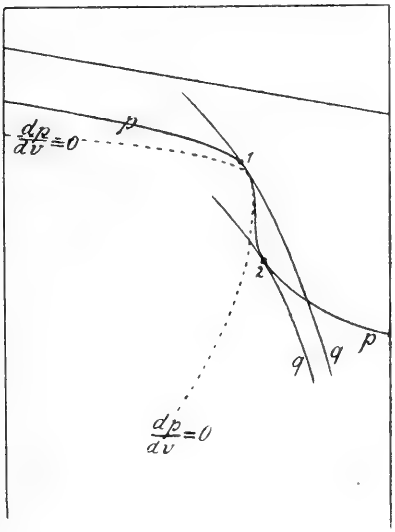

Fig. 7b.

The following remark may not be superfluous. In point (2) $\left(\frac{d^2v}{dx^2}\right)_p$ is not only smaller than $\left(\frac{d^2v}{dx^2}\right)_q$, but even negative. In order to find the plaitpoint, the point in which 2 points of contact for the q and the p-lines coincide, and so $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ have the same value, $\left(\frac{d^2v}{dx^2}\right)_p$ must first reverse its sign in the point (2) with increase of the value of p for the isobar before the equality with $\left(\frac{d^2v}{dx^2}\right)_q$ can be obtained. And that, at least in this case, this reversal of sign must take place with point (2) and not with point (1), appears from the positive value of $\left(\frac{d^2v}{dx^2}\right)_q$. So we arrive here at the already known theses that in the plaitpoint the isobar surrounds the spinodal curve, and also the binodal one.

As

$$dv_p = \left(\frac{dv}{dx}\right)_p dx + \frac{1}{1.2}\left(\frac{d^2v}{dx^2}\right)_p dx^2 + \frac{1}{1.2.3}\left(\frac{d^2v}{dx^3}\right)_p dx^3 \text{ etc.}$$

and

$$dv_q = \left(\frac{dv}{dx}\right)_q dx + \frac{1}{1.2}\left(\frac{d^2v}{dx^2}\right)_q dx^2 + \frac{1}{1.2.3}\left(\frac{d^3v}{dx^3}\right)_q dx^3 \text{ etc.}$$

we find for a plaitpoint:

$$dv_p - dv_q = \frac{1}{1.2.3}\left\{\left(\frac{d^3v}{dx^3}\right)_p - \left(\frac{d^3v}{dx^3}\right)_q\right\} dx^3 \text{ etc.}$$

So the p- and the q-lines meet and intersect in a plaitpoint, and this is not always changed when a point should be a double plaitpoint. We shall, namely, see later on that the criterion for a double plaitpoint is sometimes as follows:

$$\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$$

and

$$\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q = 0\cdot$$

Let us now proceed to the discussion of the case represented by fig. 8. Here it is assumed that T lies below the temperature at which $\frac{d^2\psi}{dx^2} = 0$ vanishes, so that this locus exists, it being moreover supposed that it intersects the curve $\frac{dp}{dv} = 0$. It appears from the drawing that for the q-lines for which maximum and minimum volume occurs, two new points of contact with the p-lines are necessarily found in the neighbourhood of the points of largest and smallest volumes at least for so far as these points lie on the liquid side of $\frac{dp}{dv} = 0$.

So there is a group of q-lines on which 4 points of the spinodal curve occur, and which will therefore intersect the spinodal curve in 4 points. The two new points of contact lie on either side of $\frac{d^2\psi}{dx^2} = 0$, and these two new points of contact do not move far away from this curve, the two old points of contact not being far removed from $\frac{dp}{dv} = 0$.

If we raise the value of q, the two new points of contact draw nearer to each other. Thus e. g. the q-line which touches $\frac{d^2\psi}{dx^2}$ in its highest point, and for which $\left(\frac{dv}{dx}\right)_q = 0$ and also $\left(\frac{d^2v}{dx^2}\right)_q = 0$ in that point has also been drawn in the figure. Also this q-line may still be touched by two different p-lines, which, however, have not been represented in the drawing. For a still higher q-line these points would coincide, and in consequence of the coincidence of two points of the spinodal curve a plaitpoint would then be formed. $\left(\frac{d^2 v}{dx^2}\right)_v$ always being positive, $\left(\frac{d^2 v}{dx^2}\right)_q$, which has been negative for a long time in the point lying on the left side, must first reverse its sign before it can coincide with the point lying on the right — a remark analogous to that which we made for the plaitpoint that we discussed above.

If on the other hand the value of q is made to descend, the point of contact lying most to the left will move further and further from the curve $\frac{d^2\psi}{dx^2} = 0$, and nearer and nearer to the curve $\frac{dp}{dv} = 0$, till for q-lines of very low degree, for which as we shall presently see, the number of points of contact has again descended to two, the whole bears the character of a point of contact lying on the liquid side.

But something special may be remarked about the two inner points of contact of the four found on the above q-line. When the q-line descends in degree, these points will approach each other, and they will coincide on a certain q-line. Then we have again a plaitpoint. In this case neither $\left(\frac{d^2 v}{dx^2}\right)_q$, nor $\left(\frac{d^2 v}{dx^2}\right)_p$ need reverse its sign because these quantities have always the same sign for each of the two points of contact which have not yet coincided, i. e. in this case the positive sign. But in this case, too, there is again besides contact, also intersection of the p- and q-lines. On the left of this plaitpoint the q-line lies at larger volumes, on the right on the other hand at smaller volumes than the p-line, the latter changing its course soon after again from one going to the right into one going to the left.

This plaitpoint, however, is not to be realised. With the two plaitpoints discussed above all the p-line and all the q-line, at least in the neighbourhood of that point, lie outside the spinodal curve, and so in the stable region. In this case they lie within the unstable region.

Summarizing what has been said about fig. 8, we see that there is a group of q-lines which cut the spinodal curve in four points. The outside lines of this group pass through plaitpoints. That with the highest value of q passes through the plaitpoint that is to be realised; that with the lowest value of q passes through the plaitpoint that is not to be realised. All the q-lines lying outside this group intersect the spinodal curve only in two points. If, however, the temperature chosen should lie above $(T_k)_2$ the q-lines of still higher degree than of that, passing through the vapour-liquid-plaitpoint, will no longer cut the spinodal curve.

And finally one more remark on the spinodal curve, which may occur in the case of fig. 8. By making the line $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ intersect, we have a region, in which both $\frac{d^2\psi}{dv^2}$ and $\frac{d^2\psi}{dx^2}$ is negative. In such a region the product of these quantities is again positive, and it may become equal to $\left(\frac{d^2\psi}{dx\,dv}\right)^2$. If this should be the case, it takes again place in a locus which forms a closed curve. Within this region there is then again a portion of the spinodal curve which is quite isolated from the spinodal curve considered. With regard to the p- and q-lines this implies, that there both $\frac{dv}{dx_p}$ and $\frac{dv}{dx_q}$ is negative; and so that contact is not impossible. Such a portion of a spinodal curve encloses then a portion of the ψ-surface which is concave-concave seen from below. If we consider the points lying within the spinodal curve as representing unstable equilibria, the points within this isolated portion of the spinodal curve are a fortiori unstable. The presence of such a portion of a spinodal curve not being conducive to the insight of the states which are liable to realisation, we shall devote no more attention to them.

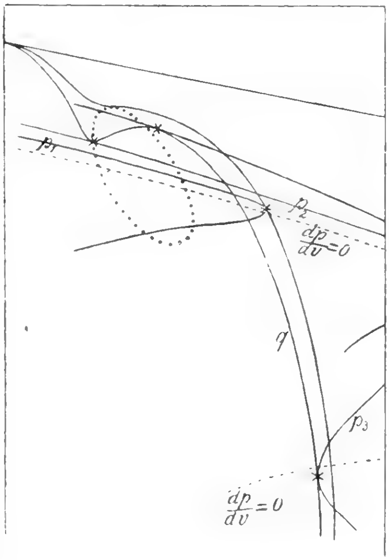

Fig. 8.

It appears from this description and from the drawing (fig. 8) that in this case the spinodal curve has a more complicated course than it would have if the curve $\frac{d^2\psi}{dx^2} = 0$ did not exist. It has a portion on the liquid side in which it is forced towards smaller volumes. There is, however, no reason to speak here of a longitudinal plait. We might speak of a more or less complicated plait here. But we shall only use the name of longitudinal plait, when we meet with a portion that is quite detached from the ordinary plait, which portion will then on the whole run in the direction of the v-axis.

There remains an important question to be answered: "What happens to the spinodal curve and to the plaitpoints with increase of temperature?"

At the temperature somewhat higher than $(T_k)_2$ there exist 3 plaitpoints in the diagram. 1. The realisable one on the side of the liquid volumes. 2. The hidden plaitpoint also on the side of the liquid volumes. 3. The realisable vapour-liquid plaitpoint. Let us call them successively P_1, P_2 and P_3. Now there are two possibilities, viz. 1. that with rise of the temperature P_1 and P_2 approach each other and coincide, and the plait has resumed its simple shape before P_3 disappears at $T = (T_k)_1$; and 2. that with rise of T the points P_2 and P_3 coincide and disappear, and also in that case the plait has resumed a simple shape. In the latter case, however, the plaitpoint is to be expected at very small volumes, and so also at very high pressure. Then, too, all heterogeneous equilibria have disappeared at $T = (T_k)_1$. Perhaps there may be still a third possibility, viz. when the locus $\frac{d^2\psi}{dx^2} = 0$ would disappear at a temperature higher than $(T_k)_1$. Besides the plaitpoint P_1 another new plaitpoint would then make its appearance at $T = (T_k)_1$ on the side of the first component. This would transform the plait into an entirely closed one, and only above the temperature, at which $\frac{d^2\psi}{dx^2} = 0$ vanishes, all heterogeneous equilibria would have disappeared.

Let us now briefly discuss these different possibilities. We shall restrict ourselves to the description of what happens in those cases, and at least for the present leave the question unsettled on what properties of the two components it depends whether one thing or another takes place. If P_1 and P_2 coincide, the portion of the locus $\frac{d^2\psi}{dx^2} = 0$ which we have drawn in fig. 8 for smaller volumes than that of $\frac{d^2\psi}{dv^2} = 0$, must have got entirely or almost entirely within the region where $\frac{d^2\psi}{dv^2}$ is negative in consequence of the rise of temperature, or the whole locus $\frac{d^2\psi}{dx^2} = 0$ may have disappeared with rise of T.

Now at P_1 in the previously given equation:

$$dv_p - dv_q = \frac{1}{1.2.3}\left\{\left(\frac{d^3v}{dx^3}\right)_p - \left(\frac{d^3v}{dx^3}\right)_q\right\} dx^3$$

the factor of dx^3 is negative, but at P_2 this factor is positive. If the points P_1 and P_2 coincide, this factor $= 0$. With coincidence of these plaitpoints, called *heterogeneous* plaitpoints by KORTEWEG, besides $\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$ and $\left(\frac{d^2x}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$, also $\left(\frac{d^3v}{dx^3}\right)_p = \left(\frac{d^3v}{dx^3}\right)_q$.

If P_2 and P_3 coincide, $\frac{d^2\psi}{dv^2} = 0$ has contracted with rise of temperature. Also $\frac{d^2\psi}{dx^2} = 0$ contracts with rise of the temperature and is displaced as a whole, as I hope to demonstrate further. But the contraction of $\frac{d^2\psi}{dv^2} = 0$, whose top moves to the left, happens relatively quicker, so that e.g. the top falls within the region in which $\frac{d^2\psi}{dx^2}$ is negative. The existence of the point P_3 requires that $\left(\frac{dv}{dx}\right)_q$ is positive. The point P_2 lies on the right of $\frac{d^2\psi}{dx^2} = 0$ and above $\frac{d^2\psi}{dv^2} = 0$.

If the top of $\frac{d^2\psi}{dv^2} = 0$ lies within the curve $\frac{d^2\psi}{dx^2} = 0$, neither P_2 nor P_3 can exist any longer. Before this relative position of the two curves they have, therefore, already disappeared in consequence of their coinciding. Also in this case the coincidence of *heterogeneous* plaitpoints holds. At P_2 the factor of dx^3 was positive, and at P_3 this factor is negative. In case of coincidence $\left(\frac{d^3v}{dx^3}\right)_p = \left(\frac{d^3v}{dx^3}\right)_q$. With further rise of T, however, the top of $\frac{d^2\psi}{dv^2} = 0$ will have to get again outside the region where $\frac{d^2\psi}{dx^2}$ is negative. The curve $\frac{d^2\psi}{dx^2} = 0$, namely, cannot extend to $x = 0$, and the curve $\frac{d^2\psi}{dv^2} = 0$ at $T = (T_k)$, has its top at $x = 0$. We draw from this the conclusion, that

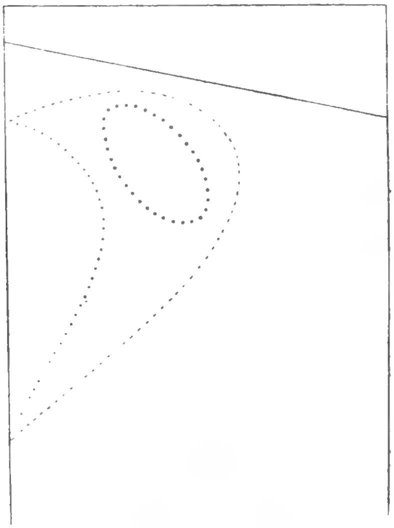

Fig. 9.

with continued increase of temperature the curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$ will no longer intersect, but will assume the position indicated by fig. 9.

The spinodal line runs round the two curves, and so in consequence of the presence of $\frac{d^2\psi}{dx^2}=0$ it is forced to remain at an exceedingly large distance from the curve $\frac{d^2\psi}{dv^2}=0$. The question may be raised whether the spinodal curve cannot split up into two separated parts, one part enclosing the curve $\frac{d^2\psi}{dv^2}=0$, the other part passing round $\frac{d^2\psi}{dv^2}=0$. The answer must then be: probably not. In the points between the two curves $\frac{d^2\psi}{dv^2}$ and $\frac{d^2\psi}{dx^2}$ are indeed, positive, but still small, whereas $\frac{d^2\psi}{dx\,dv}$ does not at all occur in the figure, and will, therefore, in general, be large. Now if the temperature at which $\frac{d^2\psi}{dx^2}=0$ disappears, should lie above $(T_k)_1$, $\frac{d^2\psi}{dv^2}=0$ shifts to the left, till it leaves the figure, and the spinodal curve is closed at $x=0$ and $T=(T_k)_1$, and the new plaitpoint makes its appearance, which we mentioned above. From this moment we have a spinodal curve with two realisable plaitpoints. The graphical representation of the curvature of the p- and the q-lines is in this case very difficult, because both groups of lines have only a slight curvature. If, however, we keep to the rule, that the p- and the q-lines envelop the spinodal curve at realisable plaitpoints, we conclude that the value of $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ is positive in P_1, and negative in the other plaitpoint. When these points, called *homogeneous* plaitpoints by KORTEWEG, coincide, $\left(\frac{d^2v}{dx^2}\right)_p=\left(\frac{d^2v}{dx^2}\right)_q=0$. Above the temperature at which this takes place, the p- and the q-lines have no longer any point of contact. In consequence of the disappearance of the locus $\frac{d^2\psi}{dv^2}=0$, the course of the p-lines has become chiefly from left to right, so in the direction of the x-axis. On account of the disappearance of the locus

$\frac{d^2\psi}{dx^2}=0$ the course of the q-lines has also been simplified, and at least with a volume which is somewhat above the limiting volume, they run chiefly in the direction of the v-axis.

Many of the results obtained about the course of the spinodal curve, and about the place of the plaitpoints, at which we have arrived in the foregoing discussion by examining the way in which the p- and the q-lines may be brought into mutual contact, may be tested by the differential equation of the spinodal line. This will, of course, also be serviceable when we choose another region than that discussed as yet.

From:

$$\frac{d^2\psi}{dv^2}\,\frac{d^2\psi}{dx^2}-\left(\frac{d^2\psi}{dxdv}\right)^2=0.$$

we derive:

$$\left\{\frac{d^2\psi}{dx^2}\,\frac{d^2\psi}{dv^2}+\frac{d^2\psi}{dv^2}\,\frac{d^3\psi}{dx^2dv}-2\,\frac{d^2\psi}{dxdv}\,\frac{d^3\psi}{dxdv^2}\right\}dv+$$

$$+\left\{\frac{d^3\psi}{dx^3}\,\frac{d^2\psi}{dv^2}+\frac{d^2\psi}{dx^2}\,\frac{d^3\psi}{dxdv^2}-2\,\frac{d^2\psi}{dx^2}\,\frac{d^3\psi}{dx^2dv}\right\}dx+$$

$$+\left\{-\frac{d^2\eta}{dx^2}\,\frac{d^2\psi}{dv^2}-\frac{d^2\eta}{dv^2}\,\frac{d^2\psi}{dx^2}+2\,\frac{d^2\eta}{dxdv}\,\frac{d^2\psi}{dxdv}\right\}dT=0.$$

We arrive at the shape of the factor of dT by considering that from:

$$d\varepsilon = T\,d\eta - p\,dv + q\,dx$$

follows:

$$d\psi = -\eta\,dT - p\,dv + q\,dx$$

so that $\left(\frac{d\psi}{dT}\right)_{v,x}=-\eta$ and so $\frac{d^3\psi}{dTdv^2}=-\left(\frac{d^2\eta}{dv^2}\right)_{x,T}$ etc.

This very complicated differential equation may be reduced to a simple shape.

Let us for this purpose first consider the factor of dv. By substituting in it the quantity $\frac{\left(\frac{d^2\psi}{dxdv}\right)^2}{\frac{d^2\psi}{dv^2}}$ for $\frac{d^2\psi}{dx^2}$, and $\left(\frac{dv}{dx}\right)_p$ for $-\frac{\frac{d^2\psi}{dx\,dv}}{\frac{d^2\psi}{dv^2}}$

this factor becomes:

$$\frac{d^2\psi}{dv^2}\left\{\frac{d^3\psi}{dv^3}\left(\frac{dv}{dx}\right)_p^2+2\,\frac{d^3\psi}{dxdv^2}\left(\frac{dv}{dx}\right)_p+\frac{d^2\psi}{dx^2dv}\right\}.$$

From $p=-\frac{d\psi}{dv}$ we derive:

$$\frac{d^2\psi}{dv^3}\left(\frac{dv}{dx}\right)_p+\frac{d^2\psi}{dxdv}=0$$

and

$$\frac{d^2\psi}{dv^2}\left(\frac{d^2v}{dx^2}\right)_p+\left\{\frac{d^3\psi}{dv^3}\left(\frac{dv}{dx}\right)_p^2+2\,\frac{d^3\psi}{dv^2dx}\left(\frac{dv}{dx}\right)_p+\frac{d^3\psi}{dx^2dv}\right\}$$

from which appears that we can write the factor of dv in the form of:

$$-\left(\frac{d^2\psi}{dv^2}\right)^2\left(\frac{d^2v}{dx^2}\right)_p.$$

We might proceed in a similar way with regard to the factor of dx, but we can immediately find the shape of this factor by substituting the quantity x for v and q for p in the factor of dv. We find then:

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

As long as we keep T constant, and this is necessary for the course of a spinodal curve, the differential equation, therefore, may be written:

$$-\left(\frac{d^2\psi}{dv^2}\right)^2\left(\frac{d^2v}{dx^2}\right)_p dv-\left(\frac{d^2\psi}{dx^2}\right)^2\left(\frac{d^2x}{dv^2}\right)_q dx=0.$$

By taking into account that $\left(\frac{d^2x}{dv^2}\right)_q=-\left(\frac{dx}{dv}\right)_q^3\left(\frac{d^2v}{dx^2}\right)_q$, we obtain after some reductions which do not call for any explanation, the simple equation:

$$\left(\frac{dv}{dx}\right)_{spin}=\left(\frac{dv}{dx}\right)_{p=q}\frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p}.$$

As a first result we derive from this equation the thesis, that $\left(\frac{dv}{dx}\right)_{spin}$ and $\left(\frac{dv}{dx}\right)_{p=q}$ must have the same sign, if $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ have the same sign and vice versa. Thus on the vapour side in fig. 7 $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ have always reversed sign, and $\left(\frac{dv}{dx}\right)_{p=q}$ being negative, $\left(\frac{dv}{dx}\right)_{spin}$ is negative on the vapour branch of the spinodal curve. Reversely the curvatures of the p and q-lines have the same sign on the liquid side, and $\left(\frac{dv}{dx}\right)_{bin}=\left(\frac{dv}{dx}\right)_{p=q}=$ positive. If, however,

$\left(\frac{d^2v}{dx^2}\right)_q$ should have been indeed negative there, as was accidentally represented in point 2 of the spinodal curve, the spinodal curve runs towards smaller volumes with increasing value of x. So if there occur points with maximum or minimum volume on the spinodal curve, $\left(\frac{d^2v}{dx^2}\right)_q = 0$ in those points. If on the other hand $\left(\frac{dv}{dx}\right)_{spin}$ is infinitely large, which occurs in the case under consideration when the spinodal curve is closed on the right side for $T > (T_k)_2$ then $\left(\frac{d^2v}{dx^2}\right)_p$ must be $= 0$, and so the p-line must have a point of inflection in such a point, to which we had moreover already concluded before in another way. A great number of other results may be derived from this differential equation of the spinodal line. We shall, however, only call attention to what follows. In a plaitpoint $\left(\frac{dv}{dx}\right)_{spin} = \left(\frac{dv}{dx}\right)_{p=q}$. For a plaitpoint it follows from this that $\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$.

If for a point of a spinodal curve $\left(\frac{dv}{dx}\right)_{spin}$ is indefinite, both $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ must be equal to 0. This takes place in two cases: 1. in a case discussed above when the whole of the spinodal line is reduced to one single point. 2. when a spinodal line splits up into two branches, as is the case for mixtures for which also T_k minimum is found. In the former case the disappearing point has the properties of an isolated point, in the second case of a double point.

In the differential equation of the spinodal line the factor of dT may be written:

$$-\frac{1}{T}\left\{\left(\frac{d^2T\eta}{dx^2}\right)_{vT}\frac{d^2\psi}{dv^2} - 2\left(\frac{d^2T\eta}{dxdv}\right)_T\frac{d^2\psi}{dxdv} + \left(\frac{d^2T\eta}{dv^2}\right)_{Tx}\frac{d^2\psi}{dx^2}\right\}$$

and by putting $\varepsilon - \psi$ for $T\eta$ it may be reduced to:

$$-\frac{1}{T}\left\{\frac{d^2\psi}{dv^2}\frac{d^2\varepsilon}{dx^2} - 2\frac{d^2\psi}{dxdv}\frac{d^2\varepsilon}{dxdv} + \frac{d^2\psi}{dx^2}\frac{d^2\varepsilon}{dv^2}\right\}$$

or to

$$-\frac{1}{T}\frac{d^2\psi}{dv^2}\left\{\frac{d^2\varepsilon}{dv^2}\left(\frac{dv}{dx}\right)^2_{p=q} + 2\frac{d^2\varepsilon}{dxdv}\left(\frac{dv}{dx}\right)_{p=q} + \frac{d^2\varepsilon}{dx^2}\right\}.$$

The factor by which $-\frac{1}{T}\frac{d^2\psi}{dv^2}$ is to be multiplied, occurs for the first time in formula (4) Verslag K. A. v. W. Mei 1895, and at the close of that communication I have written this factor in the form:

$$-\frac{2a}{v}\left\{\left(\frac{1}{v}\frac{dv}{dx_v}-\frac{1}{2a}\frac{da}{dx}\right)^2+\frac{a_1a_2-a_{12}^2}{a^2}\right\},$$

from which appears that in any case when $a_1a_2 > a_{12}^2$, this factor is negative. Here, too, I shall assume this factor to be always negative, but I may give a fuller discussion later on.

In consequence of these reductions the differential equation of the spinodal curve may be written as follows:

$$\frac{d^2\psi}{dv^2}\left(\frac{d^2v}{dx^2}\right)_{pT}dv+\frac{d^2\psi}{dxdv}\left(\frac{d^2v}{dx^2}\right)_{qT}dx+\frac{dT}{T}\left(-\right)=0.$$

From this equation follows inter alia this rule concerning the displacement of the spinodal curve with increase of T, that on the side where $\left(\frac{d^2v}{dx^2}\right)_p$ is positive, the value of v with constant value of x, increases, and the reverse. So the two branches of a spinodal curve approach each other with increase of the temperature. But I shall not enter into a discussion of the further particulars which might occur when this formula is applied. By elimination of dv I shall only derive the differential equation of the spinodal line when we think it given by a relation between p, x and T. We find then:

$$\left(\frac{d^2v}{dx^2}\right)dp=\left(\frac{dp}{dx}\right)_{v,T}\left[\left(\frac{d^2v}{dx^2}\right)_{p,T}-\left(\frac{d^2v}{dx^2}\right)_{q,T}\right]dx+\frac{dT}{T}\left[(-)+T\left(\frac{dT}{dp}\right)_{v,x}\left(\frac{d^2v}{dx^2}\right)_{pT}\right]$$

for a plaitpoint the factor of dx disappears, and we find back the equation (4). Verslag K. A. v. W. Mei 1895, for the plaitpoint curve. At constant temperature we find for the spinodal curve:

$$\left(\frac{dp}{dx}\right)_{spin}=\left(\frac{dp}{dx}\right)_v\left\{1-\frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p}\right\}.$$

(*To be continued*).

Physics. — *"The shape of the empiric isotherm for the condensation of a binary mixture"*. By Prof. J. D. VAN DER WAALS.

Let us imagine a molecular quantity of a binary mixture with a mass equal to $m_1(1-x)+m_2x_1$ at given temperature in a volume, so that part of it is in the liquid state, and the remaining part in the vapour state. Let us put the fraction which is found in the vapour state equal to y. The point that indicates the state of that mixture, lies then on a nodal curve which rests on the binodal curve. Let the end of the nodal line which rests on the liquid branch be denoted by the index 1, and the other end by the index 2. Let us represent the molecular volume of the end 1 by v_1, and the molecular volume of the other end by v_2, then when v represents the volume of the quantity which is in heterogeneous equilibrium:

$$v = v_1(1-y) + v_2 y$$

the constant quantity x being represented by:

$$x = x_1(1-y) + x_2 y.$$

From this we find:

$$dv = (v_2-v_1)\,dy + (1-y)\,dv_1 + y\,dv_2$$

and

$$0 = (x_2-x_1)\,dy + (1-y)\,dx_1 + y\,dx_2.$$

By elimination of dy we obtain the equation:

$$-dv = \frac{v_2-v_1}{x_2-x_1}\left\{(1-y)\,dx_1 + y\,dx_2)\right\} - (1-y)\,dv_1 - y\,dv_2.$$

Now in general $dv = \left(\frac{dv}{dx}\right)_p dx + \left(\frac{dv}{dp}\right)_x dp$. Let us apply this equation for the points 1 and 2 of the binodal curve, and let us take the course going from v_1 to v_1+dv_1 and from v_2 to v_2+dv_2 on the surface for the homogeneous phases. Then:

$$dv_1 = \left(\frac{dv_1}{dx_1}\right)_p dx_1 + \left(\frac{dv_1}{dp}\right)_{hom} dp,$$

and

$$dv_2 = \left(\frac{dv_2}{dx_2}\right)_p dx_2 + \left(\frac{dv_2}{dp}\right)_{hom} dp.$$

The quantities $\left(\frac{dv_1}{dx_1}\right)_p$ and $\left(\frac{dv_2}{dx_2}\right)_p$ must then be taken along an isobar.

If we substitute the values of dv_1 and dv_2 in the equation for dv, it becomes:

$$- dv = (1-y) \left\{ \left[\frac{v_2-v_1}{x_2-x_1} - \left(\frac{dv_1}{dx_1}\right)_p \right] dx_1 - \left(\frac{dv_1}{dp}\right)_{hom} dp \right\} +$$

$$+ \quad y \quad \left\{ \left[\frac{v_2-v_1}{x_2-x_1} - \left(\frac{dv_2}{dx_2}\right)_p \right] dx_2 - \left(\frac{dv_2}{dp}\right)_{hom} dp \right\}$$

or

$$-\left(\frac{dv}{dp}\right)_{het} = (1-y) \left\{ \left[\frac{v_2-v_1}{x_2-x_1} - \left(\frac{dv_1}{dx_1}\right)_p \right] \left(\frac{dx_1}{dp}\right)_{bin} - \left(\frac{dv_1}{dp}\right)_{hom} \right\} +$$

$$+ \quad y \quad \left\{ \left[\frac{v_2-v_1}{x_2-x_1} - \left(\frac{dv_2}{dx_2}\right)_p \right] \left(\frac{dx_2}{dp}\right)_{bin} - \left(\frac{dv_2}{dp}\right)_{hom} \right\}$$

Now the factor of $\left(\frac{dx_1}{dp}\right)_{bin} = \frac{v_{21}}{x_2-x_1} = \left(\frac{d^2\xi}{dx_1^{\,2}}\right)_{p,T} \left(\frac{dx_1}{dp}\right)_{bin}$, and we find:

$$-\left(\frac{dv}{dp}\right)_{het} = (1-y) \left\{ \left(\frac{d^2\xi}{dx_1^{\,2}}\right)_{p,T} \left(\frac{dx_1}{dp}\right)_{bin}^2 - \left(\frac{dv_1}{dp}\right)_{hom} \right\} +$$

$$+ \quad y \quad \left\{ \left(\frac{d^2\xi}{dx_2^{\,2}}\right)_{p,T} \left(\frac{dx_2}{dp}\right)_{bin}^2 - \left(\frac{dv_2}{dp}\right)_{hom} \right\} \quad . \quad . \quad . \quad (1)$$

If we consider the beginning of the condensation, and so $y=1$, the above equation becomes:

$$-\left(\frac{dv}{dp}\right)_{het} = \left(\frac{d^2\zeta}{dx_2^{\,2}}\right)_{p,T} \left(\frac{dx_2}{dp}\right)_{bin}^2 - \left(\frac{dv_2}{dp}\right)_{hom}$$

in which we must put $v_2 = v$ and $x_2 = x$. It appears from this equation, that never $-\left(\frac{dv}{dp}\right)_{het} = -\left(\frac{dv}{dp}\right)_{hom}$, and that there must therefore be a leap in the value of $-\frac{dv}{dp}$ or of $-\frac{dp}{dv}$ at the beginning of the condensation, unless there should be cases in which $\left(\frac{d^2\zeta}{dx^2}\right)_{p,T} \left(\frac{dx}{dp}\right)_{bin}^2$ is equal to 0. The only case in which this is so, is in the critical point of contact. There $\left(\frac{dp}{dx}\right)_{bin} = \infty$ and so $\left(\frac{dx}{dp}\right)_{bin} = 0$. But then there is properly speaking no longer condensation, and the empiric isotherm has disappeared. We might think of a plaitpoint, because $\left(\frac{d^2\zeta}{dx^2}\right)_{p,T} = 0$ in it, but on the other hand $\left(\frac{dp}{dx}\right)_{bin} = 0$ and $\left(\frac{dx}{dp}\right)_{bin} = \infty$ there. If the limiting value of $\left(\frac{d^2\zeta}{dx^2}\right)_{p,T} \left(\frac{dx}{dp}\right)_{bin}^2$ or of $\frac{\left(\frac{d^2\zeta}{dx^2}\right)_{p,T}}{\left(\frac{dp}{dx}\right)_{bin}^2}$ is sought, we find by differentiating numerator and denominator twice with respect to x:

$$\frac{\left(\frac{d^2\zeta}{dx^2}\right)_{pT}}{\left(\frac{dp}{dx}\right)^2_{bin}} = \frac{\left(\frac{d^3\zeta}{dx^3}\right)_{pT}}{2\left(\frac{dp}{dx}\right)_{bin}\left(\frac{d^2p}{dx^2}\right)_{bin}} = \frac{\left(\frac{d^4\zeta}{dx^4}\right)_{p,T}}{2\left(\frac{d^2p}{dx^2}\right)^2_{bin}}.$$

In a plaitpoint, besides $\left(\frac{d^2\zeta}{dx^2}\right)_{p,T}$ also $\left(\frac{d^3\zeta}{dx^3}\right)_{p,T} = 0$, but $\left(\frac{d^4\zeta}{dx^4}\right)_{p,T}$ will have a value differing from 0, and so there is a leap in the value of $-\frac{dv}{dp}$ in a plaitpoint too.

As $-\left(\frac{dv}{dp}\right)_{hom}$ must always be positive, also $\left(-\frac{dv}{dp}\right)_{het}$ will always be positive and larger than $\left(-\frac{dv}{dp}\right)_{hom}$ or $\left(-\frac{dp}{dv}\right)_{hom} > \left(-\frac{dp}{dv}\right)_{het}$.

At the beginning of the condensation the empiric curve will ascend less steeply with decrease of volume than that for homogeneous phases.

There are cases in which $-\left(\frac{dv}{dp}\right)_{het} = \infty$, or $\left(-\frac{dp}{dv}\right)_{het} = 0$. 1. on the sides, so for $x = 0$ and $x = 1$. Then $\left(\frac{d^2\zeta}{dx^2}\right)_{pT}$ is infinite, and is represented by the principal term $\left(\frac{MRT}{x(1-x)}\right)$. 2. if on the binodal curve $\frac{dx}{dp}$ is infinite or $\frac{dp}{dx} = 0$; this takes place for those mixtures which behave as a simple substance.

If in equation (1) we put $y = 0$ and $v_1 = v$ and $x_1 = x$ we could derive the same conclusions for the end of the condensation.

The relation between $-\left(\frac{dp}{dv}\right)_{het}$ and $-\left(\frac{dp}{dv}\right)_{hom}$ at the beginning and at the end of the condensation, could be immediately derived by applying the equation:

$$dv = \left(\frac{dv}{dp}\right)_x dp + \left(\frac{dv}{dx}\right)_p dx$$

both for the surface of the homogeneous phases and for that of the heterogeneous phases. If we then take into consideration that $\left(\frac{dv}{dx}\right)_p$ on the heterogeneous surface is equal to $\frac{v_2 - v_1}{x_2 - x_1}$, we find:

$$\frac{v_3-v_1}{x_2-x_1}\,dx+\left(\frac{dv}{dp}\right)_{het}dp=\left(\frac{dv}{dx}\right)_p dx+\left(\frac{dv}{dp}\right)_{hom}dp,$$

and from this the former relation.

From the form for $\left(-\frac{dv}{dp}\right)_{het}$ in general, so not only at the beginning or at the end of the condensation, we see that the empiric isotherm can have an element in which it has an horizontal direction only when a nodal curve is intersected, at one or the other of whose ends $\left(\frac{dx}{dp}\right)_{bin}$ is infinitely large. But as neither the sides nor the nodal curve which runs parallel to the v-axis can be intersected, it would follow that the empiric isotherm can never run horizontally in one of its elements. There *are*, however, cases which form exceptions to this rule. First of all if we widen the idea empiric isotherm, and understand by it the section of a surface // v-axis with the derived surface of the ψ-surface, also in the case of a complex plait. Then there are also nodal curves to points in which the binodal curve passes through the spinodal, and where therefore $\left(\frac{dx}{dp}\right)_{bin}=\infty$. But as such equilibria are hidden equilibria, they cannot be realised in spite of this. Instead of this we have rectilinear intersection of the surface // v-axis with the three phase triangle, and in this part $\left(\frac{dv}{dp}\right)_{het}$ is, of course, again infinitely large. But secondly, and this is a case which might, indeed, be realised, the binodal curve has a point in which $\left(\frac{dx}{dp}\right)_{bin}=\infty$, when this point is a plaitpoint which with increasing or decreasing temperature will become a hidden plaitpoint. This is a limiting form of the first mentioned case, in which the three phase triangle was intersected. Then the three phase triangle has contracted to a single line, and the above mentioned straight line has contracted to a single point. Then there is, of course, a point of inflection of the empiric isotherm in that point. With larger volumes it is curved negatively, with smaller volumes positively.

Physics. — "*Isotherms of di-atomic gases and their binary mixtures. VI. Isotherms of hydrogen between* —104° C. and —217° C." By Prof. H. Kamerlingh Onnes and C. Braak. Comm. N°. 97^a from the Physical Laboratory at Leiden.

(Communicated in the meeting of December 29th 1906).

§ 1. *Introduction.*

The investigation treated in this Communication forms part of the investigation on the equation of state of hydrogen, which has been in progress at Leiden for many years. [1])

With that part of our measurements [2]) which we now deem fit for publication, we have more directly carried on the work that H. H. Francis Hyndman had already done with one of us (K. O.) before 1904, so that, though all the observations, one for this, another for that reason, but always for the purpose of reaching the desired accuracy (which, we may add, was increased in the course of the investigation) have been repeated, an important share of the final success of the measurements is due to the said investigator.

The results obtained by us furnish data for applying the correction of the readings of the hydrogen thermometer to the absolute scale experimentally (see the following communication), and for determining the deviation between the net of isotherms of hydrogen and that of the mean reduced equation of state (see Comm. N°. 71, June 1901 and Comm. N°. 74, Arch. Néerl. 1901) [3]). The points determined in

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[1]) In Comm. N°. 69 (March 1901), where the apparatus have been described which were used in this investigation, the Communications referring to this subject, have been mentioned. Since then the isotherm for 20° C. to 60 atms. was given in Comm. N°. 70 (May and June 1901) with the accuracy of which the open standard-manometer (Comm. N°. 44 Oct. 1898) and the closed standard manometers (Comm. N°. 50 June 1899) admit, which investigation is carried on in Comm. N°. 78 (March 1902) for the isotherms of hydrogen at 20° C. and 0° C., which have been determined with the apparatus that have also been used for this investigation. The suitability of these apparatus for accurate determinations of isotherms has been shown in Comm. N°. 78, and is confirmed by this Communication for low temperatures. Several communications e. g. N^{os}. 83, 84, 94^b and 94^f, further 85 and 95^b, finally N^{os}. 89, 93 and 95 are more or less in connection with this investigation, the great importance of which, if accurately carried out, is demonstrated in Suppl. N°. 9.

[2]) We soon hope to publish the results of measurements at higher pressures and lower temperatures, and also those of supplementary determinations at lower pressures.

[3]) Definitive values for the virial coefficients B and C (§ 12 contains only provisional values) from which the difference with those according to the reduced equation may follow, are given in the following communication.

the net of isotherms are only few in number, but these few points have been determined with particular care, so that, so to say, they form normal places in the examined region of the equation of state, with which without preliminary adjustment we may set about the calculation of individual virial coefficients. Characteristic of them is that every group of such normal places obtained by determinations with the piezometer and manometer (see Comm. N^{os}. 69 and 78) lies really on the same isotherm (that of about — 104°, — 136°, — 183°, —195°, —205°, —213° and —217°), and that on these same isotherms every time a point has been obtained at small density by a determination with the hydrogen thermometer (see Comm. N°. 95^e Oct. 1906). The great difficulty [1]) of this investigation lies in obtaining the required constancy and stability of the low temperatures. Accordingly the arrangement of reliable cryostats was made a separate subject of investigation at Leiden. (cf. Comm. N^{os}. 83 and 94).

This investigation comprises three series of piezometer-determinations at densities respectively about 70, 160, and 300 times the normal. [2]) Several of the observations mentioned here lie in the neighbourhood of the curve of the minima of $p\,v$. They enable us to determine the shape of this curve pretty accurately (see § 13).

We confine ourselves in this communication to our observations themselves. A discussion of them, also in connection with the results of other observers, will be given in a following communication.

§ 2. *Survey of the apparatus used.*

a. On Pl. I in fig. 1 we find a schematic [3]) representation of the system of the apparatus for measurements and auxiliary arrangements, excepted those which serve for keeping constant the temperature in the cryostat. The compression apparatus A is the same as that mentioned in Comm. N°. 84 (March '03). For the meaning of the system of tubes, cocks and other parts we may refer to Comm. N°. 69 and N°. 84. The same figures have been used, except that in this communication c_1 is used for the cock which admits the

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[1]) Witkowski, whose important investigation on the expansion of hydrogen (Bulletin de l'Académie des Sciences de Cracovie 1905) had already appeared before the experiments mentioned in this communication had been completed, already mentions this as an explanation for the fact, that he has dropped the direct determination of isotherms at temperatures lower than — 147°.

[2]) The limits are chiefly given by the pressure under which the gas stands; they are about 20 and 60 atms.

[3]) The individual apparatus are represented on the same scale, the connections schematically.

compressed air, and c_2 for the cock which shuts off the level glass. Of the compression tube, provided with the system of cocks, mercury-reservoir and level-glass belonging to it a front-view is given in fig. 3 of Pl. I. The piezometer with the connections g_1 and g_2 has been represented in detail in fig. 2 of Pl. I.

The arrangement of the cryostat B which has served for the determinations mentioned in this communication, is described in Comm. N°. 94^a.

For the description of the apparatus serving for keeping the temperature in the cryostat constant, we may also refer to this last communication. Fig. 4 of Pl. I may also serve for elucidating this description for the special case that our piezometer is placed in the cryostat.

The pressure is conveyed (see fig. 1, Pl. I) from the compression-tube to the manometer along c_{11}, c_8, c_{12}, c_{13}, c_{14} and c_{15}. By closing and opening c_{12} the differential-manometer E [1]) may be shunted in and out. By means of the cocks c_8 and c_{13} it may be shut off from the rest of the pressure-conduit, when great differences in pressure are brought about, or are to be feared. [2]) [3]). The apparatus are placed in two rooms as has been indicated in the figure by a dotted line. By closing one of the cocks c_{13} and c_{14} the two parts may be treated as independent systems. This was done when the manometer was compared with the open manometer connected at c_{17}. The manometer C is the same as served for the investigations of Comm. N°. 78. The reservoir D serves, if necessary, for eliminating the injurious influence of small leaks, for which purpose it is placed in ice. At c_{16} it can be coupled to the system. In the experiments of this communication there was no need to use it [4]). The pressure is exerted by compressed air, which enters through c_1 and c_{19} along the drying tubes F and G; and is regulated by blowing off along c_{24}. The cocks c_{15}, c_{18}, c_{20}, c_{21}, c_{22} and c_{23} have analagous meaning to c_{11}, c_7, c_3, c_4, c_5 and c_6.

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[1]) This manometer, which was formerly used with the open standard-manometer, (see C fig. 1 Comm. N⁰. 44) and had now been removed to the piezometer, was of great use for finding leaks.

[2]) A couple of mercury-receptacles, which served for receiving the mercury that might overflow, have not been represented in the figure.

[3]) The system which we have so far described and which belongs to the piezometer, is placed in one of the rooms of the laboratory, situated in the immediate neighbourhood of the cryogen department. The remaining apparatus which chiefly belong to the manometer are erected in the room with the standard-manometer.

[4]) The adjustment of trays of oil for the different couplings rendered the search for leakages so easy, that an injurious leak needed never to remain.

All couplings of the conducting tubes in which air is to be kept at constant pressure, have been placed (cf. the plate to Comm. N°. 94^b) in trays filled with oil, according to what has been said in Comm. N°. 94^b.

b. With regard to the means for keeping a constant temperature in the cryostat, the system of pumps and auxiliary arrangements for the regulation of the temperature, belonging to the circulation of oxygen, has been represented in fig. 4 of Pl. I. For a description we refer to Comm. N°. 94.

Some particulars about the ethylene circulation used for the determinations of Series I, are to be found in Comm. N°. 94^f XIII § 1.

§ 3. *The manometer.*

The pressure measurements were performed by means of the closed auxiliary manometer described in Comm. N°. 78^c. As a comparison of this manometer made in 1904 with the standard manometer A IV (of Comm. N°. 78 § 17), yielded an unsatisfactory result, and led us to expect that the auxiliary manometer was no longer reliable, it was compared at four points with the open standard manometer, to which the improvements mentioned in Comm. N°. 94^b were applied [1]). The results of this comparison have been combined in the subjoined table.

Column *C* like column *C* of table XVII of Comm. N°. 78^c represents the reading of the pressure determined with the open manometer (Comm. N°. 44). Every value is the mean of two observations. Column *F* gives the pressure read by means of our closed auxiliary manometer. Each of the values has been obtained as a mean from three observations. In the calculation the calibration derived in Comm. N°. 78^c has been used. In column *G* the difference of the columns *F* and *G* is represented, column *H* contains this same difference expressed in the numbers of column *C* as unity. The pressure given by the auxiliary manometer appears to be too high for all pressures observed. It was obvious to ascribe this to a too high value assumed for the normal volume [2]).

If we take the mean of the values in column *H*, we find 0.00087. If we diminish the normal-volume and so also the pressures by this part of the original amount, the differences represented in

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[1]) In the investigations with this manometer of Comm. N°. 70 the total absence of leaks was rare; here, however, it was easily brought about. Also the improved coupling of the steel capillaries to the glass-capillaries of the open manometer by platinizing proved satisfactory. (See Comm. N°. 94^b).

[2]) In connection with this diminution of the normal volume see also Comm. N°. 95^e, § 11.

column K remain between the indications of the auxiliary manometer and the open standard manometer. These differences, considerably smaller than those in table XVII of Comm. N°. 78c, remain within the limits of accuracy fixed for this investigation, and justify us to estimate the mean error in the pressure measurements at $\pm \frac{1}{3000}$.

In the following the pressures have been calculated with this new value of the normal volume.

TABLE I. Manometer.

C	F	G	H	K
24.247	24.264	+ 0.017	0.00070	— 0.00017
36.290	36.333	+ 0.043	0.00120	+ 0.00033
47.960	48.004	+ 0.044	0.00092	+ 0.00005
60.022	60.061	+ 0.039	0.00065	— 0.00023

§ 4. *The piezometers and auxiliary apparatus.*

The piezometer used in the first series for the observations at a density 70 and the temperatures —104°, —136°, —183°, —195°, was of about the same dimensions as that used for the observations of Comm. N°. 78. In the subjoined table, just as in the corresponding table II of that communication, the dimensions are given to facilitate a survey of the amount and the influence of the many corrections.

TABLE II. Data H_2, Series I.

$U_1 = 6.4110$ cm³. $\beta_1 = 5.0 \, . \, 10^{-6}$ [1]
$U_2 = 0.0530$ » $\beta_4 = 4.7 \, . \, 10^{-6}$
$V_3 = U_3 = 1.198$ »
$V_4 = 6.0174$ »
U_4 has been determined from a calibration table
$V_5 = 576.077$ cm³.
$v' = 0.722$ » per cm.

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[1] The values of β given here have been determined for the ordinary temperature and those for lower temperatures have been put equal to them. We hope soon to determine β also for lower temperatures.

The stem b_4 (see Pl. II Comm. N°. 69), on which the volume U_4 is read, was 30 cm. long in order to enable us to determine every time three points on the isotherm which did not lie too near each other [1]). In others of our piezometers it was taken still longer.

For the series II and III a piezometer of larger dimensions was used.

The necessity of the use of a larger gas-volume for determinations at densities higher than 120 times the normal has already been mentioned in § 19 of Comm. N°. 84. The volumenometer described there was not used, but just as in Series I the normal-volume was determined in the piezometer itself.

As in the preceding table the dimensions of the piezometer are given here.

TABLE III. Data H_2, Series III.

$U_1 = 5.1583$ cm³.	$\beta_1 = 3.7 \,.\, 10^{-6}$
$U_2 = 0.0382$ »	$\beta_4 = 4.7 \,.\, 10^{-6}$
$V_3 = U_3 = 1.407$ »	
$V_4 = 10.9645$ »	
$U_4 =$ (see preceding table)	
$V_5 = 2063.30$ cm³.	
$v' = 1.617$ » per cm.	

In Series II the piezometer-reservoir had a volume of 10.343 cM³, but for the rest it had the same dimensions as in Table III.

To detect any escaping of gas during the measurements at high pressure in consequence of leakages at the connections g_2 and g_3 (see Pl. II Comm. N°. 69), cylindric glass oil-trays were placed round these couplings (see Pl. I fig. 2) which enabled us to discover immediately even the slightest leakage; everywhere the oil-trays rendered excellent services, but here they were of the greatest importance for obtaining reliable results [2]).

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[1]) They may serve, inter alia, to give us information about the curvature and the inclination of the isotherms at the middle point.

[2]) Once the oil-trays near the couplings g_1 and g_2 rendered good services, when before the determinations of Series III gas escaped in consequence of the nut g_2 being imperfectly screwed on. From a determination of the normal-volume made immediately afterwards, it proved to have changed so much that the previous determinations had to be rejected.

§ 5. *The hydrogen.*

The filling was accomplished for Series III with all the improvements described in Comm. N°. 94^e § 2. For the first series the purification by means of cooling in liquid air was not yet applied, in the second series it was, but without application of high pressure.

§ 6. *The temperatures.*

The temperatures t_4 and t_3 respectively of the divided stem b_1 and the steel capillary g_1 (see Comm. N°. 69 Pl. II) were determined in the same way as in Comm. N°. 78 § 13. In series I three thermometers were placed along the steel capillary, and one at the part of the glass capillary f_2 that remained outside the cryostat. The refrigerating action of the cryostat proving to be very slight even in the immediate neighbourhood, only three thermometers were used in the following two series, two at the ends and one in the middle of the steel capillary. The influence of an error of 1° C. in the temperature of the capillary (comp. Comm. N°. 78 § 13) is only $\frac{1}{4000}$ of the total compressed volume at $-100°$ and $\frac{1}{10000}$ at $-200°$. For the temperature of the glass capillary we assumed here that indicated by the thermometer at the end of the steel capillary. This simplification is the more admissible as the temperature in the cryostat is lower, and hence the volumes outside it contain less gas.

The temperature of the glass capillary in the cryostat has been determined in the same way as was followed in the investigations with the hydrogen thermometer mentioned in Comm. N°. 95^e. As the arrangement of the cryostat was the same in the two cases, and the measuring-apparatus placed in it had almost the same form, there was no objection to start from the previously found data for the determination of the temperature of the capillary. (see Comm. N°. 95^e § 4). This method gives sufficient accuracy, as, reasoning in a similar way to that followed in the said communication, we arrive at the result, that an error of 50° in the temperature of the part of the stem that is taken into consideration still gives a negligible error in the final result, viz. less than $\frac{1}{5000}$.

The temperature t_1 of the piezometer-reservoir was determined by means of the resistance-thermometer, which (cf. Comm. N°. 95^c) had beforehand been compared with the hydrogen-thermometer.

They differ little from those at which the calibration of the resistance-thermometer took place. Hence the reductions are simple and may be effected with great accuracy.

The temperatures were not calculated directly from the resistance formula of comm. N°. 95 § 6, but they were based on the separate readings of the hydrogen-thermometer, because the latter must also serve as points of the isotherms. From the above mentioned formula $\frac{dt}{dw}$ was determined, and by the aid of this factor the reduction was effected.

The difference of temperature for which the reduction was made amounting to less than 0.°3, this method of calculation is perfectly sufficient; only for the temperature of — 135°.71, where the difference amounts to 4°, another correction of 0.°01 was required.

In the subjoined table[1]) the method of calculation has been represented for one determination of the temperature. The first column contains the observed resistance W, in the following column W_c represents the resistance at which the resistance-thermometer has been compared with the hydrogen-thermometer (of comm. N°. 95^c Table I § 6), and T represents the corresponding reading of the hydrogen-thermometer. From the value $\frac{dt}{dw}$ and $W—W_c$ follows now the temperature-correction Δt which is to be added to T_c in order to give t_1 on the hydrogen-thermometer-scale.

TABLE IV. Temperature of the bath during observation N°. 7 of Series III.

W	W_c	T_c	$\frac{dt}{dw}$	Δt	t_1
17.295	17.290	— 212°.832	1.750	+ 0°.009	— 212°.82

§ 7. *The measurements.*

At the beginning and the end of every series the normal-volume was determined in the way described in Comm. No. 78 § 12, only with this difference that in the series mentioned here every determination of the normal-volume was supplemented with a reading in the U-tube b_2 and one of the barometer. In this way two determinations were generally made before and after every series. The values found before and after every series, differ nowhere more than $\frac{1}{2000}$.

The tables V and VI are analogous to the tables VII and VIII of Comm. N°. 78. In the former the results are represented referring to

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[1]) The difference of the numbers in this table with those of the Dutch text is due to an improved calculation. The influence of this improvement enters also in some numbers of the last part of this communication.

the determination of the normal-volume for series III, the latter comprises the three series.

TABLE V. Normal volume H_2, Series III.

N°.	Volume.	Pressure.	$p\,v_A$	Mean.	Mean.	Difference.
1	1955.78	75.546	1945.56	1945.58		— 0.17
2	1955.82	75.545	1945.60		1945.73	— 0.13
9	1961.39	75.342	1945.87	1945.87		+ 0.14
10	[1962.04	75.327	1946.13 1)			+ 0.40]
11	[1962.31	75.317	1946.14			+ 0.41]

TABLE VI. Normal volumes H_2.

Determinations.		Before.	After.	Mean.	Difference.
Series I	N°. 1	544.74	544.82	544.78	— 0.05
	2				— 0.02
	10				+ 0.02
	11				+ 0.07
Series II	1				— 0.60
	2	1945.73	1946.10		— 0.46
	3				— 0.23
	11			1946.16 2)	+ 0.05
	12				— 0.18
	21	1946.10	1946.64		+ 0.39
	22				+ 0.58
	23				+ 0.47
Series III		1945.58	1945.87	1945.73	see Table V

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1) The two last determinations have been left out of account, though they show but slight deviations, because on account of variations of temperature in the room a certain cause could be assigned for the apparent rise of the normal-volume.

2) A determination of the normal volume was made in this series both before and after, and also between the determinations at high pressure. The value given here is the mean from these three determinations.

As far as the pressure permitted, three points were chosen in every series on every isotherm for the determinations of the isotherms ascending with about equal differences of density, which offers advantages for the calculation of the virial coefficients (see § 12). The readings were adjusted at these points by bringing the mercury at the bottom, in the middle and at the top of the divided stem b_4. By way of control the two points in the middle and at the bottom of the stem were for some determinations determined once more with decreasing pressure.

For every determination we waited till both the temperature and the pressure were constant, and we could assume that the equilibrium of temperature and pressure had been established. This will be the case when the meniscus in the divided stem is moving up and down within the same narrow limits. The stability of the temperature was ensured by a good regulation, and that of the pressure was easily obtained and preserved by paying attention to the oil-trays mentioned in § 2, which immediately betrayed the slightest leakage [1]).

When the above mentioned constant state had set in, some readings of the piezometer and the manometer were alternately made. If they agreed, we proceeded to the next point.

With regard to the regulation of the temperature the measurements took place under the same circumstances as the investigations with the hydrogen thermometer described in Comm. N°. 95^e (Oct. 1906). Besides the resistance-thermometer for regulation and determination of the temperature the thermo-element was also used here by way of control for the determination of the temperature. The indications of the resistance-thermometer, however, proving more reliable than those of the thermo-element, only those of the latter apparatus were used for the calculations. All possible care was always taken that the temperatures at which determinations were made, lay as close as possible to those which have been used for the calibration of the resistance-thermometer to render the corrections small, and the accuracy of the determination of the temperature as great as possible.

The regulation of the pressure took place according to the indication of the metal manometer *M* of Pl. I, fig. 1. If we passed but slowly from one pressure to the other the thermal process in the reservoir which attended it, was so slight, that the regulation and the measure-

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[1]) Formerly this often required a long and sometimes fruitless search (cf. e.g. comm. N°. 70 p. 8).

ment of the temperature did not experience any perceptible disturbance, on account of which the stability of the bath was the more ensured throughout a whole determination of an isotherm.

§ 8. *Calculation of the observations.*

The calculation is made in the same way as described in Comm. N°. 78 § 8.

For the calculation of the variability of the volume of the piezometer-reservoir U_1 at low temperatures we started from the quadratic formula for k found in Comm. N °. 95^b § 1, so that $k_1 = 23.43 \times 10^{-3}$ and $k_2 = 0.0272 \times 10^{-6}$. No correction for glass-expansion was required for the volume of the glass capillary U_2 nor for that of the steel capillary U_3. For the reduction of the gasvolume in the glass capillary U_2 to 0° we proceeded as follows: the volume was divided into 5 parts U_{2a}, U_{2b}, U_{2c}, U_{2d} and U_{2e}. U_{2a} represents the part in the liquid bath increased by 2 cm. of the capillary above the liquid, where the temperature may still be put equal to that of the bath. U_{2b} U_{2c} and U_{2d} form together the remaining part of the capillary in the cryostat above the bath, $U_{2b} + U_{2c}$ corresponds to the volume u'_2 of § 5 of Comm. N°. 95^e and U_{2d} to u''_2. U_{2e} is the volume of the capillary that is outside the cryostat. For the reduction of the volumes U_{2b}, U_{2c} and U_{2d} we started from the same determinations of the temperature as in Comm. N°. 95^e. As on account of the greater density at lower temperatures the mean temperature found cannot directly be used for the reduction, each of the above mentioned volumes is divided into 3 parts, the temperature of each of these parts is derived, and from this the mean temperature is determined according to the formula $t = \dfrac{\Sigma \frac{t}{T}}{\Sigma \frac{1}{T}}$ in which T represents the absolute temperature. The coefficients of expansion, which are required for the reduction, were determined by means of the general development into series of Comm. N°. 71 with a slight modification of the coefficients mentioned there. The results obtained in this way do not give an appreciable difference with those which were found when the reductions are made with the approximate results for the determinations of the isotherms obtained in this way.

With regard to the corrections of the temperature of the volumes U_3 and U_4 we proceeded in a way similar to that of Comm. N°. 78. For that of the reservoir at low temperature a somewhat different way was followed. As practically the temperature for every individual determination of the temperature might be considered as constant (see § 1), a number of parts of isotherms could be immediately obtained for every series separately. As they at the same time refer to about the same densities, an accurate value may be derived for $\left[\frac{d(pv_A)}{dt}\right]_{t_1 v_A}$ from the graphical representation of pv_A on $\frac{1}{v_A}$. The temperatures in the different series not differing more than 0.°2, the results could be reduced to one and the same standard-temperature in this way without the slightest difficulty. As standard-temperatures were assumed the temperatures —103°.57 and —135°.71 of series I, —182°.81 and —195°.27 of series II and —204°.70, —212°.82 and —217°.41 of series III. In the subjoined table the values of $\left(\frac{pv_{At''} \; pv_{At'}}{t''-t'}\right)_{v_A}$ are given, which served for the reduction of the remaining determinations of the isotherms to these standard temperatures t_s, which relate to the hydrogen-thermometer at constant volume and 1100 mM. pressure at 0°.

TABLE VII. H_2 $(a_p)_{t_{s_1}}^{t_{s_2}}$ Series II.

Density.	$(a_p)_{-182°.81}^{-195°.27}$	$(a_p)_{-195°.27}^{-204°.83}$	$(a_p)_{-204°.83}^{-212°.98}$
150	0.004336	0.004406	0.004501
160	0.004390	0.004458	0.004540
170	0.004440	0.004513	0.004588
184	0.004508	0.004599	0.004667

From these mean coefficients values for $\left[\frac{d(pv_A)}{dt}\right]_{t_1 v_A}$ could be derived for the different points of the respective isotherms, which for the isotherm of —212°.82 have been given in Table XI of § 10.

§ 9. *Survey of a determination.*

As an instance of determinations of isotherms at low temperatures we give here one of the measurements from the 3rd series at a density 326 times the normal, in oxygen boiling under strongly reduced pressure.

TABLE VIII. H_2 Series III N° 7. Determination in oxygen at about — 213° C.

Time 3.10—3.20	A	B	C	D	E	F	G	H	K
Piëzometer top	5.8	56.496	— 213°	20°.76	19°.5				
rim	4.8	56.360	— 188°		19°.4	21.6			
division n° 29	7.0	56.864	— 98°		19°.4				
			— 11°						
Manometer						5.0	93.97	19.98	
								20.04	
Piëzometer top	5.9	56.493		20°.76	19°.4				
rim	4.8	56.360				21.6			
					19°.3				
Manometer						5.0	93.97	20.00	
								20.05	
Float									1.3

The columns of the table agree in the main with those of table IX of Comm. N° 78^b. A and B have the same meaning, C denotes the temperature t_1 of the piezometer-reservoir in the bath, and the temperatures t_{2b} t_{2c} and t_{2d} in the order of the parts U_{2a} U_{2b} and U_{2c} (see § 8) of the glass stem in the cryostat above the bath. The temperatures given in this column are to be considered as constant throughout the determination, and have, therefore, been mentioned only once. D gives the temperature t_4 of the waterbath round the stem b_4, E the temperatures t_3', t_3'' and t_3''' of the thermometers placed along the steel capillary. The temperature of the part U_{2e} that projects above the cryostat is put equal to t'_3. The columns F, G and H have the same meaning as in the above mentioned table. In column K the indication of the float in the cryostat has been given. All lengths are in cms.

These readings are corrected in the same way as was followed for table X of Comm. N°. 78^b. These corrected values are given in the following table. The two readings of the piezometer have afterwards been united to a mean after reduction.

TABLE IX. H_2, Series III. Determination at about —213° C. Corrected and recalculated data.

	A	B	C	D	E	F	G	H	K
Manometer mean						115.5	93.97	19.93	
Temperatures t_1, t_4, t_3			—213°	20°.70	18°.6				
t_{2b}			—188°						
t_{2c}			— 98°						
t_{2d}			— 11°						
Piëzometer	28.634	0.135				82.3			
	28.631	0.132							
Surface of the liquid									1.9

The columns from *A* to *H* (*H* included), have the same meaning as those of table X of Comm. N°. 78^b. *K* denotes the position of the liquid level above the boundary of the piezometer-reservoir and the glass stem, derived from the indications of the float.

From this the following table is obtained, which gives the corrections of volume and pressure required for the calculation of pv_A. It corresponds to table XI of Comm. N°. 78.

The volumes of the parts of the glass capillary with their corrections have been separately given. Moreover the corrections u'_3 and h have been added, the former is a consequence of the packings being pressed down at g_1 and g_2, the latter accounts for the weight of the compressed air in the connecting tube between the manometer and the piezometer. The vertical distance of the levels of the mercury is about 0.5 meters. Instead of the mean coefficient of expansion k, the double term $k_1 + k_2 t$ has been assumed (cf. § 8) for the computation of the correction w_1.

Here we must point out that as standard temperature t_x for the reduction of the parts into which the glass capillary is divided, + 20° has been assumed, so that the differences $t_x—t_2$ are not very small here. The method of interpolation applied in Comm. N°. 78 for small values of $t_x—t_2$ will be used as soon as we have tables for d_{xp_2} at our disposal. The values have been directly determined here by calculation.

TABLE X, H_2. Series III. Corrections and final result.

$U_1 =$ 4.4904 cm³.	$p_m =$ 61.004 atm.
$w_1 =$ 0.0003 »	$H_p =$ 0.434 »
$w'_1 =$ 0.0014 »	$h = -$ 0.004 »
$u_1 = -$ 0.0104 »	
$u_3 =$ 0.0018 »	$u'_3 = -$ 0.0005 cm³.
$U_{2a} =$ 0.0018 »	$u_{2a} =$ 0.0059 »
$U_{2b} =$ 0.0020 »	$u_{2b} =$ 0.0049 »
$U_{2c} =$ 0.0025 »	$u_{2c} =$ 0.0024 »
$U_{2d} =$ 0.0129 »	$u_{2d} =$ 0.0015 »
$U_{2e} =$ 0.0190 »	$u_{2e} =$ 0.0001 »
$w_1 = -$ 0.0239 »	$w'_1 =$ 0.0012 »
$(pv_A)_{t_1} =$ 0.18863	$t_1 = -$ 212°.82
$(pv_A)_{-212°.82} =$ 0.18863	for $p =$ 61.434 atms.

The total value of the correction of the stem appears to be very small, so that we might apply the law of GAY—LUSSAC down to —217° without introducing appreciable errors.

§ 10. *Values of pv_A.*

The values of pv_A obtained in this way for the different determinations have been represented for the isotherm of —212°.82 in the following table. The values in the last columm refer to the reduction to the standard-temperature t_s (cf. the conclusion of § 8).

The values of this table have been obtained, as appears from table IX, by calculation with the mean values of the separate readings. The deviations in these separate readings which may be due both to oscillations of the pressure and the temperature and to errors in the readings themselves, amount nowhere to more than $\frac{1}{2000}$.

The result found for about the same point at the beginning and at the end of one determination of an isotherm are in very good accordance, as moreover is to be seen by comparing observation

TABLE XI. H_2. Results for the isotherm of —212°.82.

N°.		t_1	p	pv_A	d_A	$\left[\frac{d(pv_A)}{dt}\right]_{t_1 v_A}$
Series II	17	— 212°.98	30.591	0.19406	157.64	0.00458
	18		35.426	0.19134	185.15	0.00473
	19		33.071	0.19264	171.68	0.00465
	20		30.554	0.19405	157.46	0.00458
Series III	6	— 212°.82	51.632	0.18767	275.12	
	7		61.434	0.18863	325.68	

N°. 17 and N°. 20 of table XI. The results are reduced to the same standard-temperature by means of the values of $\left[\frac{d(pv_A)}{dt}\right]_{t_1 v_A}$ given in the last column.

In table XII the results obtained in this way are also given for the remaining isotherms. Those belonging to series I are less certain and will be repeated.

The results obtained at the beginning and at the end of a determination of an isotherm at about the same density have been united to a mean.

For every temperature we have added to the results of the determinations of isotherms those of the readings of the hydrogen-thermometer to which the former are in direct relation.

The numbers do not agree with those of the preceding table, because some determinations have been united to a mean, for which reason they are indicated by ( ).

The points of the hydrogen-thermometer have been obtained in the following way. From SCHALKWIJK's determinations of isotherms follows for 20° C.

$$pv_A = 1.07258 + 0.000667\, d_A + 0.00000099\, d_A^2.$$

If we suppose the mean pressure-coefficient from 0° to 20° not to deviate appreciably from the value 0.0036627 between 0° and 100°, which is permissible on account of the insignificant deviations of the indications of the hydrogen-thermometer of constant volume from the absolute scale, it follows from this that:

$$(pv_A)_{0°,\,1100\,mm.} = 1.000275.$$

The value given in Comm. N°. 60 having been taken for the pressure-coefficient of hydrogen for the calculation of the hydrogen

TABLE XII, H_2. Values for $(pv_A)_{t_s}$.

N⁰.	t_s	p	pv_A	d_A
H_2 therm. (1)	— 103°.57	0.896	0.62082	1.444
Series I (2)		32.985	0.63467	51.971
(3)		39.659	0.63765	62.193
(4)		49.897	0.64274	77.632
H_2 therm. (1)	— 135°.71	0.727	0.50307	1.445
Series I (2)		28.592	0.51064	55.991
(3)		33.437	0.51258	65 231
H_2 therm. (1)	— 182°.81	0.479	0.33051	1.448
Series II (2)		46.572	0.32700	142.42
(3)		55.293	0.32822	168.46
H_2 therm. (1)	— 195°.27	0.413	0.28486	1.449
Series II (2)		40.599	0.27367	148.35
(3)		45.484	0 27337	166.36
(4)		49.998	0.27343	182.85
H_2 therm. (1)	— 204° 70	0 363	0.25031	1.449
Series II (2)		35.487	0.23189	153 03
(3)		38.640	0.23097	167.30
(4)		42.438	0.23010	184.43
Series III (5)		61.917	0.23009	269.10
H_2 therm. (1)	— 212°.82	0 320	0.22056	1.450
Series II (2)		30.689	0.19480	157.64
(3)		33.200	0.19339	171.68
(4)		35.566	0.19210	185.15
Series III (5)		51.632	0.18767	275.12
(6)		61.434	0.18863	325 68
H_2 therm. (1)	— 217°.41	0.295	0 20375	1.450
Series III (2)		46.419	0.16381	283.81
(3)		52 898	0.16336	323 80
(4)		58.971	0.16424	359.04

thermometer-temperatures, the value of pv_A at t_s now follows from the formula

$$(pv_A)_{t_s} = (pv_A)_0 \, (1 + 0.0036627 \, t_s).$$

§ 11. *Probable error of a determination.*

The mean error in the calibration of the large volume of the piezometer may be estimated at $\pm \frac{1}{4000}$. As to the volume into which the gas is compressed during the measurements, the greater density of the gas in the reservoir at low temperatures may be allowed for by reckoning only with $\frac{1}{3}$ of the amount of the volumes at the temperature of the room. The errors in these volumes being predominant with respect to those in the volume of the piezometer reservoir, the mean error for measurements below —180° with piezometers of 5 c.M^3 may be put equal to $\pm \frac{1}{3000}$ of the compressed volume in accordance with the degree of accuracy as was calculated in Comm. N^0. 69, where for measurements at the ordinary temperature the mean error is estimated at $\pm \frac{1}{1000}$ for piezometers of 5 c.M^3. For —100° the mean error will be $\pm \frac{1}{2000}$.

The mean error of the determinations of the normal volume is $\pm \frac{1}{3000}$, that of the measurements of the pressure may also be estimated at $\pm \frac{1}{3000}$.

In the determination of the temperature there is no appreciable error. The observations made for one point show that the mean error due to variations of temperature and faulty readings of the position of the mercury in the stem, may be put smaller than $\pm \frac{1}{5000}$.

The mean error of the determination of temperature in the stem remains below $\pm \frac{1}{6000}$.

The mean error caused by all these sources of errors together amounts to $\pm \frac{1}{1500}$ for piezometers of 5 c.M.^{3} and not very low temperature, to $\pm \frac{1}{1700}$ for larger piezometers and very low tempeure. The different points on one and the same isotherm must show smaller discrepancies inter se than corresponds with the said mean error. The mean error namely, for a determination, apart from the errors in the determination of the normal volume and the calibration of the large volume is ± from $\frac{1}{2000}$ to ± $\frac{1}{2400}$.

All this does not apply to the isotherms of — 103°.57 and — 135°.71. These belonging to series I are the earliest determinations and for different reasons less accurate than the later ones.

§ 12. *Provisional individual virial coefficients.*

If the temperatures had not been given as readings on the hydrogen-thermometer of constant volume at 1100 mm. pressure, but on the absolute scale, the coefficients A_A, B_A etc. calculated from the equation

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v^2_A} + \frac{D_A}{v^4_A} + \frac{E_A}{v^6_A} + \frac{F_A}{v^8_A} \quad . \quad . \quad . \quad (1)$$

with the values of pv_A from table XII, could be immediately compared with those derived in Comm. N°. 71 [1]). However, this is not the case, because the latter relate to the absolute scale of temperature. From the outset it has been our purpose to derive the correction of the hydrogen scale on the absolute scale experimentally from our measurements themselves. This might be attained by first neglecting the correction, and by calculating provisional values A'_A, B'_A, C'_A etc. for each of the isotherms, which serve then for finding provisional corrections for the hydrogen-thermometer; after this the calculation is repeated with the corrected temperatures, etc., till further repetition would not bring about any change. A similar treatment has been applied for the determination of the corrections of the readings of the hydrogen-thermometer to the absolute scale, where we purposed to draw through the observations for every isotherm a curve, which does not only correspond as closely as possible to the observations, but also to the general equation of state. In this §

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[1]) We must call attention to the fact that in the calculations of Comm. N⁰. 71 we began by taking 273°.04 by first approximation for the absolute zero-point; we should find the correction to this from the results of the calculations of isotherms, and then proceed to a second approximation. We have still retained 273°.04 in VI. 1 Suppl. N⁰. 8 and in VI. 2 Comm. N⁰. 92. Since then, however, a set of coefficients VII. 1, which will be published in the following communication, have been calculated with the further approximation for the absolute temperature, viz. the more accurate value 273°.09, and corrections have, moreover, been applied in critical quantities etc.

the method of least squares has been applied directly to the individual isotherms, in order to obtain a formula which represents the observations as accurately as possible.

The number of points on each isotherm not being large enough for all six coefficients to be determined at once, definite values were assumed for the last three values. F_A was put $= 0$, and values were calculated for D_A and E_A from the sets of coefficients VII.1 [1]), which was chosen instead of V of Comm. N°. 71. This assumption means, that a definite course was prescribed for the isotherms at higher densities, which corresponds as closely as possible to the law of the corresponding states. The results of these calculations are laid down in the subjoined table. D_A and E_A are the values assumed for the calculation according to the above.

TABLE XIII. H_2. Provisional virial coefficients.

t_s	A'_A	$10^3 . B'_A$	$10^6 . C'_A$	$10^{12} . D'_A$	$10^{18} . E'_A$
— 103°.57	0.62048	0.24271	0.5584	0.9113	— 0.648
— 135°.71	[0.50303	0.03234	1.7974	0.7028	— 0.408]
— 182°.81	0.33063	— 0.08384	0.4021	0.3809	— 0.088
— 195°.27	0.28503	— 0.13051	0.3565	0.2892	— 0.016
— 204°.70	0.25058	— 0.18030	0.3710	0.2166	0.031
— 212°.82	0.22090	— 0.22433	0.3668	0.1514	0.066
— 217°.41	0.20410	— 0.25013	0.3715	0.1122	0.082

It appears from the table, that the coefficients of the same column vary regularly with the temperature, except for — 135°.71, for which we may account by taking into consideration that the two piezometer-determinations which had to be used for the calculation, lie so close together, that a slight difference in their relative situation already produces a large difference in B'_A and C'_A.

By the aid of the coefficients the values of pv_A were determined anew according to formula (1). The divergencies for every isotherm between the assumed values of pv_A, W_i and the R_{oi} calculated with A'_A, B'_A and C'_A ($pv_A = 1$ for 0° and 760 mm.), where i indicates the number of that observation in table XII, have been represented in the subjoined table.

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[1]) For the calculation of D_A and E_A the uncorrected reading of the hydrogen thermometer was used (see preceding note).

TABLE XIV H_2. Deviation from formula (1).

t_s	$10^5\,(W_i - R_{oi})$						in $^0/_0$ of R_{oi}					
	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$
—103°.57	—1	+7	—9	+3			0.001	0.011	0.015	0.005		
—135°.71												
—182°.81												
—195°.27	+1	+1	—4	+2			0.004	0.004	0.014	0.007		
—204°.70	—1	+9	0	—9	+1		0.004	0.036	0.000	0.036	0.004	
—212°.82	—2	+5	+6	—2	—17	+10	0.007	0.022	0.027	0.009	0.077	0.045
—217°.41	0	0	—3	+2			0.001	0.000	0.014	0.010		

The isotherm of — 212.°82 is best adapted to give an idea of the accuracy of the mutual agreement on account of its larger number of points. The agreement proves very satisfactory. The upper limit of the mean error may be put at $\pm\dfrac{1}{2000}$.

§ 13. *Minima of pv.*

By means of the coefficients of table XIII the following minima of the *pv*-curves were derived from the data of table XII.

TABLE XV. H_2. Minima of $p\,v_A$.

t_s	$p\,v_A$	d_A	p	$W - R_0$
— 182°.81	0.32630	102.24	33.36	— 0.08
— 195°.27	0.27338	174.45	47.69	+ 0.50
— 204°.70	0.22935	227.47	52.10	— 0.75
— 212°.82	0.18780	285.55	53.63	+ 0.26
— 217°.41	0.16335	315.72	51.57	+ 0.08

By means of the method of least squares the coefficients of a parabola

$$p = P_0 + P_1\,(pv_A) + P_2\,(pv_A)^2$$

have been calculated from these data [1]). They are:

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[1]) It is to be remarked that the less certain isotherms of — 104° and — 136° are not used in this deduction.

$$P_0 = -\ 2.623$$
$$P_1 = \ 552.610$$
$$P_2 = -\ 1354.86.$$

The differences $W - R_0$ between the given values of p and those calculated with these coefficients have been represented in the last column of table XV. They amount to little more than ½ atmosphere. The results given in the table have been reproduced in a diagram on Pl. II [1]; the curve traced there is the calculated parabola.

It follows further from the values of the coefficients, that the parabola cuts the ordinate $p = 0$ in two points, where pv_A is respectively 0.00480 and 0.40307, from which follows with the formula [2])

$$(pv_A)_T = 0.99939\ \{1 + 0.0036618\ (T - 273°.09)\}$$

for the corresponding temperatures measured on the absolute scale,

$$T_1 = 1°.3 \qquad\qquad T_2 = 110°.2.$$

The top of the parabola lies at a pressure of 53.73 atms. the value of pv_A is here 0.20394, from which follows, in connection with the value of $\left(\frac{d(pv_A)}{dt}\right)_{p=53.73}$ determined from the isotherms, viz. 0.0053, for the absolute temperature of the isotherm which passes through the top that

$$T = 63°.5.\ ^{3})$$

Physics. — *"On the measurement of very low temperatures. XIV. Reduction of the readings of the hydrogen thermometer of constant volume to the absolute scale."* By Prof. H. Kamerlingh Onnes and C. Braak. Communication N°. 97^b from the Physical Laboratory at Leiden.

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

§ 1. *Introduction.*

As it is till now difficult to obtain pure helium, and very easy to obtain pure hydrogen (c.f. Comm. N°. 94^f, June 1906), the scale of the normal hydrogen thermometer (that with constant volume under a pressure of 1000 m.M. of mercury at 0°) is for the

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[1] The temperatures have been given in absolute degrees below zero. The temperatures noted down on the plate undergo slight alterations on account of a more accurate calculation of the corrections to the absolute scale. They become —103°.54, —135°.67, —182°.75, —195°.20, —204°.62, —212°.73 and —217°.32.

[2] This value of A_{AO} has been calculated from Schalkwijk's determinations of isotherms (cf. the conclusion of § 10).

[3] In this the corrections to the absolute scale have been taken into account.

present, just as when it (1896) was first mentioned as the basis of the measurement of low temperatures at Leiden in the first communication (N°. 27) on this subject, still the most suitable temperature-scale to determine low temperatures down to —259° unequivocally with numerical values, which come nearer to the absolute scale than those on any other scale. It is therefore of great importance to know the corrections with which we pass from the normal hydrogen-scale to the absolute one.

As is known they may be calculated for a certain range of temperatures, when the equation of state for this region of temperature has been determined at about normal density. Up to now we had to be satisfied for that calculation for the hydrogen thermometer below 0° with equations of state of hydrogen obtained in a theoretical way. BERTHELOT [1]) derives them by means of the law of the corresponding states from experimentally determined data of other substances in the same region of reduced temperature. CALLENDAR [2]) modifies VAN DER WAALS' equation of state so as to render it adapted to represent the results of the experiments of JOULE—KELVIN for air and nitrogen as well as those for hydrogen between 0° and 100°, and supposes that a same form of equation holds also for hydrogen outside this region. Chiefly this comes to the same thing as the application of the law of the corresponding states, albeit to a limited group of substances. Though such theoretic corrections as have been given by BERTHELOT and CALLENDAR are a welcome expedient to help us in default of other data [3]), yet an experimental determination of these corrections remains necessary.

We have obtained them in this research by using the isotherms of hydrogen between —104° C. and —217° C. given in Comm. N°. 97^a.

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[1]) Sur les thermomètres à gaz, Travaux et Mémoires du Bureau International, T. XIII.

[2]) Phil. Mag. [6] 5, 1903.

[3]) WROBLEWSKI's determinations of isotherms at the boiling point of ethylene and oxygen are not accurate enough for this purpose. In the results found for the last temperature this is immediately apparent from the irregular situation of the points on the isotherm. The values obtained at the boiling-point of ethylene give more harmonious results. And yet a correction on the absolute scale would follow from them which has the wrong sign, viz. — 0°.07.

At the temperature of liquid air TRAVERS has determined the difference of the hydrogen thermometer of constant volume and constant pressure, from which we may also derive the corrections to the absolute scale for these temperatures. It is obvious that this derivation cannot be very trustworthy.

Further it is now possible (see § 1 of Comm. N°. 97^a) to derive data on the expansion of hydrogen at low temperatures from the determinations of WITKOWSKI; they will be discussed in a following communication.

For the calculation of these corrections at a definite temperature we might start from the individual virial coefficients in the development into series of the equation of state (cf. Comm. N°. 71, 1901), which we have derived in § 12 of Communication N°. 97^a. The results obtained in this way show really a regular course[1]), in spite of the small number of points on the isotherms.

However, we wished first to adjust the results of the separate isotherms by general formulae of temperature. Both in this case and in general it is very difficult to succeed in this by application of one of the equations of state drawn up in a finite form. Very suitable for such a purpose is the general development into series (or more strictly speaking, development into a polynomial), which has already been mentioned frequently. We chose for this the form VII. 1 (cf. the footnote to § 12 of Comm. N°. 97^a). The adjustment takes place by calculating for every isotherm modifications in B and C, ΔB and ΔC, which we call individual ΔB and ΔC, with an approximate value of the correction to the absolute scale, by then representing the values of ΔC by a general formula of the temperature, and by computing new values for ΔB by successive approximation in such a way that the value for the correction on the absolute scale corresponds to the assumed value of T. Finally also the values of ΔB were represented by a general formula of the temperature.

If we put the new values of B and C obtained by the aid of these corrections, which *special* values we denote by VII. H_2. 1 in the polynomial of state, then this represents at the same time the determinations of isotherms of Comm. N°. 70 at 20° very satisfactorily, and those of Comm. N°. 78 at 0° and 20° by approximation.

By means of these general expressions the reductions on the absolute scale have been carried out.

If B and C are known there is another way to derive the absolute temperature from the observations with the hydrogen thermometer, than by applying the corrections which lead from the hydrogen scale to the absolute temperature scale. In the calculation of the temperature from the observations we may namely take at once into account, that the gas in the thermometer does not follow the law of BOYLE-CHARLES, but that pressure and volume are connected in the way, as is indicated by the development into series with the corrected values of B and C. The formula which may serve for this purpose, is given in § 5.

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[1]) Only the isotherm of — 135°.71 gives a deviating result. (See the conclusion of § 12 of the preceding communication).

§ 2. *Reduction of the readings of the hydrogen thermometer of constant volume to the absolute scale.*

If v is the volume of the gas in the thermometer, expressed in the theoretical normal volume, p the pressure in atmospheres, T the absolute temperature, the equation of state for the thermometer gas may be written in the form:

$$pv = A_T \left(1 + \frac{B'_T}{v} + \frac{C'_T}{v^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Further we put:

t the temperature on the scale of the hydrogen thermometer of constant volume

and

$$T - T_{0^\circ \text{C.}} = \theta .$$

t is determined by

$$t = \frac{(pv)_T - (pv)_0}{(pv)_0 \, \alpha_p} ,$$

where α_p represents the mean pressure-coefficient between 0° and 100° for the thermometer with the specific volume v. This is given by $\dfrac{(pv)_{100} - (pv)_0}{100 \, (pv)_0}$.

If we represent the correction on the absolute scale by:

$$\Delta t = \theta - t ,$$

we may write for this:

$$\Delta t = \frac{(T - T_0)\left(\dfrac{T_{100}B'_{100} - T_0 B'_0}{100\, v} + \dfrac{T_{100}C'_{100} - T_0 C'_0}{100\, v^2}\right) - \left(\dfrac{TB'_T - T_0 B'_0}{v} + \dfrac{TC'_T - T_0 C'_0}{v^2}\right)}{1 + \dfrac{T_{100}B'_{100} - T_0 B'_0}{100\, v} + \dfrac{T_{100}C'_{100} - T_0 C'_0}{100\, v^2}} \qquad (3)$$

In agreement with what may be derived from the mean equation of state VII. 1, it appears from our determinations, that the influence of C'_T is very slight, and down to — 217° does not amount to more than 0°.0003, so that it has not to be taken into account. Therefore in what follows will be put $C'_T = 0$, as is also done by BERTHELOT but without proof.

For the absolute zero point the value 273°.09 ¹) is assumed, from

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¹) From AMAGAT's experiments with the development into series of Comm N^o. 71 (cf. the note to § 12 of Comm. N^o. 97^a) 1.26×10^{-5} was found for the difference between the pressure-coefficients of nitrogen at 1000 mm. pressure and 0 mm. pressure, from which follows with CHAPPUIS' pressure-coefficient for 1000 mM., i. e. 0.0036744 the value 0.0036618 for the limiting value at 0 mM. pressure, corresponding to the absolute zero point — 273°.09. In the same way hydrogen gives for the difference of the pressure-coefficients at 1090 mM. and 0 mM. 2.1×10^{-6}, which with the pressure-coefficient 0.0036629 given in Comm. N^o. 60 (see XV) gives

which follows $A_T = 0.0036618\, T$, $T_{0^\circ C.} = 273^\circ.09$ and $T_{100^\circ C.} = 373^\circ.09$.

For the reduction of the data given in Comm. N°. 97^a to the theoretical normal volume the value $\frac{v_A}{v} = 0.99939$ was taken, borrowed from the determinations of isotherms of Comm. N°. 70 (SCHALKWIJK).

The values of B'_0 and B'_{100} have been derived from the same determinations of isotherms [1]) by the aid of the pressure-coefficient 0.0036629 (see XV at the end of this Communication), neglecting the correction to the absolute scale for 20°. These values are: [2])

$$B'_0 = 0.000607 \qquad B'_{100} = 0.000664$$

The values of B'_T were found from the VII. H_2. 1 already more fully discussed in § 1, which gives in a reduced form [3])

$$10^8\, \mathfrak{B} = +\,173.247\, t - 462.956 - 706.416 \frac{1}{t} + 384.2458 \frac{1}{t^3} - 4.2530 \frac{1}{t^5}$$

whereas VII. 1 gives:

$$10^8\, \mathfrak{B} = 157.9500\, t - 305.7713 - 231.8247 \frac{1}{t} - 97.5686 \frac{1}{t^3} - 4.2530 \frac{1}{t^5}$$

From this the values of B'_T have been calculated for the standard temperatures of the isotherms.

The subjoined table contains in the first column these standard temperatures t_s measured on the scale of *our* hydrogen thermometer,[4])

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the limiting value 0.0036608. The same value as was found above from nitrogen, was derived by BERTHELOT (loc. cit.) from CHAPPUIS' results for nitrogen and those for hydrogen obtained with a thermometer-reservoir of hard glass. In the same paper he derives the value 273°.08 for the absolute zero-point for the case that also the less concordant results found by CHAPPUIS for hydrogen with a platinum-thermometer are taken into account. Afterwards (see Zeitschrift für Elektrochemie N°. 34, 1904) the first mentioned value 273°.09 is again found by taking the mean of the above values for nitrogen and hydrogen, and those which may be derived by means of the experiments of KELVIN and JOULE.

[1]) Compare the conclusion of § 10 of Comm. N°. 97^a.

[2]) The values found by CHAPPUIS are resp. 0.000579 and 0.000606.
Those of WITKOWSKI are 0.000616 and 0.000688.
Those derived in Comm. N°. 71 from the observations of AMAGAT are 0.000669 and 0.000774.

[3]) According to DEWAR, $p_K = 15$ atms. and $T_K = 29^\circ$ are used for the calculation, which also served for the derivation of VII. 1.
Further have been put $A_{A0} = 0.99939$ and $A_A = A_{A0}\,(1 + 0.0036618\, t)$.

[4]) The slight differences with the value of table XII of Comm. N°. 97^a are due to a correction (see XV) in consequence of the application of the improved pressure-coefficient 0.0036629 and the influence of the dead space on the determinations of the temperature, which will be more fully discussed in the last part of this communication.

in the second column the same temperatures measured on the absolute scale. The two following columns contain the corresponding values of the special B'_T and of the corrections to the absolute scale $\Delta\, t_s$ calculated according to formula (2) for a hydrogen-thermometer of constant volume with 1090 mm. zero-point-pressure. The last column gives the corrections for the *normal* hydrogen-thermometer.

The values for — 103°.56 and — 135°.70 are less certain than the others (compare § 10 and § 11 of the preceding communication).

TABLE XVI. H_2. Corrections to the absolute scale.

t_s	ϑ	$B'_T.10^3$	$\Delta\, t_s$	$\Delta\, t$
— 103°.56	— 103°.54	+ 0.3892	0°.0214	0°.0196
— 135°.70	— 135°.67	+ 0.2368	0°.0316	0°.0290
— 182°.80	— 182°.75	— 0.2327	0°.0530	0°.0486
— 195°.26	— 195°.20	— 0.4734	0°.0611	0°.0561
— 204°.69	— 204°.62	— 0.7244	0°.0683	0°.0627
— 212°.81[1]	— 212°.73	— 1.0112	0°.0752	0°.0690
— 217°.40	— 217°.32	— 1.2167	0°.0796	0°.0730

With very close approximation the results of the last column may be represented by the formula:

$$\Delta t = a\,\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + d\left(\frac{t}{100}\right)^4 \quad . \quad . \quad . \quad (4)$$

where:

$$a = -\ 0.0143307$$
$$b = +\ 0.0066906$$
$$c = +\ 0.0049175$$
$$d = +\ 0.0027197$$

The greatest deviation is three units of the last decimal.

The formula gives the value $\Delta t = 0$, both for $t = +100°$ and for $t = 0°$, while $\Delta t = +0°.14$ would follow from it for $t = -273°$.

§ 3. *Accuracy of the corrections.*

The influences which may cause errors in the corrections, are of two kinds.

1. Errors in the values of B'_T.
2. Errors in the data which have been used in the further derivation.

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[1] The difference with Comm. N°. 97*a* remaining after the correction of the preceding note is the consequence of an improvement applied in the calculation.

The latter may be reduced to the error in B'_0 and the difference of the pressure-coefficients used for the density $= 0$ and that at 0° and 1090 mM. If for the mean error in B'_0 we compare the values of B'_0 which may be derived from the data of Comm. N^os^. 70 and 78 and from those of CHAPPUIS, a mean error of ± 0.000034 (about agreeing with the error per cent derived for the pv in § 11 of Comm. N°. 97[a]) follows from their deviations inter se, which corresponds with a mean error of ± 0°.008 at — 100° and of ± 0°.003 at — 200° for Δt.

We may further assume that the mean error in the pressure-coefficients 0.0036618 and 0.0036629 amounts to one unit of the last decimal for the first and to two units for the second, which corresponds with a mean error in Δt of ± 0°.003 and ± 0°.006 at — 100° and of ± 0°.005 and ± 0°.011 at — 200°.

If we further put the mean error in B'_T equal to that of B'_0, a mean error in Δt corresponds to this of ± 0°.006 at — 100° and of ± 0°.002 at — 200°.

The total mean error in consequence of all these mean errors together will amount to ±0°.012 for —100° and ±0°.013 for —200°.

§ 4. *Comparison of the results with those which have been theoretically derived.*

Table XVII contains the corrections concerning the normal hydrogen

TABLE XVII. H_2. Corrections to the absolute scale.

t	Δt		t	Δt		
	experimental values	according to VII. 1		according to Callendar	according to Berthelot	from experimental values
— 103°.56	0°.0196	0°.0017	— 10°	0°.00021		0°.0015
— 135°.70	0°.0290	0°.0032	— 20°	0°.00048		0°.0031
— 182°.80	0°.0486	0°.0082	— 50°	0°.00164		0°.0082
— 195°.26	0°.0561	0°.0108	— 100°	0°.0054	0°.008	0°.0187
— 204°.69	0°.0627	0°.0136	— 150°	0°.0132		0°.0337
— 212°.81	0°.0690	0°.0168	— 200°	0°.0311	0°.06	0°.0593
— 217°.40	0°.0730	0°.0192	— 240°		0°.18	
240°		0°.0470	— 250°	0°.1005		
— 250°		0°.0925				

thermometer. Besides the above mentioned values of Δt, which were directly found from the observation it contains the corrections determined according to the serial formula VII. 1 and those calculated by CALLENDAR and BERTHELOT. Moreover in the last column the corrections, which may be calculated from the experimental values adjusted with VII. H_2 according to formula (4) are given for a comparison.

Besides the corrections derived from this investigation for the zero-point-pressure of 1000 m.M., also the values found by **BERTHELOT** and CALLENDAR are represented on the plate. The three curves have been indicated by I, II and III in the above mentioned order. Also II and III refer to a zero-point-pressure of 1000 m.M.

The values derived by CALLENDAR and BERTHELOT by means of the law of the corresponding states appear to deviate systematically from the experimental ones. With regard to the corrections according to VII. 1., in the derivation of which formula agreement in the region of the equation of state (between 0° and —217° for hydrogen) treated here, was not aimed at, we may observe that a modification is required for VII. 1 to give as good an agreement as possible also in this region. In the first place this agreement would require that for the calculation of VII. 1 those values were assumed for the critical quantities of H_2 which follow from the data of Comm. N°. 97^a. They are $p_k = 15$ atms. and $T_k = 43°$. This value of T_k would considerably increase the corrections given in table XVII according to VII. 1.

§ 5. *Formula to derive the temperature directly from the observations with the gas thermometer of constant volume.*

We suppose that the correction for the difference in pressure at the mercury meniscus and the thermometer-reservoir in consequence of the weight of the thermometer-gas is applied to H_T, and that it is so small that it may be neglected for the small volumes.

The fundamental formula for the reduction is [1]:

$$pv = A_T\left(1 + \frac{B_T}{v} + \frac{C_T}{v^2}\right)$$

which may also be written in the form :

$$pv = A_T\left(1 + B_T^{(p)}\,p + C_T^{(p)}\,p^2\right) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We start from this latter formula. The equation for the gas-thermometer (cf. formula (1) of § 5 of Comm. N°. 95^c) becomes now :

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[1] Here v is expressed in the theoretical normal volume and hence $A_T = 1 + 0.0036618\,\theta$. We call the value for 0° C., at which $\theta = 0$, A_{T_0}. It is 1.

$$H_T\left[\frac{V_0(1+k_1\,t+k_2\,t^2)+\beta_1+u_1}{A_T(1+B^p_T\,H_T+C^p_T\,H^2_T)}+\frac{u_2'}{A_{t_2'}(1+B^p_{t_2'}\,H^2_T)}+\right.$$

$$\left.+\frac{u_2''}{A_{t_2''}(1+B^p_{t_2''}\,H_T)}+\frac{u_3}{A_{t_3}(1+B^p_{t_3}\,H_T)}+\frac{u_4}{A_{t_4}(1+B^p_{t_4}\,H_T)}\right]=$$

$$=H_0\left[\frac{V_0+\beta_2+u_1+u_3'+u_2''+u_2'''}{A_{T_0}(1+B^p_{T_0}\,H_0+C^p_{T_0}\,H^2_0)}+\frac{u}{A_{15}(1+B^p_{15}\,H_0)}\right]\quad . \quad . \quad . \quad (6)$$

This formula holds also for the carbonic acid thermometer up to the number of decimals given by CHAPPUIS. In XV we shall further discuss the deviation of the formula used by CHAPPUIS.

With a sufficient degree of approximation the formula for the determination of the temperature down to 0°.001 with a hydrogen thermometer of 1100 m.M. zero point pressure and a dead space $\frac{u}{V_0} < 0.01$ may be written in the simpler form:

$$H_T\left[\frac{V_0(1+k_1\,t+k_2\,t^2)+\beta_1+u_1}{A_T(1+B^p_T\,H_T)}+\frac{u_2'}{1+0.00366\,t_2'}+\right.$$

$$\left.+\frac{u_2''}{1+0.00366\,t_2''}+\frac{u_3}{1+0.00366\,t_3}+\frac{u_4}{1+0.00366\,t_4}\right]=$$

$$=H_0\left[\frac{V_0+\beta_2+u_1+u_2'+u_2''+u_2'''}{A_{T_0}(1+B^p_{T_0}\,H_0)}+\frac{u}{1+0.00366\times 15}\right]\quad . \quad . \quad . \quad (7)$$

First an approximate value may be assumed for B^p_T. With the approximate value of the temperature found in this way a better value of B^p_T may be determined, and the correction term for the expansion of glass calculated.

Thus we find A_T, from which the value of θ follows through

$$\frac{A_T-A_{T_0}}{0.0036618}=\theta.$$

XV. Influence of the deviation from the law of BOYLE—CHARLES *on the temperature, measured with the scale of the gas thermometer of constant volume according to the observations with this apparatus.*

§ 1. When the formulae are drawn for the calculation of the temperature on the scale of the gas thermometer of constant volume the variation of pressure of the gas both in the thermometer-reservoir and in the dead space has as yet (see e.g. CHAPPUIS) been generally entered into the calculation as if it took place at perfectly constant density.

The error committed in this way, is so slight for the permanent gases for small values of the dead space, that it manifests itself only in the last of the decimals given by CHAPPUIS. For CHAPPUIS' carbonic acid thermometer, however, it attains an appreciable value (the influence extends here to the last decimal but one), so that it was of importance to examine in how far it is permissible to neglect it. This appears when CHAPPUIS' formula is more closely compared with formula (6) of XIV.

The density not being constant, either in the thermometer-reservoir nor in the dead space, on account of the fact that e.g. at low temperatures gas passes from the dead space to the reservoir, and *pv* as well as the pressure-coefficient varies with the density, four approximations are applied in this treatment (two for reservoir and two for dead space), all giving an error in the same direction. (Adsorption is left out of account).

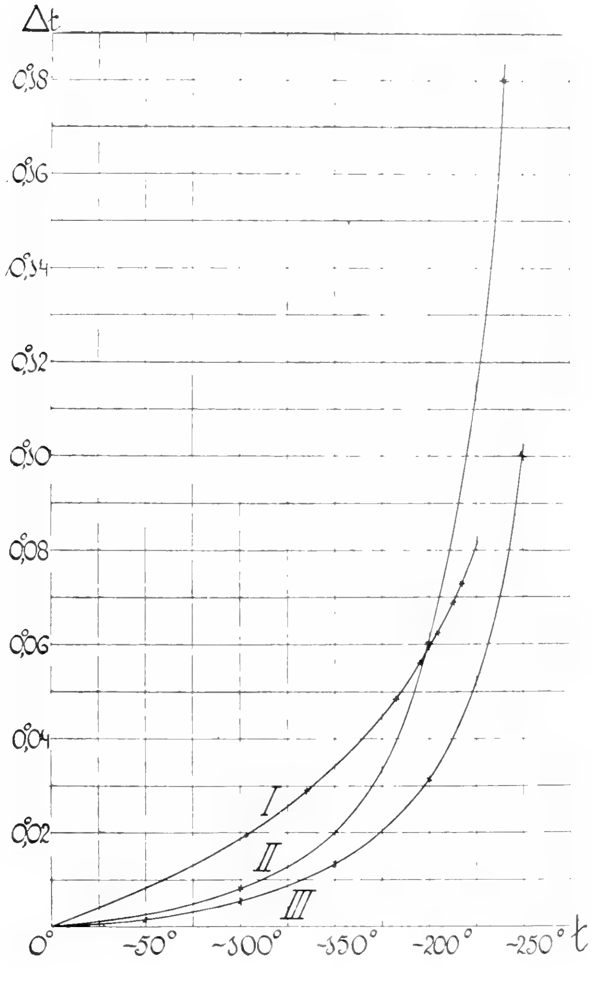
The errors caused by these approximations, are of the same order of magnitude for the reservoir and the dead space, the first applying to a large volume and a small difference of density, the second to a small volume and a large difference of density. The correction which is to be applied to the determination of temperature on account of these errors, only amounts to — 0°.001 at — 100° for a hydrogen-thermometer with 1000 mm. zero-point-pressure and a dead space of $0.01\,V_0$, to somewhat less for lower temperatures, and so it may be neglected below 0°.

Formula (6) differs from the preceding formula by one correction more, which is independent of the size of the dead space, and which is the result of the variation of density in the reservoir caused by the expansion of the glass. This error is of no importance for the determination of the temperature by the hydrogen-thermometer, but may exercise an appreciable influence in some cases. (cf. § 3).

The approximations mentioned have also an influence on the determination of the mean pressure-coefficient. The discussion, perfectly analogous to that for the influence on the determination of the temperature, gives + 0.00000019 as correction for our thermometer, which remains below the limit of accuracy given in Comm. N°. 60. Hence the value 0.0036627 derived in Comm. N°. 60 for hydrogen at 1090 mm. changes into the corrected value 0.0036629.

§ 2. We may pass from the temperatures derived in the way

Prof. H. KAMERLINGH ONNES and C. BRAAK. On the measurement of very low temperatures. **XIV.** Reduction of the readings of the hydrogen thermometer of constant volume to the absolute scale.



mentioned in Comm. N°. 95^e to those on the normal hydrogen-thermometer by availing ourselves of the subjoined table, in which the corrections required for this have been given. These corrections give an account of the variation in the assumed pressure-coefficient and (with regard to the number of decimals given) of the influence of the dead space.

TABLE XVIII. Corrections for the temperatures calculated according to Comm. N°. 95^e to those on the normal hydrogen scale.

t	Δt	t	Δt
— 50°	+ 0°.003	— 200°	+ 0°.016
— 100°	+ 0°.006	— 220°	+ 0°.019
— 150°	+ 0°.010	— 250°	+ 0°.020

By means of the fifth column of table XVI the corrections to the absolute scale are found. Thus the tables XVI and XVIII enable us to reduce the temperatures calculated according to Comm. N°. 95^e and used in Comm. N^os^ 95^a, 95^c and 95^d both to the normal hydrogen scale and to the absolute scale.

The temperatures t_s occurring in Comm. N°. 97^a, already corrected in the first column of table XVI for the application of the corrected pressure-coefficient 0.0036629 and the influence of the dead space, are adjusted to the absolute scale by the corrections in the fourth column of table XVI.

§ 3. The values found by CHAPPUIS and TRAVERS for the pressure-coefficient of hydrogen (cf. the footnote to § 7 of Comm. N°. 95^e) are corrected to 0.00366266 and 0.00366297 (number of decimals the same as given by them).

For the pression-coefficient of carbonic acid found by CHAPPUIS the correction is more considerable and amounts (because the dead space is small here, the correction on account of the variation of density caused by expansion of the glass is here about of the same value as that on account of the variation of density by the dead space) to -0.25×10^{-6}, so that the value found by CHAPPUIS [1]) 0.00372624 is corrected to 0.00372599.

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[1]) Nouvelles Etudes, Travaux et Mémoires du Bureau International. T. XIII, p. 48.

Physics. — *"Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. *XV. The case that one component is a gas without cohesion with molecules that have extension. Limited miscibility of two gases."* By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Supplement N°. 15 to the communications from the Physical Laboratory at Leiden.

(Communicated in the meeting of Februari 23, 1907).

§ 1. *Introduction.* In the Proceedings of Dec. '06, p. **502.** (Comm. N°. 96*b*) it was mentioned that the investigation of the ψ-surface of binary mixtures in which the molecules of one component have extension but do not exert any attraction, would be taken in hand as a simpler case for a comparison with what the observations yield concerning mixtures of He, whose molecules are almost without cohesion. Before long we hope to give a fuller discussion of such a ψ-surface [1]). In the meantime some results have already been obtained in this investigation, which we shall give here.

Thus it has appeared, that at suitable temperatures, at least if the suppositions concerning the applicability of VAN DER WAALS' equation of state with a and b not depending on v and T for constant x, mentioned in § 2 hold for these mixtures, [2]) *two different phases may be in equilibrium which must be both considered as gasphases.* Then the two substances which are the components of these mixtures, are not *miscible in all proportions even in the gas state.* And if certain conditions are fulfilled this may continue to be the case when the one component is not perfectly without cohesion, but possesses still some degree of cohesion, which, however, must be very slight.

From the considerations of VAN DER WAALS, Contin. II p. **41** et sqq. and p. **104**, follows that the mixing of two substances in the fluid state is brought about in consequence of the molecular motion depending on the temperature T, and promoted by the mutual attraction of the molecules of the two components determined by the quantity a_{12}, whereas the attractions of the molecules of each component inter se determined by a_{11} and a_{22}, oppose the mixing.

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[1]) VAN LAAR, These Proc. May '05, p. 38, cf. p. 39 footnote 1, treated the projection of the plaitpoint curve on the v, x-plane for such a mixture, without, however, further investigating the shape of the spinodal curve and of the plait.

[2]) The possibility of the occurrence of a longitudinal plait at temperatures above the critical ones of both components was supposed by VAN DER WAALS in his treatment of the influence of the longitudinal plait on critical phenomena. (Zittingsversl. Kon. Akad. v. Wetensch. Amst. Nov. 1894, p. 133). [Added in the English translation].

If the mutual attraction of the molecules of the two components a_{12} is small compared with the attraction of the molecules of one of the components inter se, a_{11}, the appearance of complete miscibility will be determined solely by the molecular motion, and then the temperature will have to be raised to an amount which, if some proportions of the b's can occur then, may greatly exceed the critical temperature of the least volatile component, T_{k_1}[1]), and with it the critical temperatures of all mixtures of these components. Thus from the equation (a) of VAN DER WAALS, Contin. II p. 43, follows $T_{km} = 1.6875\ T_{k_1}$ for the critical temperature of complete miscibility (VAN DER WAALS l. c.) T_{km}, if $a_{22} = a_{12} = 0$ and $b_{11} = b_{22}$ may be put. At a lower temperature the two substances considered are only partially miscible, whereas for such a temperature above T_{k_1} there may be coexistence of two phases which, as will be further explained in § 3 and 4, are to be considered as gas phases.

Now it seems to follow from the nature of most of the substances known to us, most likely from the structure of their atoms, that b_{22} is also small, when a_{22} becomes very small; hence for a gas without cohesion b_{22} may not be put equal to b_{11} of a gas with cohesion, and as according to the equation cited of VAN DER WAALS a small value of b_{22} furthers the mixing greatly, the critical temperature of complete miscibility cannot rise as high as was derived just now. But though most likely the case mentioned just now as example does not occur in nature, yet it is certainly conducive to a better insight of what is to be expected for gases of exceedingly slight cohesion.

§ 2. *The shape of the spinodal curves and the form of the plait on the ψ-surface for binary mixtures of which one component is a gas with molecules with extension and without cohesion.* In fig. 1 Pl. I the spinodal curves are represented for such a case. The figure refers to the ψ-surface for the unity of weight of the mixtures, as we hope to give a further discussion of such a ψ-surface (comp. § 1), also with a view to the treatment of the barotropic phenomena which may occur for these mixtures [2]) in case of a suitable proportion of the molecular volumes of the components, for which treatment the use of the ψ-surface for the unity of weight readily suggests itself. As was also mentioned in Comm. N^0. 96 b, the conditions for

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[1] VAN DER WAALS, in the paper cited p. 786 footnote [1], brought this in connection with the great amount of heat absorbed at the mixing of such substances. [Added in the English translation].

[2] Cf. Comm. N^0. 96a (Nov. '06), 96b (Dec. '06) and 96c (Dec. '06, Febr. '07).

coexistence may be studied by the aid of the ψ-surface for the unity of weight in the same way as by the aid of that for the molecular quantity; moreover it is easy to pass from the former to the latter, which offers advantages for the treatment of many problems (cf. § 6) if this is desired.

The equation of the spinodal curve on the ψ-surface for the unity of weight of mixtures, for which VAN DER WAALS' equation of state for binary mixtures with a and b not depending on v and T for constant x may be applied, and for which $a_{12} = \sqrt{a_{11} a_{22}}$, $b_{12M} = {}^1/_2 (b_{11M} + b_{22M})$ (cf. Comm. No. 96 *c*, Dec. '06, p. 510) may be put, [1]) runs:

$$R_1 R_2 T v^3 = 2 R_2 (1-x) \{ v \sqrt{a_{11}} - b_{11} \sqrt{a} \}^2 + 2 R_1 x \{ v \sqrt{a_{22}} - b_{22} \sqrt{a} \}^2 .$$

Here R_1 and R_2 are the gas constants for the unity of weight of the components concerned. For $a_{22} = 0$ this equation passes into:

$$4 \tau \omega^3 = (1-x) \left[\{ 3 \omega - (1-x) \}^2 + \frac{R_1}{R_2} \cdot \frac{b^2{}_{22}}{b^2{}_{11}} x (1-x) \right]$$

if we put $\dfrac{T}{T_{k_1}} = \tau$, $\dfrac{v}{v_{k_1}} = \omega$. The roots of this equation in ω have been determined by a graphical way for definite values of x and τ. The figure has been construed for mixtures for which $R_2/R_1 = {}^1/_2$, $b_{22}/b_{11} = {}^1/_4$ (cf. Comm. N°. 96*c*, Febr. '07, p. 600, footnote 2).

With reference to Fig. 1 we point out that for $T < T_{km}$ $(= 1.299\ T_{k_1})$ and $> T_{k_1}$ a spinodal curve closed on the side of the increasing v's, and together with it a similar plait, extends on the ψ-surface from the side of the small v's. At $T = T_{k_1}$ this plait reaches the side of the least volatile component. At lower T the spinodal curve has two distinct branches, and the plait runs in a slanting direction from the line $v = b$ to the side of the least volatile component.

Thus the investigation of mixtures with a gas without cohesion calls attention to a plait that starts from the side of the small volumes, and at lower temperature runs in an oblique direction to the side of the figure, which plait can be distinguished from the transverse and from the longitudinal plait.

The spinodal curve for $\tau = 1.040$ has a barotropic plaitpoint P_b. (see Fig. 1). For $1.299 < \tau < 1.040$ the angle with the v-axis of the tangent to the plait in the plaitpoint [2]) $\theta_{pl} > \frac{\pi}{2}$, for $1.040 < \tau < 1$ is $\theta_{pl} < \frac{\pi}{2}$. The barotropic phenomena for such a plait will be further

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[1]) The quantities a_{11}, a_{22}, a_{12}, b_{11}, b_{22}, b_{12}, etc. relate to the unity of weight, $a_{11}{}^M$, a_{22M} etc. to the molecular quantity.

[2]) Cf. Comm. N°. 96*b*.

discussed in a following communication (cf. N°. 96*c* Febr. '07, p. 660, footnote 1).

In Fig. 2 the course of the plait has been schematically represented for a temperature between the barotropic plaitpoint temperature and the critical temperature of the first component. The — - — - - curves denote the pressure curves, the — — — — curve the spinodal curve, the continuous curve the connode. The straight line AB is the tangent chord joining the coexisting phases A and B, CD is the barotropic tangent chord (Comm. 96*b*).

§ 3. *Limited miscibility of two gases.* For mixtures where as in fig. 2 a plait giving rise to phases *separated by a meniscus* which coexist in pairs, represented in the figure e.g. by A and B, while mixtures in intermediate concentrations are not stable, extends on the ψ-surface from the side of the small v's at temperatures above the critical temperature of the least volatile component, we shall call not only the phase B a gas phase, for which it is a matter of course, but also the other A; so the latter may be called a *second gas phase*, and we may speak of *equilibria between two gaseous mixtures* at those temperatures. That there is every reason to do so in the case treated in § 2 appears already from this, that the reduced temperature of the phase A, calculated with the critical temperature of the unsplit mixture with the concentration of A, is so high that already through its whole character the phase must immediately make the impression of a gas phase (so a second one).

The shape of the p-lines in fig. 2 shows further, how the two coexisting gas phases may be obtained by isopiestic and isothermic mixing, in which nothing would indicate a transition to the liquid state, from the gas phases M and N of the simple substances [1]).

We shall explain in the following § that it is really in accordance with the distinction between gas state and liquid state for binary mixtures in general, when we call A a second gas phase.

§ 4. *Distinction between gas and liquid state for binary mixtures.* It is true that since the continuity of the gas and the liquid state of aggregation has been ascertained, it may be said with a certain degree of justice that it is no longer possible to draw the line between the two states, but when in the definition of what is to be understood by liquid and what by gas we wish properly to express the difference and the continuity in the character of the heterogeneous region and the homogeneous region and to preclude con-

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[1]) Cf. footnote 1 p. 792.

clusions[1]) which are irreconcilable with the most obvious conception of phenomena, then the limits allowed for making this definition, are very narrow.

Thus for a simple substance no other distinction will be possible than by means of the isotherm of the critical temperature, and the border curve (connodal curve on GIBBS' surface), which is divided into two branches by the critical state (plaitpoint of the connodal curve), of which the branch with the larger volumes is to be defined as gas branch, that with the smaller volumes as liquid branch[2]). Liquid phases are only those which by isothermic expansion may pass into such as lie on the liquid branch of the connodal curve, and also the metastable[3]) phases lying between the connodal and the spinodal curves, which may be brought on the liquid branch of the connodal curve by isothermic compression[4]).

For binary mixtures the consideration of the ψ-surface of VAN DER WAALS leads in many cases to definitions which are just as binding.

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[1]) So THIESEN's definition, Z.S. für compr. und fl. Gase 1 (1897) p. 86, according to which e.g. strongly compressed hydrogen at ordinary temperatures would have to be called a liquid.

[2]) This is in harmony with the principle of *continuity of phase along the border curve* according to which a change of the character of the phases on a border curve can only occur in a critical point. For substances which at temperatures near the critical one, in states represented by points on, or in the vicinity of that branch of the connodal curve on GIBBS's surface which connects the liquid states at low temperatures with the plaitpoint, should be associated to multiple molecules of which the volume is *greater* than the volumes of the composing molecules together, this principle would admit the possibility that on the liquid branch of the border curve liquid phases should occur with greater volume than the coexisting gasphase. Such simple substances would then show the barotropic phenomenon, till now only found for binary mixtures. There is nothing known that points in the direction, of making the existence of such simple substances probable but there can be no more given a reason why it should be impossible. [Added in the translation].

[3]) The metastable states have not been included in BOLTZMANN's definition Gastheorie II, p. 45.

[4]) We do not accept the principle of the distinction of LEHMAN, Ann. d. Phys. 22 (1907) p. 474: "Erst die unterhalb der betrachteten Isotherme liegenden Kurven, welche in ihrem *S*-förmigen Teil unter die Abszissenachse hinunterreichen, entsprechen wahrer (tropfbarer) Flüssigkeit, d. h. einem Zustand, der negativen Druck zu ertragen im stande is", as depending on the meaning that the existence of capillary surface tension in liquids which can form drops, would presuppose that these liquids can bear external tensile forces, i. e. negative pressures without splitting up (cf. ibid p. 472 in the middle, and p. 475 at the top). [Added in the translation].

When discussing this we shall leave out of account the case of solid states of aggregation and three phase equilibria.

In the first place gas states are all the states on the ψ-surfaces on which there are no plaits. As criterion to divide states which belong to the stable or metastable [1]) region of ψ-surfaces which show plaits, into gas states and liquid states, analogy with the simple substance indicates their relation with the connodal curves of those plaits while for the metastable states the help of spinodal curves is to be called in.

For this first of all the distinction between the two branches of the connodal curve of a plait is required. For in the first place we shall have to give the same name to each of the two branches of a connodal curve separated by one or two plaitpoints throughout its length [2]).

Now, on account of the existence of the barotropic phenomenon we cannot simply call gas branch of the connodal curve that at which one of the isopiestically connected states has the smallest density [3]). It is therefore the question to indicate if possible on each branch a state whose nature is already known through the definition holding for simple substances or for those which behave as such when splitting up into two phases. In this different cases are to be distinguished.

For the case that the considered plait [4]) extends from one of the side planes $x=0$ or $x=1$ over the ψ-surface, follows from the definition of gas phase and liquid phase of a single substance that the branch of the connodal curve from the gas state of the pure substance to the plaitpoint is to be called gas branch, and also that the branch from the liquid phase of the simple substance to the plaitpoint is to be called liquid branch. The gas branch and the liquid branch of the spinodal curve may be distinguished in the same way as those of the connodal curve.

Let us restrict ourselves for the present to the distinction of gas and liquid in this case. In the first place we make use for this purpose of the isomignic (Comm. N°. 96*b*) compression and expansion.

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[1]) It follows from the nature of the case that unstable states have not to be considered here.

[2]) Cf. p. 790 footnote [2].

[3]) Even it if we wish to leave gravity out of account, and pay only attention to the molecular volume of the phase, the barotropic phenomena have yet called attention to the possibility that we may find the gas volume first larger and then smaller than the liquid volume when passing along the same connodal curve.

[4]) The case of the two plaits at minimum critical temperature is comprised in this.

Every phase which cannot be brought on the connodal curve through this operation, or if it can, comes on the gas branch, will have to be called a gas phase, every phase which is made to lie on the liquid branch through isomignic expansion is a liquid phase. Besides the phases lying between the connodal and the spinodal curve which isomignically may be brought on the liquid branch of the connodal are metastable liquid phases.

Besides the isothermic and isomignic compression without splitting there is another operation already mentioned in § 3, which may help us to form an opinion about the similarity of different phases, viz. the isopiestic and isothermic mixing. [1]) With regard to this phases which have been obtained by isopiestic admixing without splitting from phases of which it has been ascertained that they are to be called liquid phases, must be called liquid phases until in another way, (e. g. because no splitting takes place with isomignic compression and expansion) they have been proved to have passed into gas phases. [2]).

Proceeding to the case that the plait from higher temperature appears as a closed plait on the ψ-surface, as long as the plaitpoint which first comes into contact with the side with decrease of temperature, has not yet come into contact, and with decrease of temperature the plait has not yet reached a mixture which on splitting behaves as a simple substance, and for which the distinction in liquid state and gas state is therefore fixed, we shall have to consider that branch of the connodal curve on the side of this plaitpoint, which passes into that of the gas phase at lower temperature, as belonging to the ordinary gas phase, whereas the branch which passes into the liquid branch at lower temperature may be looked upon as a *second gas phase*, and we are the more justified in doing so as the temperature should lie further above the critical tempera-

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[1]) With the continuous isothermic and isopiestic mixing of two similar phases a and b the case may present itself (divided plait in the case of minimum crit. temp.), that an intermediate phase c of the other kind is obtained. So in general we cannot conclude to the similarity of c from the isothermic and isopiestic mixing of similar a and b.

[2]) This criterion is particularly of application to the retrograde condensation 2nd kind. For then phases on the connodal curve between the plaitpoint and the critical point of contact are liquid phases, phases on the p-curve through the plaitpoint and phases with the same x as the critical point of contact just the transitions to gas phases. The phases within the triangle bounded by these two lines and the connodal curve are also to be considered as liquid phases.

Here we abstract from the small uncertainties which would be caused in these definitions when capillarity ought to be taken into account. [Added in the translation].

tures of the unsplit mixtures belonging to the phases lying on them.

Whereas in the case, that at a temperature comparatively little lower also the other side of the ψ-surface is reached by the originally closed plait, the difference of the second gas phase with a liquid phase is still not very conspicuous, this may become very clear for the case of § 2, to which we have now got at last, that viz. with decreasing temperature a plait comes from the side $v = b_x$ on the ψ-surface, and the plait appears for the first time as longitudinal plait. Now we may again call *PBDF* the branch of the first gas phase, *PACE* the branch of the second gas phase. It will certainly be obvious to speak of gas phases when *all* the parts of the plait are found above the critical temperatures of the unsplit mixtures, and we shall decidedly *have* to speak of two gas phases, when the second branch of the connodal curve is intersected all over its length by isomignic lines on which beyond this plait no splitting up occurs, or if it is at most touched by one of them in the point $v = b$. For then it is beyond doubt that the final point of that branch must be called a gas phase.

Possibly also phases between the isomignic line of the critical point of contact, the line $v = b_x$ and the second gas branch belong to the second gas phase.

§ 5. *The surface of saturation for equilibria on the gas-gasplait.* In fig. 3, 4 and 5 the sections $T =$ const. of the p, T, x-surface of saturation for equilibria on the gas-gasplait have been schematically drawn for a mixture in which one component is a gas without, or almost without cohesion, in fig. 3 and 4 for temperatures higher than the critical temperature of the first component, in fig. 5 for this last temperature.

In these figures too the division of a gas phase into two gas phases, and the transition of a part of the gas region into the liquid region at $T = T_{k_1}$ is clearly set forth. The — — — — curve is the locus of the plaitpoints.

In a following communication, in which the properties of the ψ-surface for such mixtures will be further discussed, T, x-sections etc. will be drawn of this surface of saturation. At the same time it will then have to appear in how far *retrograde* unmixing of a phase into two other phases is to be expected.

That one of these phases may be called a second gas phase, appears in § 4.

§ 6. *On the conditions which must be fulfilled that limited mis-*

cibility of two gases may be expected. Now that it has appeared that on the suppositions mentioned in § 2 for mixtures in which one component is a gas without cohesion with molecules with extension, limited miscibility might be expected in the gas state, the question rises whether this phenomenon is also to be expected for mixtures with a gas of feeble cohesion. As on the said suppositions no maximum critical temp. is to be expected, this will be the case when $T_{km} > T_{k_1}$ is found. [1]) We have treated this question by the aid of the ψ-surface for the molecular quantity (cf. § 2). We arrive then at the equations developed by VAN DER WAALS Contin. II p. 43. The condition that $T_{km} > T_{k_1}$ is:

$$\{b_{22M}/b_{11M} - \sqrt{a_{22M}/a_{11M}}\}^2 > \frac{4}{27} b^3_M / b^3_{11M} \cdot \frac{1}{x_M(1-x_M)}$$

in which b_M and $x_M(1-x_M)$ follow from the equations given by VAN DER WAALS loc. cit. We find from this [2]) $T_{km} > T_{k_1}$,

for	$b_{22M}/b_{11M} = 2$	, if	$a_{22M}/a_{11M} < 0.58$
	1		0.053
	$^1/_2$		0.0037
	$^1/_4$		0.00023
	$^1/_8$		0.000015

It appears on investigation that only for few pairs of substances the ratios of the a's and b's [3]) will be able to satisfy this condition. The still unknown relations between a and b for a same substance, to which we alluded in § 1, and from which ensues that in general substances with small a also possess a small b, and that as a rule large b goes together with large a, seem to prevent this. He, which with a b which is still not very small compared with H_2 possesses a very small a, so feeble cohesion, and H_2O, which taking the value of a into consideration, has a comparatively small b, so a molecule of small volume, constitute exceptions to this general rule which are favourable for the phenomenon treated here.

If for He — H_2 : $b_{22M}/b_{11M} = {}^1/_2$, and $a_{22M}/a_{11M} = {}^1/_{175}$ (Comm. N°. 96*c*, Febr. '07. p. 660 footnote 2), $T_{km} < T_{k_1}$ must be expected on the above suppositions. Also for helium-argon and helium-oxygen e. g. the same thing must be expected. Most likely the ratios are

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[1]) Whether limited miscibility in the gas state may also occur if $T_{km} < T_{k_1}$ in certain cases and at suitable temperatures, will be discussed in § 7.

[2]) For $b_{22M}/b_{11M} = {}^1/_8$ e g. we find also $T_{km} > T_{k_1}$ for $0.125 > a_{22M}/a_{11M} > 0.061$. These cases will be further discussed.

[3]) See e. g KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen.

more favourable for mixtures of helium and neon[1]) than for those o helium and hydrogen.

For mixtures of helium and water the ratios for the above assumed a_{He} and b_{He} are such that for them limited miscibility in the gas state is to be expected, if the suppositions mentioned in § 2 are to be applied.

The coefficients of viscosity and of conduction of heat (cf. Comm. N°. 96*c*, Febr. '07 p. 660 footnote 2) admit a value of b_{He} which is still somewhat though only little higher; this might render it possible to realise the said phenomenon perhaps also for the other pairs of substances mentioned, especially when we bear in mind that its appearance is not excluded for $T_{km} < T_{k_1}$ (cf. p. 794 footnote 1).

The experimental investigation of these mixtures has been taken in hand in the Leiden Laboratory.

(Communicated in the meeting of March 30).

§ 7. *The shape of the spinodal curves and of the plaits for the case that the molecules of one component exert some, though still feeble attraction.* With very small value of the mutual attraction a_{12} of the molecules of the two components, in connection with the feeble attraction a_{22} of the molecules of one component inter se, the spinodal curve will with decreasing temperature extend more and more on the ψ-surface as in Pl. I fig. 1 from the side of the small v's, come into contact with the line $x=0$ at $T=T_{k_1}$, and then cross from the line $v=b$ to the side $x=0$ in two isolated branches[2]). We leave here out of account what takes place at lower temperatures when the spinodal curve approaches and reaches the side $x=1$ too.

To examine what shape the spinodal curve can have with greater attraction of the most volatile component, we shall avail ourselves of the suppositions introduced in § 2 and also applied in § 6 con-

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[1]) Cf. Ramsay and Travers, Phil. Trans. A. 197 (1901) p. 47 for data concerning refractive power and critical temperature of neon.

[2]) Here $\frac{dT_{xpl}}{dx} > 0$ for $x=0$. We see here that Verschaffelt's conclusion (These Proc. March 1906 p. 751) concerning the maximum temperature in the plaitpoint curve for mixtures, for which the component is indicated by a point from the region *OHK* (see fig. 2) must be supplemented by the possibility that he branch of the plaitpoint curve starting from the first component, goes to infinite pressures.

cerning the equation of state and the quantities a_{12} [1]) and b_{12}. In the net of spinodal curves for a given pair of substances 2 singular points may then occur, belonging to the spinodal curves for different temperatures. The values of x for these are determined by the equation:

$$\frac{x_M}{1-x_M} = \frac{3b_{11M}\sqrt{a_{22M}} \mp 2b_{11M}\sqrt[4]{a_{11M}a_{22M}} - b_{22M}\sqrt{a_{11M}}}{-b_{11M}\sqrt{a_{22M}} \mp 2b_{22M}\sqrt[4]{a_{11M}a_{22M}} + 3b_{22M}\sqrt{a_{11M}}} \qquad (1)$$

For very small a_{22} we find from this two singular points with $x > 1$, so not belonging to that part of the ψ-surface which can denote phases of mixtures. Of these two singular points that for which the lowest signs hold, passes through infinity for increasing a_{22}, and then approaches the line $x = 0$ on the other side of the ψ-surface. This line is reached for:

$$\sqrt[4]{a_{22M}/a_{11M}} = \frac{1}{3}\left\{-1 + \sqrt{1 + 3\, b_{22M}/b_{11M}}\right\} = m_1 \quad . \quad (2)$$

With increasing a_{22}/a_{11} the singular point, which appears to be a double point for this region, approaches the line $v = b$, which line is reached for:

$$\sqrt[4]{a_{22M}/a_{11M}} = -(1 - b_{22M}\, b_{11M}) + \sqrt{1 - b_{22M}/b_{11M} + (b_{22M}/b_{11M})^2} = m_2 \quad (3)$$

In this we assume $b_{22M} < b_{11M}$ [2]).

So if the mutual attraction of the molecules of the most volatile component and those of the other in connection with the attractions inter se attains a certain value — on the assumptions made for the calculations for $m = \sqrt[4]{a_{22M}/a_{11M}} = m_1$ — the spinodal curve for $T = T_{k_1}$ will no longer touch the side in K_1 (cf. fig. 1 Pl. I), but it

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[1]) In this first investigation of what may be expected for mixtures of helium, with a view of forming some opinion as to the conditions under which the experiments for this purpose are to be made, we put (§ 2), $b_{12M} = \frac{1}{2}(b_{11M} + b_{22M})$ $a_{12M} = \sqrt{a_{11M}a_{22M}}$ (cf. Comm. Suppl. No. 8, These Proc. Sept. '04 p. 227) in the calculations, no data concerning a_{12} and b_{12} for those mixtures being available as yet. Also VAN DER WAALS (These Proc. Febr. '07, p. 630) assumes that as a rule $a_{12M} < (a_{11M} + a_{22M})$. It will be necessary for a complete survey concerning the different possibilities to make also other suppositions about a_{12M} (cf. VAN DER WAALS l.c., KOHNSTAMM ibid p. 642), at the same time taking care that a and b are not put independent of v and T, at least not both (cf. VAN DER WAALS, These Proc. Sept. '05 p. 289) and that they may only be put quadratic functions of x by approximation.

If also for mixtures with very small a_{22}, a_{12M} might be $< \sqrt{a_{11M}a_{22M}}$ (cf. KOHNSTAMM l c.), the phenomena of limited miscibility under discussion might still be sooner expected.

[2]) For $b_{22M} > b_{11M}$ the other singular point comes from side $x = 1$ on the ψ-surface for a smaller value of a_{22M}/a_{11M}. As probably this case does not present itself for the pairs of substances with small a_{22}/a_{11} known to us, we shall not discuss it.

will have a double point there, in which the two branches of the spinodal curve intersect each other and the line $x=0$ at an angle. In this case the critical temperature of the least volatile component is not changed in first approximation by small quantities of admixtures.

With greater attraction of the most volatile component — on the suppositions mentioned for $m_1 < m < m_2$ — a spinodal curve on the ψ-surface will have a double point. This will lie the nearer to the side of the small v's, the more the attraction of the most volatile component increases. With a certain value of the attraction — $m = m_2$ — the spinodal curve reaches the line $v=b$ with a double point, with greater attraction the spinodal curve will proceed from $x=0$ on the ψ-surface with decreasing T, and touch the line $v=b$ at $T=T_{km}$. On the suppositions mentioned for $b_{22M}/b_{11M} < {}^{16}/_{21}$ the contact with the line $v=b$ will here take place at temperatures $> T_{k_2}$, for $b_{22M}/b_{11M} > {}^{16}/_{21}$ at $T < T_{k_2}$, so that in the latter case the spinodal curve comes first into contact with the line $x=1$.

In the first case $(b_{22M}/b_{11M} < {}^{16}/_{21})$ a plait will come from $x=0$ and at lower T, whereas for larger m a branch plait directed to the side $x=1$ may develop: if $m < m_2$ it will be united through an homogeneous double plaitpoint (KORTEWEG, *Archiv. Neerl.* 24 (1891)), with a plait coming from $v=b$ to a plait that crosses from one side to the other, if $m > m_2$ it will pass into such a plait by contact with $v=b$.

In the second case the plait which becomes from $x=0$ will again united with one coming from $v=b$ for smaller m; for larger m a branch plait will have developed before this union takes place or before the spinodal curve touches the line $v=b$.

The shape of the spinodal curve for these cases with always greater attraction of the most volatile component, where we shall have to consider three phase equilibria, need not be discussed for the present, as they do not belong to the case of a component with feeble attraction [1]).

For some values of b_{22M}/b_{11M} table I gives the values $a_{22M}/a_{11M} = m^4$, calculated from the equations (2) and (3). If we compare with this the values of a_{22M}/a_{11M} for which $T_{km} = T_{k1}$ (§ 6) we see that they really lie between those calculated here.

The shape of the spinodal curves for a case, in which $m_1 < m < m_2$, has been represented on plate II, for the ψ-surface of the unity of weight (cf. § 2), with the relations and data assumed in § 2, except that $a_{22}/a_{11} = 0.00049$ (or $a_{22M}/a_{11M} = 0.00196$).

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[1]) Cf. moreover VAN LAAR, Arch. TEYLER (2) 10 (1906), These Proc. Sept. '06 p. 226.

TABLE I.

b_{22M}/b_{11M}	$m_1{}^4$	$m_2{}^4$
1/2	0.0014	0.0179
1/4	0.000134	0.000527
1/8	0.000011	0.000022

The plait extending on the ψ-surface from $v=b$ for a temperature $> T_{k1}$, will have to be considered as a gas-gasplait according to § 4 (cf. § 6). Also a similar plait for $T < T_{k_1}$, if the connodal curve is not touched by an isomignic line, and is nowhere cut by an isomignic line which intersects the connodal curve of the plait coming from $x=0$ [1]. According to § 4 we shall be justified in considering also the plait lying on the side of the small v's for $T_{k_1} > T > T_{dpl}$ (temperature for which the double plaitpoint considered occurs) as gas-gasplait, if the temperature is above the critical temperatures of the unsplit mixtures for all parts of that plait. That there can be some reason for doing so, appears when we calculate the reduced temperature for the double plaitpoint for some cases, e.g. for the ratios b_{22M}/b_{11M} and the m_2 belonging to it, mentioned in Table I.

Putting $b_{22M}/b_{11M}=n$ the double plaitpoint temperature is determined by:

$$T_{dpl}/T_{k_1}=\frac{27}{4}\,m\,(1+m)\,\frac{(n-m^2)^2}{(n+m)^3}$$

and

$$v_{dpl}\;v_{k_1}=\frac{2}{3}\,\frac{m}{(1+m)^2}\cdot\frac{(n+m)^2}{m\,(2-m)-n\,(1-2m)}$$

So for the case represented on Plate II we find:

$$x_{dpl}=0.587,\;\; T_{dpl}/T_{k_1}=0.966,\;\; T_{dpl}/T_{kx}=2.17.$$

(*To be continued*).

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[1] Here it appears that a gas-gasplait can occur also if $T_{km} < T_{k_1}$, and for temperatures $T < T_{k_1}$ with $T_{km} > T_{k_1}$, (cf. p. 794 note 1 and p. 794).

(April 25, 1907).

H. KAMERLINGH ONNES and W. H. KEESOM. Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XV. The case that one component is a gas without cohesion with molecules that have extension. Limited miscibility of two gases.

Plate

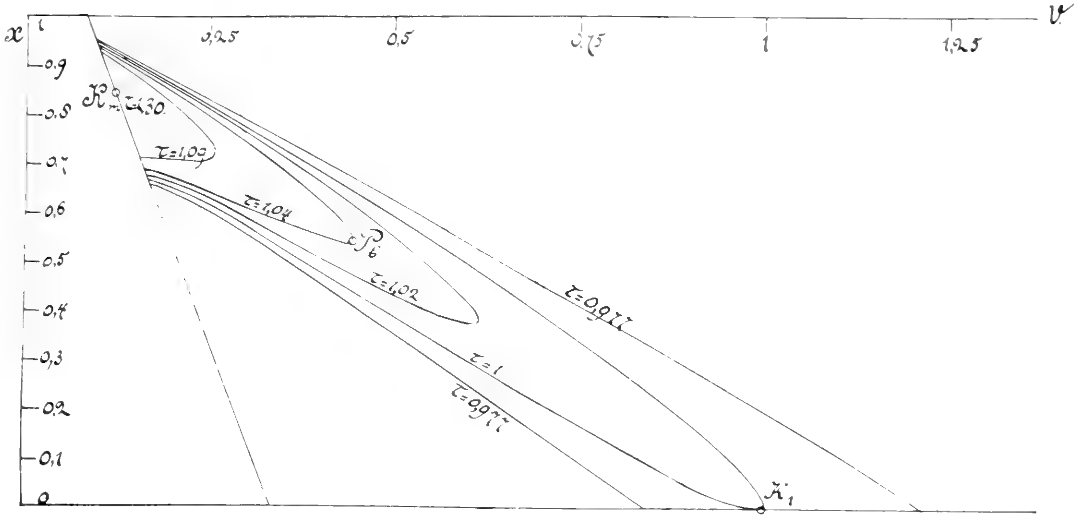


Fig. 1

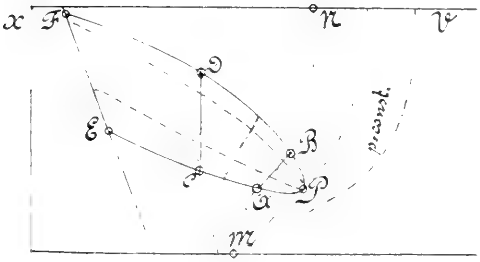


Fig. 2.

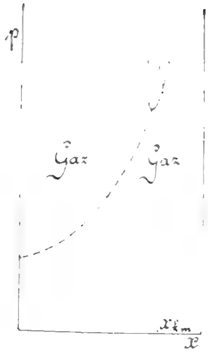


Fig. 3.

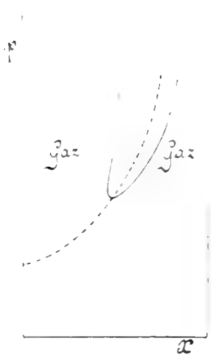


Fig. 4.

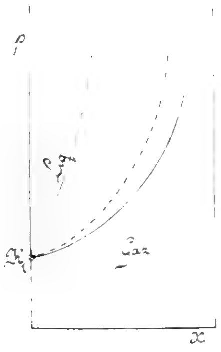
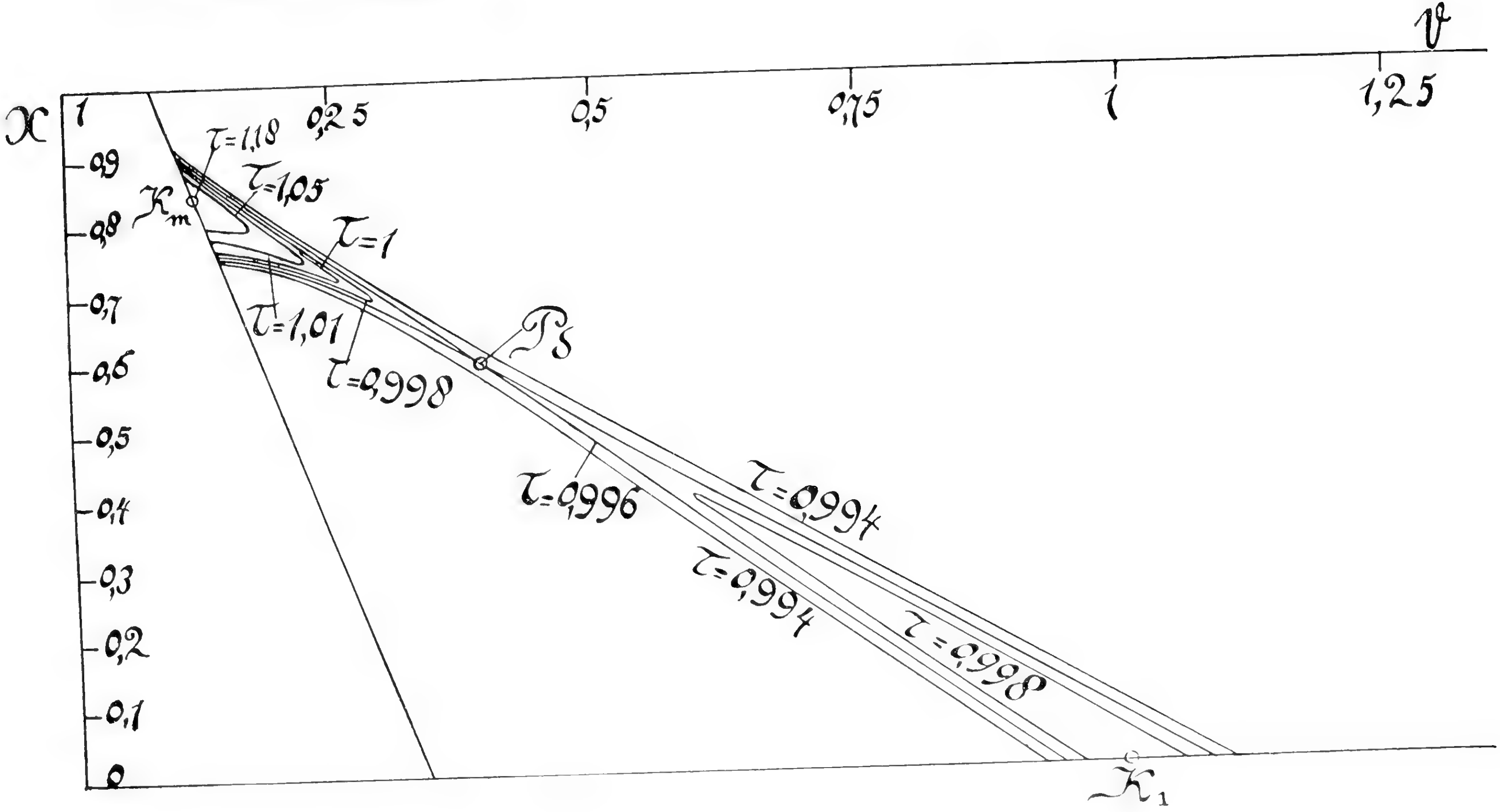


Fig. 5.

H. KAMERLINGH ONNES and **W. H. KEESOM**. Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XV. The case that one component is a gas without cohesion with molecules that have extension. Limited miscibility of two gases.

Plate II.



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Friday April 26, 1907.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Vrijdag 26 April 1907, Dl. XV).

CONTENTS.

Zoology. — "*On gastrulation and the covering of the yolk in the teleostean egg.*" By Dr. J. Boeke. (Communicated by Prof. A. A. W. Hubrecht).

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

1. Generally the process of gastrulation in teleosts is described by the greater part of the embryologists as a folding in of the margin of the blastoderm and the forming, partly by this process of folding and partly by delamination, of a mass of cells that contains the elements both of the chorda and mesoderm and of the entoderm. Only Waclaw Berent, M. v. Kowalewski (in his paper of 1885), F. B. Sumner and myself have described a more or less independent origin of mesoderm and chorda on one side and the entoderm on the other side. Sumner called the mass of cells lying at the posterior end of the embryo, from which the entoderm originates, prostomal thickening; I kept the same name for them and regarded these cells as being derived from the periblast.

The large pelagic eggs of Muraenoids, which I could collect in large quantities at Naples, offer an extraordinarily good object for the study of these processes, much better than the eggs of Salmonides, studied chiefly by French and German authors [1]). The formation of chorda and mesodermic plates out of the folded portion of the blastoderm, and of the entoderm out of the "prostomal thickening", the mass of cells that lie at the hind-end of the embryo and are connected with the superficial layer and with the periblast, is clearly to be seen from the beginning of the formation of the embryo until the closure of the yolk-blastopore (confirmed by Sumner in his paper of 1904) and after a renewed careful study of these eggs [2]) I can only confirm entirely and in full the conclusions arrived at in my former paper [3]) and the observations described there at some length.

But in accordance with the new and better definition of gastrula-

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[1]) Neither Henneguy, nor Kopsch or Jablonowski, to take a few examples, did see anything of these differentiations. Sumner gives however of Salvelinus very clear figures and descriptions. (Arch. f. Entwickelungsmech. Bd 17. 1903).

[2]) During the last 2 or 3 years Muraenoid-eggs seemed to have disappeared entirely from the Gulf of Naples. Now (summer 1906) I found them again in sufficient quantities. When comparing the different eggs with each other, it seemed to me that they belong to a still larger number of different species than I concluded in my former paper (9), and that there must be distinguished at least 10 different species of Muraenoid eggs in the Gulf of Naples. Dr. Sanzo at Messina came to the same conclusion.

[3]) Petrus Camper, Vol. 2, page 135—210 1902.

tion in vertebrates, given by HUBRECHT and KEIBEL and confirmed by a number of other embryologists, this process in the teleostean egg too must be revised and more sharply defined.

In my former paper I was led to divide the process of gastrulation into two "phases", one by which the gut-entoderm is formed and one by which chorda and mesoderm are differentiated. But now I think the line must be drawn still sharper and the second phase must be separated entirely from the process of gastrulation sensu strictiori.

According to the definition given by HUBRECHT gastrulation is a process by which a gut-entoderm is differentiated from an ectodermic layer, and thus the germ consists of two distinct layers. The process of formation of chorda and mesodermic plates, which follows directly on the process of gastrulation proper (notogenese HUBRECHT) is a secondary complication of the process, characteristic of the vertebrate embryo.

The most primitive mode of formation of the entoderm, according to HUBRECHT, is by delamination and not by invagination. But after all it is chiefly the outcome, the formation of the two germ-layers, that is of interest. As soon as these two layers are formed and may be distinctly separated from each other, the process of gastrulation is finished.

This is for example in amphioxus already the case at that stage of development, in which the gastrula is cap-shaped, the two layers (ectoderm and entoderm) are lying close against each other, the segmentation-cavity has disappeared, but the blastopore still extends over the entire breadth of the original blastula-vesicle. All the following processes until the closure of the blastopore ("Rückenmund" of HUBRECHT) are notogenesis and lead to the formation of the back (chorda) and of the mesodermic plates and to the closure of the gastrula-mouth.

When we study again the teleostean gastrulation-process from this point of view, we come to the conclusion, that in this case the process of gastrulation is ended as soon as the prostomal thickening has been formed, viz. at the beginning of the covering of the yolk. At that moment the "Anlage" of the entoderm is clearly differentiated, and the ectodermal cells begin to invaginate to form the chorda and mesodermic plates; the concentration of the cells towards the median line begins, the long and slender embryo is formed out of the broad and short embryonic shield. The blastula-cavity, in the cases in which it is developed, has disappeared as such; all the following processes, the longitudinal growth of the embryo, the covering of the yolk by the blastoderm ring, the closure of the yolk blastopore, belong to the notogenesis and we are no more entitled to reckon these processes to gastrulation proper as we are to do that of the covering of the yolk by the entoderm in sauropsids. During this longitudinal growth of the embryo new cells are produced by the prostomal thickening and pushed inwards to form the entoderm, but this may not be called gastrulation any more. The period of development, during which the yolk is being covered by the blastodermring, differs much in different embryos. In muraenoids at the time the yolk-blastopore is closed the embryo possesses from 5 to 10 pairs of primitive segments; the issuing larvae possess 58 to 75 segments. In salmonidae at the closure of the yolk-blastopore of the 57 to 60 segments 18 to 28 are differentiated. The other organs too are developed to a greater or lesser degree. To use the term gastrulation for the processes during this whole period of development leads us into difficulties.

The first question we have to answer, when we study closer the process of gastrulation in teleosts, is: at what time does the process of gastrulation begin in the large meroblastic eggs?

Recently Brachet [1]) has called attention to a process, which he calls "clivage gastruléen", and which he describes for the eggs of Rana fusca as the formation of a circular groove at the base of the segmentation-cavity around the yolk-mass, before there is to be seen a trace of a blastopore (Rusconic groove) at the outside of the egg: "immédiatement [2]) avant que la gastrulation ne commence, la cavité de segmentation, sphérique ou à peu près, occupe l'hémisphère supérieur de l'oeuf (de Rana fusca).... Bientôt, sur tout le pourtour du plancher de la cavité de segmentation, une fente se produit par clivage; cette fente 's enfonce entre les cellules de la zône marginale et les divise en deux couches: l'une, superficielle, prolonge directement la voûte de la cavité de segmentation, mais est formé par des cellules plus volumineuses et plus claires qu' au pôle supérieur; l'autre, profonde, fait corps avec les éléments du plancher. C'est ce clivage, que j'ai appelé "clivage gastruléen", c'est lui, qui caractérise la première phase de la gastrulation, parce qu'il amène, en dessous de l'équateur de l'oeuf, la formation d'un feuillet enveloppant et d'une masse cellulaire enveloppée, d'un ectoblaste et d'un endoblaste." And farther on: "lorsque ce clivage est achevé, il est clair, qu'a sa limite inférieure, l'ectoblaste et l'endoblaste se continuent l'un dans l'autre, comme le faisaient antérieurement la voûte et le plancher de la cavité de segmentation."

This line of continuity Brachet calls "blastopore virtuel"; after a short time this virtual blastopore is converted into a real blastopore

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[1]) Archives de Biologie Tome 19 1902 and Anatom. Anzeiger. Bd. 27 1905.

[2]) Anat. Anzeiger Bd. 27, p. 215.

by the formation of the groove that leads to the formation of the archenteric cavity. This groove is formed by delamination; until now there is no trace of invagination. This begins in what Brachet calls the second phase of the gastrulation process, which leads to the formation of the archenteric cavity in its entire width, and is synchronic with the process of notogenesis, of the formation of the back of the embryo; "quand les lèvres blastoporales se soulèvent, quand de virtuelles elles deviennent réelles, c'est que le blastopore va commencer à se fermer, c'est que le dos de l'embryon va commencer à se former" (l.c. 1902, p. 225).

Brachet is right here. Also there, where be draws a sharp line between the entirely embryogenic blastoporus of the holoblastic eggs and the blastoporus of the meroblastic eggs with a large amount of yolk, which is divided into two parts, an embryogenic blastoporus and a yolk-blastoporus.

But when he reckons these processes, which occur in the selachian and teleostean egg during the covering of the large mass of yolk and the closure of the blastopore, still to gastrulation, when he calls the entire process of covering of the yolk "clivage gastruléen", and calls the whole blastoderm ring "blastopore virtuel", he goes too far, and forgets the significance of the phenomena, occurring at the end of segmentation and during the formation of the periblast.

For the answer to the question, at what time does the gastrulation in the teleostean egg begin, his analysis of the phenomena of this process in the amphibian egg is extremely interesting.

The segmentation of the teleostean eggs is not regular during all its phases. When we combine the very accurate observations of Kopsch on this account, we see, that in the segmenting blastoderm at a definite moment, about that of the 10th division of the embryonic cells, there occurs an important alteration.

Until the end of the 10th cell-division (in Belone) the different cells divide wholly synchronic; in Torpedo Rückert found synchronism until the 9th division. By the tenth division the yolk-sac entoblast is formed (in Gobius, Crenilabrus, Belone), the two nuclei of the marginal segments, resulting from this division, remaining in the undivided protoplasm; where this does not occur at the tenth division the deviation is very small (in Cristiceps argentatus it partly begins at the 9th division, in Trutta fario at the eleventh division). Synchronically with the differentiation of yolk-sac entoblast the superficial layer ("Deckschicht") is differentiated. At the end of the 10th division all at once the blastoderm alters its form: it gets higher, more hill-shaped and the diameter is lessened; the mass of cells concentrates, the superficial layer is still more clearly visible as a definite enveloping layer of cells. It is just the synchronic differentiation of the superficial layer, which shuts off the blastoderm from the surrounding medium and is the only way by which the developing cells may get the oxygenium from the perivitelline fluid, on one side, and of the periblast, by means of which the blastoderm is nourished by the yolk, on the other side, which seems to me to be important; by this synchronic differentiation a new phase in the developmental process is initiated, and the series of changes have begun that lead to gastrulation.

Very soon the blastoderm-disc flattens, at first only because the superficial layer contracts a little, and the blastoderm sinks a little into the yolk-sphere (fig. 8) but after that because the blastodisc itself spreads out, flattens (fig. 9). The cells come closer together, and soon the unilateral thickening that forms the first outwardly recognisable beginning of the building of the embryo, becomes visible.

During these changes it is of no account whether a blastula-cavity is formed, or not. As I have described elsewhere, in different muraenoids during this stage a distinct blastula-cavity is formed, which may be seen in the living egg. Afterwards follows the flattening of the blastodisc and the disappearance of the cavity as such. The closer study of young stages of the eggs of muraena N°. 7 [1]) showed me however, that in these eggs no blastula-cavity is formed, and that in this case the blastoderm, that takes just the same conical shape as the hollow blastoderm in the other muraenoid eggs, remains solid and is built up of a mass of loosely arranged cells. The further development is the same as in the other series (c.f. fig. 1—3 on plate 1).

This flattening of the blastodisc, following on the stage just described, coinciding with the concentration of the cells of the blastoderm towards the side where in later stages the embryo is formed, and coming before the invagination (and partial delamination) of the blastoderm cells, that leads to the formation of the chorda and the mesodermic plates, is already a part of the gastrulation process and must be compared with the "clivage gastruléen" of the amphibian egg.

Immediately on this "clivage gastruléen" follows the formation of the prostomal thickening (that is the "blastopore réel" of **Brachet**), there where the superficial layer or pavement layer is connected with the periblast, out of the surperficial cells of the periblast [2]) (c.f.

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[1]) Comp. Petrus Camper, Vol. II p. 150.

[2]) Sumner (l. c. page 145) saw evidences for this mode of origin in the egg of Salvelinus, but not in that of Noturus or Schilbeodes. On these two forms I can-

fig. 4, 5 and 6 on plate 1). It seems probable, that at least in some cases entodermcells are formed by delamination from the periblast at some distance from the surface in front of the prostomal thickening (fig. 5*e*). So here, as in many vertebrates, the entoderm is formed by delamination. At the moment of the differentiation of the prostomal thickening (figs. 2, 4), there is still no trace of the invagination of the mesodermcells, only a thickening of the mass of cells lying just overhead of the cells of the prostomal thickening. Immediately afterwards however a distinct differentiation of the mesoderm becomes visible. At that stage the notogenesis begins and the gastrulation process is finished. The prostomal thickening is the ventral lip of the "blastopore réel" of the Amphibian egg. For the developmental processes following on this stage I can contain myself with referring to my former paper. That here only a small, not very prominent tail-knob is formed and no far-reaching projecting tail-folds appear, as in the selachean embryo, is caused by the relation of the pavement-layer to the blastoderm and the periblast, which influence the development of teleostean egg ("développement massif" of HENNEGUY).

2. To determine the direction of growth of the blastodermring during the covering of the yolk, I used in my former paper the oil-drops in the yolk of the muraenoid eggs as a point of orientation, on the contention that these oildrops maintain (in the muraenoid egg) a constant position in the yolk. On this basis I constructed a scheme of the mode of growth of the blastoderm in the yolk. ¹) Both SUMNER and KOPSCH rejected this contention and the scheme, SUMNER because of the fact, that by inverting the egg of *Fundulus heteroclitus* in a compress, the oil-drops may be caused to rise through the yolk and assume a position antipodal to their original one, which shows, that here the oil-drop may not be regarded as a constant point of orientation in the egg. In this SUMNER is perfectly right. Not only in Fundulus, but in several marine pelagic eggs too the oil-drops may be seen travelling through the yolk by converting the egg or bringing the young larva (in some species) in an abnormal position. In the muraenoid egg however the case is entirely different. Here the structure of the periblast and of the

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not judge, but I will only mention here, that the figures, drawn by the author, are taken of much too late stages of development, to be convincing. And after all, where the blastodermcells are so much alike, as is the case in most teleostean eggs, one positive result in a favourable case as is offered in the muraenoid egg, is more convincing than several negative results in less favourable eggs.

¹) l. c. page 142.

yolk-mass, which I described at full length in my former paper, completely checks the displacement of the oil-drops. This is to be concluded already from the behaviour of the normal egg. So in the eggs of Muraena No. 4 a large number of rather large oil-drops are lying at about equal distances from each other at the surface of the yolk-mass. During the entire process of covering of the yolk, the distance of these oil-drops remains the same, they maintain their relative position absolutely, and only during the slight disfigurement of the yolk-sphere, caused by the contraction of the blastodermring during the circumgrowth of the yolk (fig. 4 on plate 2) the position of the oil-drops is changed a little, only to become the same as before, after the yolk has regained its spherical form. When these oil-drops were lying loose in the yolk or in the periblast, they would have crowded together at the upper pole of the egg, or at least their relative position would have undergone a change during the covering of the yolk. Only when the yolk-mass in the developing embryo becomes pear-shaped and very much elongated (l.c. plate 2, fig. 6, 7), the oildrops of course change their position. Even then, however, they remain scattered through the yolk.

Experiments also show the constant fixed position of the oil-drops in the muraenoid eggs. When we transfix the egg-capsule carefully with a fine needle, it is possible to lift one of the oil-drops or a small portion of the peripheral yolk out of the egg. The other oil-drops retain their normal position, and in most cases such eggs develop normally and give rise to normal embryos. When we operate very carefully under a low-power dissecting-microscope, it is possible to leave the oil-drop connected with the periblast by means of a thin protoplasmatic thread. When we do this in a very early stage of development, at the beginning of the gastrulation-process, we see that this oil-drop, which surely may be regarded as a fixed point on the surface of the egg, retains its position in relation to the other oil-drops, until it is cut off from the periblast by the growing blastodermring. In fig. 2*a*, 2*b*, 2*c* and 2*d* on plate 2 I have drawn from life several stages of this process in an egg of Muraena No. 1. During my stay at the Stazione Zoologica at Naples, in August and September 1906, I performed several of these experiments with different muraenoid eggs. They all led to the same result, and confirmed my former statements. And so I believe that my contention was right and that the scheme I figured is a true representation of the facts. Of course only in a general sense, for there are many individual variations (so for example the case figured in fig. 3 on plate 2). And after all, when we compare this scheme with that given by KOPSCH for the trout, we see that they do not differ so very much, and that the displacement of the hinder end of the embryo is almost the same. In the text of my former paper however I expressed myself rather ambiguously, and brought my view into a too close contact with that expressed by OELLACHER. The figures however show that my scheme differs rather much from that of OELLACHER.

But I differ from KOPSCH in his supposition that the head-end of the developing embryo is a fixed point on the periphery of the egg. I find myself here quite in harmony with SUMNER, who draws from the large series of his extremely careful and exact experiments the conclusion, that "the head end also grows, or at least moves, forward, though to a much smaller extent" (l. c. page 115), and says: "I regard it as highly probable (see Exp. 1, 3, 34, 35, 36 and Fig. 32) that the primary head end grows — or is pushed — forward from an original position on the margin" (l. c. page 139).

From different experiments of the author we may draw the conclusion, that in many cases this forward growth of the head-end is rather extensive (exp. No. 6, 10, 11 (partly), 26, 35, fig. 10), and experiment N°. 6 (table VIII) among others shows, that under circumstances the direction of growth may be entirely reversed, so that the tail-knob of the embryo remains at the same place, and the head-end bends round the surface of the yolk.

KOPSCH too, in his paper: "Ueber die morphologische Bedeutung des Keimhautrandes und die Embryobildung bei der Forelle", describes an experiment with simular results in the trout.

So it is not unreasonable to suppose, that in the spherical egg of the Muraenoids during the covering of the yolk the head end of the embryo is moving forward, and to a certain extent follows the growing blastodermring, which is the case chiefly during the later stages of the covering of the yolkmass, as I showed in my scheme. During the first stages of development it is chiefly the tail-end of the embryo which travels backwards, (see the scheme in my former paper and fig. 1—3 or plate 2), and KOPSCH is right to locate here the centre of growth of the embryo.

The conclusion of SUMNER, that for some time prior to the closure of the blastopore, the ventral lip of the latter (former anterior margin of the blastoderm) travels much faster than the dorsal lip (l. e. p. 115) is quite in harmony with my results for the muraenoid egg described in my former paper. [1])

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[1]) PETRUS CAMPER, l. c. p. 196.

3. At the end of the covering of the yolk, at the closure of the blastopore, Kupffer's vesicle is formed after the manner described at length in my former paper. By Swaen and Brachet[2]) and by Sumner the narrow passage connecting this vesicle with the exterior, through the closing blastopore, is regarded as representing the neurenteric canal. I do not think they are in the right here. Kupffer's vesicle is a ventral formation. Dorsally it is separated from the cells of the medulla by the cells of the prostomal thickening and the pavement layer. An open canalis neurentericus is not found even in these forms. Kupffer himself called the vesicle allantois. Hubrecht followed him in this. In my former paper I compared the vesicle with the allantois of amniota on physiological grounds, and I think it is a very good thought of Hubrecht to take up the old name of Kupffer and compare the vesicle with the allantois on morphological grounds.

DESCRIPTION OF FIGURES ON PLATE 1 AND 2.

Plate 1.

Figg. 1—4. Median sections through eggs of Muraena N^{0}. 1 on different stages of gastrulation. In fig. 3 gastrulation is finished and notogenesis is begun. In fig. 2 the structure of the yolk is drawn. Enlargement 40 times. Fig. 4*a*, 5 and 6 give median sections through the developing prostomal thickening and adjoining parts, seen under a higher power.

Figg. 7—9. The flattening of the blastodisc at the beginning of gastrulation in eggs of Muraena N^{0}. 7. Enlargement 40 times.

Plate 2.

All the figures on this plate are drawn from life as accurately as possible.

Fig. 1*a*—1*e*. Covering of the yolk in an egg of Muraena N^{0}. 1.

Fig. 2*a*—2*d*. Covering of the yolk and closure of the blastopore in an egg of Muraena N^{0}. 1. By means of a fine needle one of the oil-drops is nearly severed from the surface of the yolk, remaining connected with the periblast only by means of a thin protoplasmatic thread. In fig. 2*c* this oil-drop is cut off from the surface of the egg by the travelling blastodermring and is lying close against the egg-capsule EK. In fig. 2*d* (closure of the blastopore) this oil-drop is no more drawn in the figure.

Fig. 3. Unusually fargoing dislocation of the hinder end of an embryo during the covering of the yolk. The head end lies approximately at the former centre of the blastodisc.

Fig. 4. Compression of the yolk-sphere by the growing blastodermring in an egg of Muraena N^{0}. 4. The oil-drops only temporarily changed their relative distances a little.

OD = oildrop.
pv = prostomal thickening
per = periblast.
Bl = blastoderm.
D = pavement layer
e = entoderm

Leiden, 17 January 1907.

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[2]) Archives de Biologie T. 20. 1904. page 601.

Physics. — *"On the influence which irradiation exerts on the electrical conductivity of Antimonite from Japan"*. By Dr. F. M. Jaeger. (Communicated by Prof. P. Zeeman).

(Communicated in the meeting of February 23, 1907).

§ 1. Having been occupied for a considerable time with the determination of the specific electrical resistance in the three crystallographic main directions of the *antimonite* from Shikoku (Japan), I had already found that with this substance, which belongs to the very bad conductors, inexplicable irregularities presented themselves, when the resistance was determined several times anew during a long time, with identical electromotive force.

Generally the obtained deflection of the galvanometer first became larger and larger, and decreased again in course of time, after which, as I found, periodical increase and decrease sometimes followed. It was impossible to detect any connection between tension, intensity of current, and time.

As for rods of a length of some centimeters and a section of about a quarter of a square centimeter, resistances were found in the different directions lying between 500 and 20000 millions of Ohms, I first thought of an impregnation of the electrical charge in the ill-conducting material. On account of its opposed direction, however, an eventual polarisation current would have to cause an apparent *increase* of the resistance, whereas experience generally showed a *decrease* of the initial resistance.

§ 2. While I was trying to ascertain the cause of these deviations, a sunbeam fell through an aperture of the curtain on the piece of mirror-glass which closed the Thomson-galvanometer, and was partially reflected to the apparatus containing the piece of antimonite, cut with its longitudinal direction parallel to the crystallographic b-axis. The needle of the galvanometer deflected immediately towards that side in which the total deflection was *increased*. At first I thought that the heat of the sun penetrating the galvanometer on one side had changed the cocoon thread so much as to cause a torsion. Some moments later, however, when I happened to light a match in the neighbourhood of the preparation, the *increase* of the already existing deflection was repeated, and now in the same sense as before, and at the same time stronger.

§ 3. So we have met here with a new phenomenon. Either the radiation of light, or the heat must be the cause of the phenomenon.

I then undertook the following set of experiments.

A rod of antimonite quite covered by paraffin, and cut parallel to the *b*-axis, was shunted into the circuit of a dynamo, the tension being kept at exactly 35 Volts by means of a resistance of incandescent lamps. When shunting in the THOMSON-galvanometer [1]), which had been hung up in an antivibration apparatus of JULIUS, and which was so sensitive, that at a distance of mirror of two meters, it still gave a deflection (double) of 26,5 mm. for a current of 0,000000006 Ampères, — we obtained a constant, single deflection of 10,7 cm. on the left of the zero point.

An incandescent lamp (of 110 Volts), placed at about 2 meters' distance from the preparation, gave an *increase* of this deflection of 4 m.m., i. e. 3,7 $^0/_0$ — agreeing in this case with a decrease of resistance of about 53 millions of Ohms.

When the same lamp was placed at 1 meter's distance it brought about an increase of the deflection of 11 m.m.; at $^1/_2$ meter's distance of about 20 m.m., and held near the rod for a short moment, of more than 220 m.m., i. e. an increase of the conductivity of resp. ± 10 $^0/_0$, ± 18,7 $^0/_0$ and 206 $^0/_0$! [2])

Then the lamp was removed, and after the deflection had resumed about its original value, one of the curtains at the window was drawn aside, so that the diffuse daylight (overcast sky) fell on the apparatus. Instantly the deflection was increased by more than 4 m.m. i.e. about 3,7$^0/_0$. Then a wooden box was placed over the apparatus, and then removed. Every time the experiment was repeated the constant deflections in the light were found from 3 to 8 m.m. *larger* than those in the dark.

§ 4. In the foregoing experiments only exceedingly little light fell on the rod of antimonite, as it was quite covered by a coat of paraffin [3]) about 0,4 c.m. thick, and so only the light penetrating the half transparent coating could have any effect.

Then the experiment was repeated as follows.

A lamella [4]) of antimonite was clasped between two much larger copper plates, which two plates were well insulated. The condensator (fig. 1) obtained in this way was suspended on silk threads. [3])

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[1]) The internal resistance of this instrument amounted to 6681 Ohms.

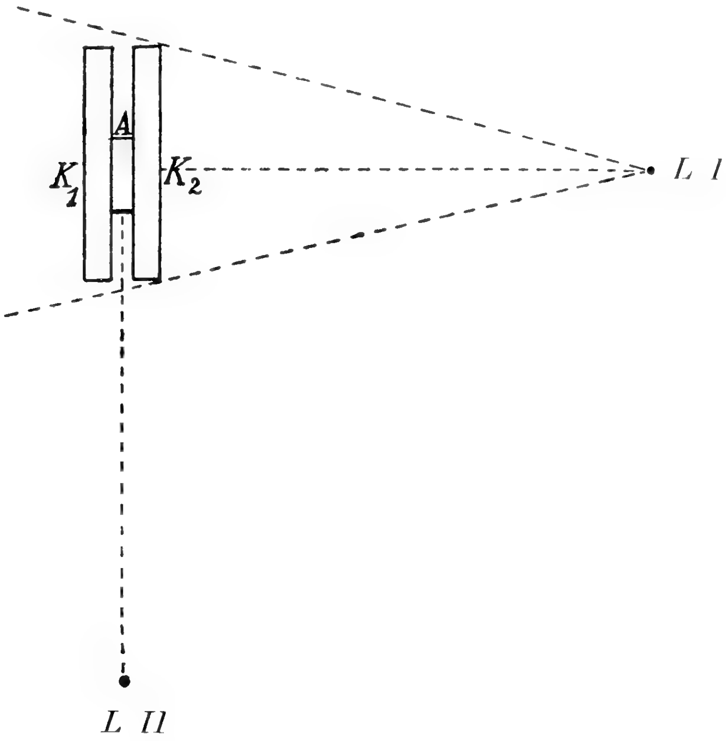
[2]) The resistance of the rod was diminished by an amount of more than 950 millions of Ohms in the latter case.

[3]) The purpose of these precautions will be explained later on in a paper written in conjunction with Mr. VAS NUNES.

[4]) The antimonite splits perfectly // (010), so ⊥ *b*-axis.

The antimonite plate had a thickness of about 1 m.m. and a section which may have amounted to about $^1/_4$ c.m^2.

Now if a source of light was placed at I, the remaining deflection of about 1,8 c.m. obtained at a 10,5 Volts' tension was only increased by 2 m.m., i. e. by about 11 $^0/_0$. If, however, the light was placed *at the same distance* in II, the increase amounted to about 11,5 m.m., i. e. 64 $^0/_0$.



In the former case the plate A is viz. in the shadow of K_2, and so receives but very little light reflected by the walls; in the latter case, however, the radiation is direct.

§ 5. If a thick plate of colourless plate-glass is placed between the source of light in II and the apparatus, the remarkable fact presents itself that the deflection is considerably *increased.* The explanation of this phenomenon was obvious. For a copper bar, heated to some hundreds of degrees, and brought near the apparatus, immediately *diminished* the obtained deflection greatly. Hence — and this is a most remarkable result — *rise of temperature has an influence directly opposed* to that of radiation of light: it enlarges the resistance instead of diminishing it, as rays of light do.

If the plate is again removed, the deflection decreases again to the value it had before the plate was placed between etc. So this fully proves that it is the *radiation of light* which influences the conductivity of antimonite in so high a degree, and *not* the heat; for the latter diminishes the conductivity, in contrast with the former.

§ 6. Finally glass plates of different colours were interposed between the source of light and the rod.

It then appeared that the influence of the differently coloured light was very different. The antimonite namely proved to be subjected to hardly any change by *green* light; for *red* light the increase was pretty large, for *yellow* light a little more, for *green* very small, for *violet* light again stronger. In each of these cases the deflection appeared to have resumed its original value after removal of the source of light[1]). With violet radiation I obtained an increase ot conductivity which amounted to about 150 % of the original value; with white light with interposed glass plate one of about 250 %.

To get some insight into the *quantitative* action for a special case, the following experiments were made. An ordinary electrical incandescent lamp was adjusted at 16 cms'. distance from an antimonite rod covered with a coat of paraffin 1 cm. thick. First of all it was ascertained that action of light by itself did not excite an electrical current. It then appeared that the deflection of the galvanometer was increased just as much irrespective of the direction of the current. So the decrease of resistance is independent of the direction of the current. By interposition of coloured glass plates I got a rough estimation of the relative influence of the different colours of the spectrum. Thus I found:

White light, placed at 16cms'. distance, makes the conductivity rise to 200% of its original value
Red ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, 194% ,, ,, ,, ,,
Orange ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, 153% ,, ,, ,, ,,
Green ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, 116% ,, ,, ,, ,,
Blue ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, 176% ,, ,, ,, ,,

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[1]) Not quite the original value. The substance shows hysteresis to a certain amount, which, however, is smaller than for selenium. Already 20 à 40 minutes after the source of light had been removed, the original deflection was sometimes found back. The mineral seems to be quite free from any admixture of selenium, as a qualitative investigation taught me. Remarkable in a high degree is the fact, that on melting the natural mineral, it obtains, when solidified as a conglomerate of little crystals, a specific resistance, which is many thousand times less than before, while at the same time it has lost its sensibility to light-radiation quite. On heating the antimonite however, without melting, it conserves this property. Analysis has taught me, that there are present the elements: Sb, S, Ca, Ba, Sr, Si and, as Prof. KLEY found, traces of Zn and Co; also SiO_2-crystals are included. (Added in the English translation).

As heat-rays have only an exceedingly slight effect, and, as I ascertained later on in conjunction with Mr. VAS NUNES, also the ultraviolet light emitted by cadmium poles causes only a small increase of the conductivity, the dependence of wave-length and decrease of resistance is evidently represented by a curve whose minima lie in the ultrared, in the green and in the ultraviolet, and whose maxima are situated in the red and in the blue part of the spectrum [1]).

Later on when the determinations of the resistance of this substance will have led to favourable results, we shall make some closer communication on the relation between thermal and electric motion in this conductor.

§ 7. The phenomenon discovered here reminds strongly of that observed for *selenium* [2]). It is, however, noteworthy, that though the dependence of the increase of the conductivity on the radiation of light, and even on the wave-length of the light manifests itself in a perfectly analogous way to that for antimonite, yet the two differ in some respects. First of all for the selenium *polymorphous changes*, and the displacement of equilibrium attending them play an important part; then, however, the resistance always decreases here with rise of temperature, so exactly the reverse of what happens in my investigations, in which moreover there is no question whatever of polymorphous changes, as far as is known. An analogy between the two cases is to be found in the fact already discovered by ADAMS [3]), that the resistance decreases with rising electromotive force, also after continued action of it; such a deviation from the law of OHM is also found for the antimonite.

On the other hand the behaviour of antimonite from Japan seems to present a closer analogy with that of the crystallised *tellurium;*

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[1]) Though it is not intended as an explanation, I will yet call to mind that it follows from MÜLLER's investigation (N. Jahrb. f. Miner. u. s. w. Beil. Bd. **17**, 187—251) on the optical constants of the antimonite from Japan, that the indices of refraction n_1 and n_2 have their maximum values exactly for the *green* rays (between the lines E and F) (viz. $n_1 = 5{,}47—5{,}53$ and $n_2 = 4{,}52—4{,}49$), while also the double refraction reaches its maximum value for these rays. The polarisation of the reflected rays is right-elliptic (negative). However, on using polarized light, we could not find any influence of the direction of vibration: the variation of the electric resistance was in the two cases the same. (Added in the English translation).

[2]) G. WIEDEMANN, Die Lehre v. d. Elektricität (1882). I. p. 544—553).

[3]) SALE, Phil. Mag. [4]. **47**. 216. (1874); Pogg. Ann. **150**. 333; Chem. News. **33**. 1. (1876).

[4]) ADAMS, Phil. Trans. **157**.; Pogg. Ann. **159**. 621. (1876), Phil. Mag. [5]. **1**. 115

here, too, the resistance increases with heating, decreases with exposure to light [1]).

In conjunction with Mr. VAS NUNES I hope shortly to publish also some quantitative data on the phenomenon discovered by me, and also on the behaviour of the melted and again solidified antimonite and the analogous selenium compound. This investigation has been made in the Physical Laboratory at Amsterdam.

Anatomy. — *"On the influence of the fins upon the form of the trunk-myotome".* By B. VAN TRICHT. (Communicated by Prof. G. C. J. VOSMAER). (From the Anatomical Institute at Leyden).

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

This research forms a direct sequel to Professor LANGELAAN's work "On the Form of the Trunk-myotome", and is intended to show the influence of the fins upon the form of the myotome. The method which I followed, was based upon the chief result of the foregoing research viz. that the differentiation of the myotome takes place in a continuous manner by means of folding, and that it is possible to follow the process of folding in dissecting the intermyotomal tissue. Now the method of direct dissection proved to be restricted in its application, so that it was necessary partly to apply a more indirect one. This latter method rests upon the relation, which exists between the form of the myotome and the structure of the transverse sections of the animal.

Differentiation of the dorsal musculature.

From a rather large sample of Mustelus vulgaris the skin with the underlying connective tissue was removed, so that the external surface of the myotoms was laid bare (figure I). Then in the region before the first dorsal fin the parts constituting one and the same myotome were determined; the form of this myotome exhibited about the same form as in Acanthias, only the lateral part of the myotome proved to be displaced caudally; the breadth of this displacement amounted to about half the breadth of the myotome. This myotome was arbitrarily indicated by the number

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[1]) I have made an arrangement with Mr. J. W. GILTAY at Delft with regard to the mounting of antimonite preparations, and the preparation of antimonite cells for practical use.

1 and the following myotoms by subsequent numbers. After that, transverse sections of the animal were made, of 1—2 cm. thickness, and the numbering transferred to these sections, so that the lamellae belonging to one and the same myotome received the same number. For the sake of an easy description, figure II gives a hemischematic representation of the myotome, in which the peaks are indicated by numbers, the lamellae by letters. In figure III which is the transverse section, (indicated in figure I with an *A*) the peaks appear as systems of concentric lamellae marked in accordance with the marking in figure II. If we now pass to the region of the first dorsal fin (figure IV, section *B* of figure I and fig. V, section *C* of fig. I) the image of the transverse section is changed, instead of being composed by four peaks, the dorsal musculature only shows three peaks.

The peak, indicated as number 1, has disappeared and instead of this peak we find the first lamellae of the dorsal fin. Now in all subsequent sections this first peak does not reappear any more. By the method of successsive numbering it was possible to determine the first myotome losing its most dorsal peak (number 1). The external surface of this myotome is blackened in figure I. From the principle laid down in the beginning of this notice ensues, that the myotome apparently losing its first peak, gives a muscular element to the dorsal fin; this element is therefore also blackened in figure I. It may be seen in figure I that the first myotome giving an element to the fin lies a little caudally in respect to the front edge of this fin. The number of myotomes giving a part to the first dorsal fin may easily be determined, because these composing parts of the fin are separated by intersegmental tissue; that we have really to deal with intersegmental tissue follows from the fact that through these lamellae bloodvessels and extremely fine nerve fibres reach the skin (vid. v. Bisselick "On the Innervation of the Trunk-myotome"). The total number of muscular elements composing the fin, amounted to 34, so that the last myotome still giving an element to the first dorsal fin already lies in the region of the second dorsal fin. From the fact that the most dorsal peak (number 1) does not reappear any more in the transverse sections, it follows that the next myotome gives the first element to the second dorsal fin. The surface of this myotome is also blackened in figure I to show its position in relation to the front edge of the second dorsal fin. It is evident, that this myotome occupies the same position in respect to the second dorsal fin as the first myotome does in respect to the first dorsal fin. The number of myotomes composing the second dorsal fin amounts to 30.

Upon the second dorsal fin follows the dorsal part of the caudal fin. In this fin the myotomes are pressed together so closely that a direct counting of the number composing the fin is no more possible; by comparing the total number of vertebrae to the number of myotomes composing the first and second dorsal fins, we find that about 70 myotomes give an element to the dorsal part of the caudal fin.

The results obtained by this indirect method are corroborated by the result of the direct dissection. If we take a myotome giving a muscular element upon the more anterior part of the dorsal fin and begin the dissection with lamella *b* in the neighbourhood of the second peak and proceed preparing caudally, we find lamella *b* being rolled in, towards the mesial plane of the body, in the shallow excavation in which the base of the fin rests, (fig. VI). Along this way the muscular tissue becomes gradually atrophic and only a thin band remains, consisting of the connective tissue which forms the framework for the muscle fibres. In the neighbourhood of the sagittal plane of the body this lamella is folded, in such a manner, that the line of folding (figure VI L″ L″) runs parallel to the sagittal axis of the body. By this process of infolding the direction of the lamella *b* is reversed, the infolded part proceeding cranially; this part of lamella *b* passes into the dense sheath of connective tissue, which is interposed between the dorsal musculature and the base of the fin. As far as I can see this sheath of connective tissue is chiefly built up by a large number of these lamellae, but they are so inextricably united that I have not been able to follow lamella *b* in this sheath. If starting from the fin, we prepare free one muscular element of the fin, and this element is lifted up with enough precaution, it may be seen, that from the base of such a fin-element as well a thin lamella of connective tissue passes into that sheath of tissue in which we could follow the reversed part of lamella *b*. The direct continuity however of both lamellae in the sheath of dense connective tissue, I have not been able to establish.

The muscular elements composing the fin (figure VI) are triangular laminae; one side of the triangle is contiguous to the fin-rays and the connective tissue which unites these rays in the mesial plane of the body, the lateral side forms part of the lateral surface of the fin, while the base is excavated and moulded upon the shallow depression in the dorsal musculature. From the outside a septum of intermyotomal tissue (s. i. figure VI) penetrates into the muscular substance of the fin dividing this substance into a lateral (*b*) and a mesial part (*a*). This septum inserts a little above the muscular substance upon the fin-rays, and becomes thinner and thinner without reaching the base of the fin. At the base therefore the lateral and mesial parts of the muscular substance are continuous and form a peak (figure VI p. 1), lying quite near the mesial septum of the body. This peak must therefore represent the peak which is lost in the transverse section (figure IV) made at the level of the first dorsal fin. The septum penetrating into the muscular substance of the fin is therefore the intermyotomal septum stretched out between lamellae *a* and *b* of figure II.

It ensues therefore from the combined observations, that the first dorsal fin (and the same applies to the other dorsal fins) is differentiated by a process of infolding similar to the differentiation between the dorsal and the lateral and between the lateral and the ventral musculature. The line of infolding crosses lamella *b*. In that part of the lamella, which lies in the depth of the fold the muscular tissue is atrophic. Proceeding from peak 2 caudally along lamella *b* the atrophy of the musclefibres gradually increases, whilst on the other hand proceeding from peak 1 caudally along lamella *b* (as far as it lies upon the fin) the atrophy of the muscular tissue is abrupt. The position of peak 1 has not changed in respect to the mesial plane of the body, only the lamellae have changed their direction. The superior cornu (i. e. lamella *a*) is no longer directed cranially but turned upwards and this is also the case with that part of lamella *b* that has passed into the fin. In connection with this representation of the facts, I determined the direction of the muscle fibres in the fin; here they slope downwards from the intermyotomal septum. Now if we imagine the lamellae composing the fin restored to their original position, the course of the fibres in lamella *a* would be from mesial to lateral and from caudal to cranial and this was actually the direction of the muscle fibres in lamella *a* in the region cranially of the first dorsal fin.

Differentiation of the latero-ventral musculature.

The lateral musculature, as described by VAN BISSELICK, shows a peak directed caudally (peak 5, figure II and fig. VII) situated near the second line of infolding L'L'. Proceeding along the body a second peak appears directed cranially. The first myotome showing this peak (peak 6, fig. II and fig. VII), is the eleventh myotome following the first myotome giving a muscular element to the first dorsal fin. The two peaks lie near to each other in the neighbourhood of the second fold. In consequence of the infolding of the myotome at that place, they do not reach the surface of the body, being covered from the outside by the ventral musculature. Meanwhile the ventral part of the myotome undergoes a change in form, the first lamella belonging to the ventral musculature (lam. *f* figure II and fig. VII) becomes shorter and the first peak of the ventral musculature directed cranially (peak 7, figure II), more and more develops into a true peak. Now by the disappearence of lamella *f* peak 6 and 7 approach each other, remaining divided, however, by a thin lamella of connective tissue penetrating into the second fold along the line L′L′ (fig. VIII and IX). In consequence of the process of infolding peak 6 lies mesially in respect to peak 7 which covers peak 6 from the outside. At the level of myotome 15 (reckoned from the first myotome, giving an muscular element to the first dorsal fin) the second fold vanishes. Together with the disappearence of the fold we notice the vanishing of the displacement of the lateral musculature in respect to the ventral musculature, which was only a consequence of the process of infolding, so that the two peaks (6 and 7) lie side by side in the same transversal level of the body. At the place of disappearance of the second fold the two peaks unite to a single peak directed cranially. Together with the disappearance of lamella *f* we notice the further development of lamella *g*.

At the same level where the second lateral fold disappears, we find the appearance of the cartilagineous plate, uniting the two basipterygii of the pelvic fins. With its front border, this plate folds in lamella *g* (figure II and X) from the inside so that this lamella covers the front edge of this plate; in this way the pelvic fin is formed. The details of the formation of the pelvic fins I have not yet investigated. By the formation of the pelvic fin peak 8 (fig. II) and lamellae *g* and *h* pass into the musculature of the fin, so that in a transverse section through the animal, at the level of the pelvic fin, the trunkmusculature is only composed by five peaks (viz. 2. 3. 4. 5. (6 + 7) of figure II). This structure of the transverse sections does not change any more proceeding along the body caudally (figure XI and XII).

The disappearance of the first fold, dividing the dorsal from the lateral musculature, takes place in the same way as described for the second fold, at the level of myotome 45 (reckoned from the first myotome giving an element to the first dorsal fin); only the case is more simple not being complicated by the presence of two peaks.

Finally I paid attention to the influence of the abdominal cavity upon the form of the myotome. I found this influence to be very restricted, as it only determines to some extent the dimensions of the myotome, without producing any particular differentiation in its form.

In fine I wish to express my thank to Prof. LANGELAAN for his aid and assistance in these researches.

Anatomy. — *"Anatomical Research about cerebellar connections."* (Third communication). By Dr. L. J. J. Muskens (Communicated by Prof. C. Winkler).

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

The ventral cerebello-thalamic bundle.

Whereas it is nowadays generally accepted, that the direction of conduction in the superior crus cerebelli is cerebellofugal, there is no uniformity of opinion attained yet by the authors regarding the bundle, which is found degenerated in the predorsal region in the pons after cerebellar lesions. After Pellizzi and van Gehuchten, Thomas, Orestano, Cayal and Lewandowsky this bundle is built up by fibres, which take their origin from the superior crus after it has crossed the raphe in Wernekinck's commissure, the direction of conduction being rubro-fugal. Probst however, describes this bundle as the ventral cerebello-thalamic bundle, conducting nervous impulses from the cerebellar basal nuclei upward towards the red nucleus.

The problem of this bundle really has to deal with two questions; 1st. which are the two nerve centres, which are connected by means of this bundle and 2nd. what is the direction of conduction of impulses in the same.

Cats appear to be more suitable for these experiments. In two animals different parts of the cerebellar cortex, with the adjacent part of the basal nuclei, were removed, except the flocculus. In these animals there was hardly any degeneration at all in the ventral cerebello-thalamic bundle, whereas in 3 other cats in which with other parts also the flocculus was removed there was very extensive degeneration of this bundle. That these fibres do not take their origin from the cortical gray matter of the flocculus is proved by the fact, that in another cat in which the cortex of the formatio vermicularis cerebelli was injured, no degeneration of the said bundle was found.

In two cats (XXIII and LXI) a lesion was effected in the midbrain, by passing a curved knife in front of the lobus simplex cerebelli in such a way, that the predorsal region on the right side was cut, distally from the red nucleus. In none of these animals any degeneration was found in the ventral bundle. If Cayal's supposition were correct, certainly a great many of the descending collaterals of the superior crus ought to have been found degenerated.

In one cat (LVIII) a longitudinal lesion was effected in the tegmentum, the instrument (PROBST's covered hook) passing through the middle crus cerebelli. In this cat were found a certain number of fibres degenerated, which passed through the regio reticularis of the side of the lesion and then, crossing the raphe and running upward in the predorsal region of the other side, took their way towards the red nucleus. This experiment tends to show, that there are direct fibres, coming from the basal cerebellar nuclei, which do not join the superior crus, but follow the ventral course to arrive at the red nucleus. LEWANDOWSKY,s fibres O. P. (in fig. 66 and 37) are not to be identified with these fibres on account of their entirely different course.

In cat LXII the anterior crus cerebelli was partially cut, and at the same time an incision made into the middle crus. Also in this animal there was found no degeneration on the distal side of the lesion except the bundle of Monakow. Were the ventral bundle to be regarded as being formed by descending collaterals of the anterior crus this result could hardly be explained. A simular result was obtained in cat LXVIII, where hemisection of the pons was effected. Also here there was no degeneration on the distal side of the lesion.

Mathematics. — *"Equilibrium of systems of forces and rotations in Sp_4."* By Dr. S. L. VAN OSS. (Communicated by Prof. P. H. SCHOUTE).

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

Referring to the following well-known properties:

a. The coordinates p_{ij} and π_{ij} of a line p and a plane π satisfy the five relations:

$$P_i = p_{kl}\, p_{jm} + p_{lj}\, p_{km} + p_{jk}\, p_{lm} = 0 \quad , \quad \pi_i = \sum_i \pi_{kl}\, \pi_{jm} = 0, \quad . \quad (1)$$

of which relations three are mutually independent.

b. The condition that a line p and a plane π intersect each other is expressed by

$$\Sigma\, p_{ij}\, \pi_{ij} = 0\, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

c. The coordinates of the point of intersection X of two planes π, π' and that of $Sp_2 \Xi$ through two lines p, p' are:

$$x_i = \pi_{kl}\, \pi'_{jm} + \pi_{lj}\, \pi'_{km} + \pi_{jk}\, \pi'_{lm} + \pi_{jm}\, \pi'_{kl} + \pi_{km}\, \pi'_{lj} + \pi_{lm}\, \pi'_{jk}\, ;$$
$$\xi_i = \sum_i p_{kl}\, p'_{jm}\, , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

we wish to draw the attention to the following properties:

If (ij) are ten *arbitrary* quantities: i.e. not satisfying the relations

$\sum_i (jk)(lm) = 0$, we shall continually be able to break up each of these quantities into two parts $(ij)'$ and $(ij)''$, so that $\sum_i (kl)'(jm)' = \sum_i (kl)''(jm)'' = 0$. It is easy to see that this decomposition can be done in ∞^4 ways.

For each decomposition holds good :

$$\Sigma (kl)'(jm)'' = \Sigma (kl)(jm) \quad , \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for :

$$\sum_i (kl)'(jm)'' = \sum_i (kl)'\{(jm) - (jm)'\} = \sum_i (kl)'(jm),$$

likewise :

$$\sum_i (kl)'(jm)'' = \sum_i (kl)''(jm),$$

from which by addition :

$$\sum_i (kl)'(jm)'' = \sum_i (kl)(jm).$$

Giving a geometrical interpretation we regard a homogeneous system of 10 arbitrary quantities a_{ij} and α_{ij} as the coordinates of

a system a of ∞^4 lines, in pairs a', a'' conjugated by the relations :

$$a'_{ij} + a''_{ij} = a_{ij} \quad . \quad . \quad . \quad (5)$$

All these lines lie in one Sp_3 Ξ having as coordinates:

$$\xi_i = \sum_i a_{kl}\, a_{jm} \quad . \quad . \quad . \quad . \quad (6)$$

a system α of ∞^4 planes, in pairs α', α'' conjugated by the relations:

$$\alpha'_{ij} + \alpha''_{ij} = \alpha_{ij} \quad . \quad . \quad . \quad . \quad (5')$$

All these planes pass through one point X, having as coordinates:

$$x_i = \sum_i \alpha_{kl}\, \alpha_{jm} \quad . \quad . \quad . \quad . \quad (6')$$

We now annul the homogeneousness of the p-, π-, a- and α-coordinates.

This causes those elements to assume vector-nature and makes them interpretable respectively as force, as rotation, as dynam and as double-rotation. The equations (5), (5′) determine the reduction of the *vectors* a and α on the conjugate pairs of lines and of planes of the systems a and α under consideration and not yet partaking vector-nature, whose structure now becomes revealed.

II. In connection with the meaning given in b of the equation $\Sigma\, p_{ij}\, \pi_{ij} = 0$ we interpret

$$\Sigma\, \alpha_{ij}\, p_{ij} = 0 \quad . \quad . \quad . \quad . \quad (7)$$

as the condition that a line p cuts a pair of conjugated planes of system α.

$$\Sigma\, a_{ij}\, \pi_{ij} = 0 \quad . \quad . \quad . \quad . \quad (7')$$

as the condition that a plane π cuts a pair of conjugated lines of system a.

This gives us a very fair survey of the structure of the linear complex of lines and planes. The reduction of the equation of the complex of planes to its diametral space is now easy to do; likewise the further reduction to the simplest form $(kl) = \sigma\,(jm)$, assumed by the equation when the edges kl and jm, the planes $i\,jm$ and $i\,kl$ of the simplex of coordinates are conjugated elements of the systems a or α.

III. If we assign to the elements p, π, a, α vector-nature, expressions $\Sigma\, \alpha_{ij}\, p_{ij}$, $\Sigma\, a_{ij}\, \pi_{ij}$ become of importance as *virtual coefficients* (in BALL's theory of screws) and the disappearing of these coefficients then gives the *condition that the force p performs no work at a displacement in consequence of a double rotation α, resp. that the dynam a performs no work at a rotation π.*

So in BALL's notation the equations (7), (7)′ give the *condition of reciprocity between force and double rotation, resp. between dynam and rotation.*

In like manner the equation

$$\Sigma\, a \quad \alpha_{ij} = 0\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

which includes (7) and (7)′ and likewise (2), gives the condition of reciprocity between the dynam a and the double rotation α.

IV. We shall now pass to the general equilibrium of forces and rotations. It will be convenient to understand by p, π, a, α vectors *unity* and to indicate the intensity of these vectors by a factor.

It will be sufficient to limit ourselves to the equilibrium of forces, leaving the treatment of the dual case to the reader.

In the first place we regard the case of n forces, $n > 10$ working along lines given arbitrarily.

It goes without saying that for the equilibrium it is necessary and sufficient that the intensities $k^{(\nu)}$ satisfy the ten conditions:

$$\Sigma\, k^{(\nu)}\, p^{(\nu)} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

We can therefore in general bring arbitrary intensities along $n - 10$ vectors, those on the other ten then being determined by the above equation (9).

In particular for $n = 11$ the theorem holds:

To vectors along eleven lines given arbitrarily belongs in general only one distribution of ratios of intensity, so that the system on those lines is in equilibrium.

The generality of the case is circumscribed by the requirement that no ten lines can satisfy one and the same linear condition in the form $\Sigma\, \alpha_{ij}\, p^{\nu}_{ij} = 0$, where the coefficients α_{ij} do not depend on ν, in consequence of a well-known property of determinants tending to zero.

So if there are among n lines at most 10 belonging to a linear complex we can satisfy the equations (9) by choosing all intensities except those belonging to these 10 equal to 0 and then (if not all subdeterminants of order 9 tend to 0) we shall be able to bring along these last only *one* distribution of intensity differing from 0 in such a way that the system of forces obtained in this manner is in equilibrium.

We have thus at the same time arrived at the following theorems: *For the equilibrium of ten forces it is necessary that these belong to one and at most to one linear complex. In this case always one and not more than one distribution of intensity is possible.*

If we continue the investigation of the equations (9) we then obtain successively the conditions of equilibrium of 9, 8, 7, 6, 5 forces. We can express the result as follows:

In order to let n forces, $11 > n > 4$, admit only of one distribution of intensity in equilibrium, it is necessary and sufficient for them to be the common elements of exactly $21-n$ linear complexes.

In particular for $n = 5$ we find the condition that the forces must belong to a system of associated lines of SEGRE.

This has given us a connection with a former paper in which we treated this case synthetically.

V. The condition that ten forces in equilibrium belong to one complex follows almost immediately out of the interpretation of the equation $\Sigma a_{ij} p_{ij} = 0$ as condition of reciprocity of force and double rotation.

Let e.g. ten forces be given in equilibrium; nine of these forces chosen arbitrarily determine a complex, so also the double rotation a for which none of them can perform labour. The united system of ten forces, as being in equilibrium doing no labour for no motion whatever, it is necessary for the tenth force to be likewise reciprocal with respect to the double rotation a, i.e. this force belongs with the former nine to the selfsame complex.

Equally simple is the deduction of the conditions of equilibrium for nine forces.

For eight forces determine a simply-infinite pencil of complexes whose conjugate double rotations $a + \lambda a'$ are all reciprocal with respect to these eight forces. So they must also be reciprocal with respect to the ninth force in equilibrium with these, i. o. w. the latter must belong to all linear complexes to which the eight others belong.

And so on.

VI. We shall now denote still, by means of a few words, in which way we can arrive at an extension of the screw-theory of BALL by the application of the principle of exchange of space-element to the equations $\sum_{1}^{10} a_i \xi_i = 0$.

By interpreting this equation either

1st. as condition of united position of a point X and an Sp_8 Ξ in Sp_9,

2nd. as condition of reciprocity (BALL) of a dynam X and a double rotation Ξ,

we make a connection between the point- and Sp_8-geometry in Sp_9 on one hand and the geometry of dynams and double rotations on the other hand.

To each theorem of the former corresponds a theorem of the latter geometry. Nov the remarkable fact makes its appearance that *the fundamental theorems of the geometry of Sp_6 correspond to the fundamental theorems of the theory of screws of* BALL *in Sp_3.*

With this as basis we shall show, though it be but by means of some few examples of a fundamental nature, that the principles of a generalisation of the theory of screws are very easy to be arrived at by transcription of the simplest properties of the point- and Sp_8-geometry in Sp_9 which examples can at the same time be of service to explain the above observations on the theory of BALL in Sp_3.

To avoid prolixity we introduce the following notation. We call:

dynamoid the system of lines whose conjugate pairs can serve as bearers of a dynam.

rotoid the system of planes whose conjugate pairs can serve as bearers of a double rotation: So dynamoid and rotoid correspond to dynam and double rotation as in the notation of BALL "screw" to dynam and helicoidal movement.

Let the following transcriptions be sufficient to explain the application of the above principle.

σX:	Point X bearing a mass σ.	Dynamoid X bearing a dynam of intensity X.
$\sigma \Xi$:	Sp_8 Ξ with a density of mass σ.	Rotoid Ξ bearing a double rotation of intensity σ.
$(X' X'')$:	Right line, locus of the centres of gravity of variable masses in the points X' and X''.	Pencil of dynamoids, locus of the bearers of the resultants of two variable dynams on the dynamoids X' and X''.
$(\Xi' \Xi'')$:	Sp_8-pencil.	Pencil of Rotoids.
	A right line has always	A pencil of dynamoids always

a point in common with an Sp_8.	contains a dynamoid reciprocal to a given rotoid.
An Sp_8 is determined by nine points.	A rotoid can always be determined lying reciprocal with respect to nine dynamoids.
p spaces Sp_8 cut each other according to Sp_{9-p}.	The dynamoids reciprocal to the movements of a body with p degrees of freedom form a $(9-p)$-fold infinite pencil.

Etc. etc.

We shall now apply the above to the problem: "To decompose a dynam according to *ten* given dynamoids", this problem being a transcription of the following:

"To apply to ten given points a distribution of mass so that the centre of gravity finds its place in a given point."

We again put side by side the results.

To be defined successively:

a. An Sp_8 through nine of the given points.	The rotoid reciprocal to nine of the given dynamoids.
b. The right line through the remaining point and the centre of gravity.	The pencil of dynamoids through the remaining dynamoid and the bearer of the given dynam.
c. The point of intersection of this right line with the Sp_8 found in *a*.	The dynamoid on this pencil reciprocal with respect to the rotoid found in *a*.
d. The decomposition of the mass in the centre of gravity according to this point of intersection and the 10th point named in *b*, which is possible, these three points being collinear; gives at once the mass to be applied in the last named point.	The decomposition of the given dynam according to the dynamoid found in *c* and the 10th dynamoid named in *b*, which is possible, these three dynamoids belonging to one pencil, gives at once the intensity of the dynam on the last mentioned dynamoid.
The other must necessarily become the centre of gravity of the remaining nine points.	The other must necessarily bear the resultant of the dynam to be applied to the remaining nine dynamoids.
e. These treatments to be repeated for the determination of mass in the other points.	These treatments to be repeated for the determination of intensity on the other dynamoids.

Zalt-Bommel, March 28, 1907.

Physics. — *"Contribution to the theory of binary mixtures,"* *III*, by Prof. J. D. van der Waals.

Continued, see page 727.

We shall now proceed to describe the course of the spinodal curve and the place of the plaitpoints when choosing regions of fig. 1 which lie more to the right. But it has appeared from what precedes that to decide what different cases may occur, we must know the relative position of the curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$, to which now the curve $\frac{d^2\psi}{dxdv}=0$ is added; so the relative position at different temperatures of the three curves which occur in the equation of the spinodal curve.

The curves $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dxdv}=0$ may be considered as sufficiently known, and the knowledge of the relative position of these curves with regard to each other enabled us already before to elucidate sufficiently the critical phenomena of mixtures with minimum critical temperature — and though with regard to the relative position of these lines some particularities are met with, which have not expressly been set forth, I shall assume the properties of these lines to be known. But the curve $\frac{d^2\psi}{dx^2}=0$ is less known — and it has appeared from the foregoing remarks, that if we wish to understand the occurrence of complex plaits, the relative position of this curve with respect to the curve $\frac{d^2\psi}{dv^2}=0$ must be known. If this line lies altogether within the region where $\frac{d^2\psi}{dv^2}$ is negative, it has no influence to speak of on the course of the spinodal line, but if it lies either partially or entirely outside this region, the influence on the course of the spinodal curve is great, and the existence of this curve accounts for the complexity of the plait and gives rise to the phenomena of non-miscibility. I have, therefore, thought it advisable to investigate the properties of the curve $\frac{d^2\psi}{dx^2}=0$, before proceeding to the description of the course of the spinodal curve also in other regions of fig. 1. A perfectly exact investigation of this line would, of course, require a perfectly accurate knowledge of the equation of state. But the value assumed already before as an approximate equation of this line:

$$\frac{d^2\psi}{dx^2} = MRT\left\{\frac{1}{x(1-x)} + \frac{\left(\frac{db}{dx}\right)^2}{(v-b)^2}\right\} - \frac{\frac{d^2a}{dx^2}}{v} = 0$$

will prove adapted to give an insight into the different possible positions of this line with respect to $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dxdv} = 0$.

THE CURVE $\frac{d^2\psi}{dx^2} = 0$.

The differential equation of this curve:

$$\frac{d^3\psi}{dx^3}dx + \frac{d^3\psi}{dx^2dv}dv + \frac{d^3\psi}{dx^2dT}dT = 0$$

may also be written in the following forms:

$$\frac{d^3\psi}{dx^3}dx + \frac{d^3\psi}{dx^2dv}dv - \frac{d^2T\eta}{dx^2{}_{vT}}\frac{dT}{T} = 0$$

or

$$\frac{d^3\psi}{dx^3}dx + \frac{d^3\psi}{dx^2dv}dv - \frac{d^2(\varepsilon-\psi)}{dx^2{}_{vT}}\frac{dT}{T} = 0$$

or

$$\frac{d^3\psi}{dx^3}dx + \frac{d^3\psi}{dx^2dv}dv - \frac{d^2\varepsilon}{dx^2{}_{vT}}\frac{dT}{T} = 0$$

or

$$\frac{d^3\psi}{dx^3}dx + \frac{d^3\psi}{dx^2dv}dv + \frac{1}{v}\frac{d^2a}{dx^2}\frac{dT}{T} = 0.$$

The curve $\frac{d^2\psi}{dx^2} = 0$ can only be found for positive value of T when $\frac{d^2a}{dx^2}$ is positive. So we derive from the latter form that $\left(\frac{dx}{dT}\right)_v$ is positive for the points for which $\frac{d^3\psi}{dx^3}$ is negative, and the other way about.

In the same way, that $\left(\frac{dv}{dT}\right)_x$ is positive for the points for which $\frac{d^3\psi}{dvdx^2}$ is negative and vice versa. The transition of the points for which $\frac{d^3\psi}{dx^3}$ is negative or positive, takes place in the points of the curve $\frac{d^2\psi}{dx^2}=0$ with maximum or minimum volume or for which $\frac{d^3\psi}{dx^3}=0$; and the transition of the points for which $\frac{d^3\psi}{dvdx^2}=-\frac{d^2p}{dx^2}_{v,T}$ is negative or positive, takes place in the points with maximum or or minimum value of x. From all this follows that the curve $\frac{d^2\psi}{dx^2}=0$ contracts with rise of T, and has contracted to a single point for certain value of $T=T_g$. It is now necessary for our purpose to determine the value of T_g, and also the value x_g and v_g of the point at which this locus vanishes. This means analytically that we have to determine the values of T, x and v, which satisfy:

$$\frac{d^2\psi}{dx^2}=0, \qquad \frac{d^3\psi}{dx^3}=0 \quad \text{and} \quad \frac{d^3\psi}{dvdx^2}=-\frac{d^2p}{dx^2}=0$$

or the equations:

$$MRT\left\{\frac{1}{x(1-x)}+\frac{\left(\frac{db}{dx}\right)^2}{(v-b)^2}\right\}=\frac{\frac{d^2a}{dx^2}}{v} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{(1-2x)}{2x^2(1-x)^2}=\frac{\left(\frac{db}{dx}\right)^3}{(v-b)^3} \quad . \quad . \quad . \quad . \quad (2)$$

and

$$MRT\frac{\left(\frac{db}{dx}\right)^2}{(v-b)^3}=\frac{1}{2}\frac{\frac{d^2a}{dx^2}}{v^2} \quad . \quad . \quad . \quad . \quad (3)$$

If (1) is divided by (3), we get a relation between x and v, which in connection with (2) may lead to the knowledge of x_g and v_g.

Then we get:

$$\frac{(v-b)^3}{x(1-x)\left(\frac{db}{dx}\right)^2}=v+b=(v-b)+2b$$

and as $(v-b)^3=\left(\frac{db}{dx}\right)^3\frac{2x^2(1-x)^2}{1-2x}$ we find :

$$\frac{b}{\frac{db}{dx}}=\frac{x(1-x)}{1-2x}-\frac{1}{2}\left\{\frac{2x^2(1-x)^2}{1-2x}\right\}^{1/3} \quad . \quad . \quad . \quad (4)$$

and putting $b = b_1 + x\dfrac{db}{dx}$

$$\frac{b_1}{\dfrac{db}{dx}} = \frac{x^2}{1-2x} - \frac{1}{2}\left\{\frac{2x^2(1-x)^2}{1-2x}\right\}^{1/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The 1st member of this last equation representing the ratio between the size of the molecules of the first component and the difference of the sizes of the two kinds of molecules, we see that x_g depends only on the ratio between the sizes of the molecules of the two components.

If we take the two extreme cases 1st that b_1 may be put equal to 0, 2nd that b_2 is equal to b_1, we find the two extreme values of x_g.

$$\left(\frac{2x^2}{1-2x}\right)^3 = \frac{2x^2(1-x)^2}{1-2x} \text{ or } 4x^4 = (1-x)^2\,(1-2x)^2 \text{ or } 2x^2 = (1-x)(1-2x)$$

or $x = {}^1/_3$ for $b_1 = 0$. For the other extreme case $\dfrac{db}{dx} = 0$, we find $x = {}^1/_2$.

For some arbitrarily chosen values of x_g I have calculated the corresponding values of $\dfrac{b_1}{b_2 - b_1}$

x_g	$\dfrac{b_1}{b_2-b_1}$	$\dfrac{v-b}{b}$	y_g (see p. 832)
$^1/_3$	0	2	0,5
0,4	0,3704	1,115	0,358
0,45	1,5	0,505	0,216
0,46	2,08	0,457	0,186
0,47	3,06	0,363	0,154
0,48	5,04	0,265	0,117
0,49	10,91	0,191	0,0874
0,5	∞	0	0.

If on the other hand the value of x_g has been calculated by the aid of the given value of $\dfrac{b_1}{\dfrac{db}{dx}}$, v_g is determined by the aid of the equation:

$$v - b = \frac{db}{dx}\sqrt[3]{\frac{2x^2(1-x)^2}{1-2x}}\,.$$

If $\dfrac{db}{dx} = 0$, in which case $x_g = {}^1/_2$, this equation gives an indefinite value for $v - b$. So it is better to express $v - b$ in a value in which $\frac{db}{dx}$ does not occur. We write by the aid of formula (4):

$$(v-b) = b \frac{\sqrt[3]{\frac{2x^2(1-x)^2}{1-2x}}}{\frac{x(1-x)}{1-2x} - \frac{1}{2}\sqrt[3]{\frac{2x^2(1-x)^2}{1-2x}}}$$

or

$$\frac{v-b}{b} = \frac{2}{\sqrt[3]{\frac{4x(1-x)}{(1-2x)^2}} - 1}.$$

In the above table we find the values of $\frac{v-b}{b}$ calculated for arbitrarily chosen values of x_g. For values of x_g differing very little from $^1/_2$ the value of $\frac{v-b}{b}$ approaches $2\sqrt[3]{(1-2x_g)^2}$.

The value of MRT_g may be brought under the following form:

$$MRT_g = \frac{\frac{d^2a}{dx^2}}{b} x(1-x) \frac{1 - \left[\frac{(1-2x)^2}{4x(1-x)}\right]^{\frac{1}{3}}}{\left\{1 + \left[\frac{(1-2x)^2}{4x(1-x)}\right]^{\frac{1}{3}}\right\}^2}$$

So the temperature at which the locus $\frac{d^2\psi}{dx^2} = 0$ vanishes depends in the first place on the value of x at which it vanishes, and in the second place on the quantity $\frac{d^2a}{dx^2}$. As according to form. 5 x may lie between $\frac{1}{3}$ and $\frac{1}{2}$, the factor of $\frac{\frac{d^2a}{dx^2}}{b}$ may vary between $\frac{4}{81}$ and $\frac{1}{4}$. The value of that factor is therefore only determined by the ratio between b_1 and b_2. For $b_1 = 0$ the value is $\frac{4}{81}$, for $b_1 = b_2$ this value is $\frac{1}{4}$. So the greater the difference in the size of the molecules, the lower this factor, and the lower the temperature at which $\frac{d^2\psi}{dx^2} = 0$ has disappeared. And because the non-miscibility in the liquid state is to a great extent due to the existence of $\frac{d^2\psi}{dx^2} = 0$, molecules of the same size $\left(\frac{d^2a}{dx^2}\right.$ being always thought equal$\left.\right)$ will not so readily mix as those for which the size of one kind greatly exceeds the size of the other kind, a property to which we might have concluded without calculations. But in the second place the quantity $\frac{d^2a}{dx^2} = 2(a_1 + a_2 - 2a_{12})$ has great influence on the height of this temperature, and indeed, in so high a degree that if $\frac{d^2a}{dx^2}$ should be $= 0$, the locus $\frac{d^2\psi}{dx^2} = 0$ would already have disappeared at the absolute zero point. Indeed, we might have seen from the very beginning that this locus could never exist for $\frac{d^2a}{dx^2}$ negative. Everything, on the other hand that diminishes a_{12}, makes T_g rise, and so furthers non-mixing. In some limiting cases we may compare the value of T_g with that of T_k, 1st in the case that into a given substance we should press a gas as 2nd component following the laws of BOYLE and GAY-LUSSAC perfectly. For such a gas we should have to put b_1 and a_1 equal to zero, and so probably also a_{12}. The value of x of the formula for T_g is then equal to $\frac{1}{3}$. The a for the mixtures containing only one term then, and being equal to a_2x^2, $\frac{d^2a}{dx^2} = 2a_2$. The value of b_x for the mixture is then equal to b_2x. On these suppositions $MRT_g = \frac{8}{27}\frac{a_2}{b_2}$, and so T_g is equal to the critical temperature of the 2nd component. The value of T_k for every mixture taken as homogeneous, is then equal to $x(T_k)_2$. Consequently $T_g = 3(T_k)_x$. For a value of T somewhat below $(T_k)_2$ the locus $\frac{d^2\psi}{dv^2} = 0$ is restricted to a very narrow region on the side of the 2nd component, while $\frac{d^2\psi}{dx^2} = 0$ still exists, and may be compared to a small circular figure whose centre is a point with the coordinates $x = {}^1/_3$ and $v = b_2$. The spinodal curve has then an equation which may be written as follows:

$$\frac{MRT}{\left(\frac{v}{x} - b_2\right)^2} = \frac{2a_2}{\left(\frac{v}{x}\right)^3},$$

which equation shows that it consists of two straight lines, which join the point $x=0$ and $v=0$ with the points for which $-\frac{dp}{dv}=0$ for the second component. At temperatures which are not too far below $(T_k)_2$, the locus $\frac{d^2\psi}{dx^2}=0$ lies, therefore, entirely outside the curve $\frac{d^2\psi}{dv^2}=0$, and is then restricted to the left side of the figure.

2nd. As second limiting case we take $b_1=b_2$, but a_1 differing from a_2. Then $MRT_g=\frac{d^2 ax(1-x)}{dx^2 \quad b}$, and because $x=\frac{1}{2}$ $MRT_g=\frac{2(a_1+a_2-2a_{12})}{4b}$, whereas MRT_k is equal to $\frac{8}{27}\frac{a_1+a_2+2a_{12}}{4b}$ for $x={}^1/_2$. Then, too, T_g may be larger than T_k viz. when $\frac{27}{4}(a_1+a_2-2a_{12})>(a_1+a_2+2a_{12})$ or if $2a_{12}<\frac{23}{31}(a_1+a_2)$. But even if T_g should be $<T_k$, this implies by no means that shortly before its disappearance the locus $\frac{d^2\psi}{dv^2}=0$ lies in the region in which $\frac{d^2\psi}{dv^2}$ is negative. The previously calculated values of $\frac{v-b}{b}$ show that this disappearance takes place at a very small volume, which may be smaller, and in the limiting case will certainly be smaller than the liquid volumes of the curve $\frac{d^2\psi}{dv^2}=0$. To ascertain whether the disappearance of $\frac{d^2\psi}{dx^2}=0$ takes place in the region in which $\frac{d^2\psi}{dv^2}$ is negative, we may substitute the value of T_g, x_g and v_g in the form for $\frac{d^2\psi}{dv^2}$, and examine the conditions on which this value of $\frac{d^2\psi}{dv^2}$ becomes negative. If we write for $\frac{(1-2x_g)^2}{4x_g(1-x_g)}=y_g{}^3$, then:

$$MRT_g=\frac{d^2 a\,x_g(1-x_g)}{dx^2 \quad b_g}\,\frac{1-y_g}{(1+y_g)^2}, \quad \frac{v_g-b_g}{b_g}=\frac{2y_g}{1-y_g}, \quad \frac{v_g}{b_g}=\frac{1+y_g}{1-y_g}$$

and

$$\left(\frac{d^2\psi}{dv^2}\right)_g=\frac{MRT_g}{(v_g-b_g)^2}-\frac{2a}{v_g{}^3}.$$

So the sign of $\left(\frac{d^2\psi}{dv^2}\right)_g$ depends on $MRT_g - \frac{2a}{b_g}\frac{(v_g-b_g)^2}{v_g^2}\frac{b_g}{v_g}$ or on

$$\frac{d^2a}{dx^2}\frac{x_g(1-x_g)}{b_g}\frac{1-y_g}{(1+y_g)^2} - \frac{2a}{b_g}\frac{4y_g^2}{(1+y_g)^2}\frac{1-y_g}{1+y_g}$$

or on $(a_1+a_2-2a_{12})\,x_g\,(1-x_g) - a\,\frac{4y_g^2}{1+y_g}$.

For the discussion of this last quantity we first put the first mentioned limiting case, in which a_1 and a_{12} may be neglected with respect to a_2, and $a=a_2x^2$ may be put; the value of y_g being $=\frac{1}{2}$ according to the table of p. 829. With this value this quantity becomes:

$$a_2x\left\{1-x-\frac{2}{3}x\right\}$$

so positive.

For the other limiting case for which $y_g=0$, it is also positive. But for the intermediate cases, specially those for which $a_1+a_2-a_{12}$ is small with respect to a, and b_1 and b_2 are not equal, it will be negative, and shortly before its disappearance the locus $\frac{d^2\psi}{dx^2}=0$ will lie in the region in which $\frac{d^2\psi}{dv^2}$ is negative, and the existence of this locus will have little influence on the course of the spinodal curve, and accordingly it will not give rise to a complex plait [1]) or rather to a spinodal curve which diverges greatly from the curve $\frac{d^2\psi}{dv^2}=0$.

Let us now also examine where the point in which $\frac{d^2\psi}{dx^2}=0$ disappears, lies with respect to the curve $\frac{d^2\psi}{dxdv}=0$ or to $\left(\frac{dp}{dx}\right)_v=0$. Let us substitute the value of MRT_g, x_g and v_g in the expression for $\left(\frac{dp}{dx}\right)$. If this expression becomes positive, the point lies outside the curve or rather at smaller volumes than those of the curve $\left(\frac{dp}{dx}\right)_v=0$ and the other way about. Then we find for:

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[1]) I need hardly state expressly, that in this communication I no longer attribute the cause of the complexity of the plaits exclusively to the abnormal behaviour of the components, to which at one time I thought I had to ascribe it, in compliance with LEHFELD. On the other hand it would be going too far to deny the abnormality of the components any influence.

$$MRT_g \frac{\frac{db}{dx}}{(v_g-b)^2} - \frac{\frac{da}{dx}}{v^2}$$

$$\frac{d^2a}{dx^2}\frac{x_g(1-x_g)}{b}\frac{1-y_g}{(1+y_g)^2}\frac{db}{dx}\frac{1}{(v_g-b)^2} - \frac{\frac{da}{dx}}{v_g^2}$$

and after the substitution of $\frac{b}{\frac{db}{dx}} = \frac{x_g(1-x_g)}{1-2x_g}(1-y_g)$ and of $\left(\frac{v_g-b}{v_g}\right)^2 = \frac{4y_g^2}{(1+y_g)^2}$, the sign proves to depend on the expression:

$$\frac{d^2a}{dx^2}(1-2x_g) - \frac{da}{dx}4y_g^2.$$

In the first limiting case in which $\frac{d^2a}{dx^2} = 2a_2$, $\frac{da}{dx} = 2a_2x_g$, $y_g = \frac{1}{2}$ and $x_g = \frac{1}{3}$, this expression $= 0$. Also in the second limiting case, in which $x_g = \frac{1}{2}$ and $y_g = 0$. So in the limiting cases the curve $\frac{d^2\psi}{dxdv} = 0$ intersects the curve $\frac{d^2\psi}{dx^2}$ up to the last moment in which the latter disappears. Also in an intermediate case this quantity may be zero, but the value of x_g, at which this takes place, depends on $\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}$ or on $\frac{(a_2-a_{12})-(a_{12}-a_1)}{(a_{12}-a_1)(1-x_g)+x_g(a_2-a_{12})}$.

If we write $\frac{a_2-a_{12}}{a_{12}-a_2} = 1+\Delta$, then $\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}} = \frac{\Delta}{1-x_g+x_g(1+\Delta)} = \frac{\Delta}{1+x_g\Delta}$. We then derive the value of x_g for this intermediate case from the equation:

$$\frac{\Delta}{1+\Delta x_g}(1-2x_g) = 4\frac{(1-2x_g)^{4/3}}{[4x_g(1-x_g)]^{2/3}}$$

or

$$\frac{\Delta}{1+\Delta x_g} = 4\left[\frac{1-2x_g}{16x_g^2(1-x_g)^2}\right]^{1/3}.$$

For values of x_g differing little from $\frac{1}{2}$ we find approximately:

$$\frac{1}{2} - x_g = \frac{1}{128}\left(\frac{\Delta}{1+\frac{1}{2}\Delta}\right)^3.$$

If for Δ we take the value 4, which must be considered large for molecules of about the same size, then $\frac{1}{2} - x_g$ would be $= \frac{1}{54}$. The conclusion which we draw from all this as to the situation of the point in which $\frac{d^2\psi}{dx^2} = 0$ disappears, with respect to the curve $\frac{d^2\psi}{dxdv} = 0$, is the following. In most cases this point disappears within the curve $\left(\frac{dp}{dx}\right)_v = 0$, and so in the region where $\left(\frac{dp}{dx}\right)_v$ is negative, but this can also take place on the other side of $\left(\frac{dp}{dx}\right)_v = 0$, so at a volume which is smaller than that of this curve.

That at positive value of Δ, so at positive value of $\frac{a_1+a_2-2a_{12}}{a_{12}-a_1}$
$\frac{\Delta}{1+x\Delta} = 4^{1/3}\frac{(1-2x)^{1/3}}{x^{2/3}(1-x)^{2/3}}$ has always a root, appears immediately when we represent the two members of this equation graphically. The first member, namely, represents then a branch of a hyperbola which at $x=0$ has a height above the axis of x equal to that of Δ, and at $x=1$ a height equal to $\frac{\Delta}{1+\Delta}$, and which, therefore, proceeds continuously at a certain positive though decreasing height above the x-axis. The second member represents a line which for $x=0$ has a point infinitely far above, and for $x=1$ a point infinitely far below the x-axis. This line passes through the point $x = \frac{1}{2}$, and on the left and the right of this point the ordinates are equal, but with reversed sign. So intersection will certainly take place, and for positive Δ at a value of $x < \frac{1}{2}$. For the case that $\frac{d^2\psi}{dx^2} = 0$ disappears at smaller volume than that of the curve $\frac{dp}{dx} = 0$, the first member must be larger than the second. As Δ is larger, the point of intersection will be further removed from $x = \frac{1}{2}$, and so the series of the values of x for which the condition is that the first member be larger

than the second member, has increased. From this we conclude that $\frac{d^2\psi}{dx^2}=0$ may disappear also for very different size of the molecules in the region for $\frac{dp}{dx}=$ positive, if Δ has a considerable size. But for perfectly unequal size of the molecules $\left(x=\frac{1}{3}\right)$, $\frac{\Delta}{1+\frac{\Delta}{3}}$ would be >3 or $\frac{\Delta}{3+\Delta}>1$, which is not yet satisfied even at $\Delta=\infty$.

Fig. 6, in which the intersection of $\left(\frac{dp}{dx}\right)_v=0$ and $\frac{d^2\psi}{dx^2}=0$ has been drawn in both points on the left of the point in which $\left(\frac{dp}{dx}\right)_v=0$ has the minimum volume, holds for this latter case. The point in which $\frac{d^2\psi}{dx^2}=0$ disappears, must viz., lie on the line $\frac{d^2p}{dx^2}=0$. As has already been mentioned before, this line passes through the point where $\left(\frac{dp}{dx}\right)_v=0$ has its smallest volume, and as is easy to calculate $\frac{dv}{dx}$ is then always positive. If now in fig. 6 the line $\frac{d^2\psi}{dx^2}=0$ contracts, and it must vanish on $\frac{d^2p}{dx^2}=0$, then the point in which it disappears, lies at smaller volume than that of $\left(\frac{dp}{dx}\right)_v=0$. For the opposite case the two points of intersection must therefore be drawn right of the point with minimum volume. Also the intermediate case has now become clear. In this respect there is an inaccuracy in the drawing of fig. 5. The line $\frac{d^2\psi}{dx^2}=0$, which has already almost quite contracted, must be expected there on the right of the point in which $\left(\frac{dp}{dx}\right)_v=0$ has the smallest volume. So the line $\left(\frac{dp}{dx}\right)_v=0$ would have its minimum volume more to the left in fig. 5. In fact, with rise of temperature all these lines are subjected to displacements — however, not to such a degree that the relative position is much changed by it.

All these remarks seem essential to me for the following reason: we shall, namely, soon have to draw the relative position of the curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$, also in regions lying more to the right of fig. 1, in order to decide about the more or less complexity of the plaits at the different temperatures. Then we shall have to make assumptions as to this relative position, which otherwise might seem quite unjustifiable. A great many more similar questions would even have to be put and solved, before alle doubt as to the validity of the assumptions would have been removed. And it remains the question if for the present the imperfect knowledge of the equation of state for small volumes does not prevent our ascertaining with perfect certainty whether a phenomenon of mixing or non-mixing is either normal or abnormal. So, before proceeding to the applications I shall subject only one more point to a closer investigation, viz. the question whether in the critical point of a mixture taken as homogeneous, the quantity $\frac{d^2\psi}{dx^2}$ is positive or negative, so the sign of the quantity:

$$\frac{8}{27}\frac{a}{b}\left\{\frac{1}{x(1-x)}+\frac{\left(\frac{db}{dx}\right)^2}{4b^2}\right\}-\frac{\frac{d^2a}{dx^2}}{3b}$$

or of

$$\frac{1}{x(1-x)}+\frac{\left(\frac{db}{dx}\right)^2}{4b^2}-\frac{9}{8}\frac{\frac{d^2a}{dx^2}}{a}.$$

As $2a\frac{d^2a}{dx^2}=\left(\frac{da}{dx}\right)^2+4(a_1a_2-a_{12}^2)$, we may also write for the last form:

$$\frac{1}{x(1-x)}+\frac{\left(\frac{db}{dx}\right)^2}{4b^2}-\frac{9}{16}\frac{\left(\frac{da}{dx}\right)^2}{a^2}-\frac{9}{4}\frac{a_1a_2-a_{12}^2}{a^2}.$$

As a first special case we consider a substance mixed with a perfect gas; then $b_1=0$, $a_1=0$ and $a_{12}=0$. Hence $a=a_2x^2$, $b=b_2x$. With these values the above form becomes:

$$\frac{1}{x(1-x)}-\frac{2}{x^2}=\frac{3x-2}{x^2(1-x)}$$

so $\frac{d^2\psi}{dx^2}$ is negative in the critical point for values of $x<{}^2/_3$; for $x={}^2/_3$ the curve $\frac{d^2\psi}{dx^2}=0$ will pass through the critical point. But

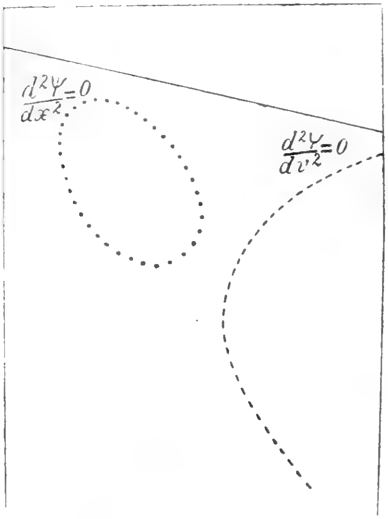

Fig. 10.

for $x > {}^2/_3$ the two curves will lie outside each other, as has been drawn in fig. 10, and already observed above. For all other cases in which a and b cannot be equal to zero, the value of the expression for $x = 0$ and $x = 1$ will be positive infinite. If it can become negative, this will, accordingly, have to be the case for two values of x. Now very different relations may exist between $\frac{1}{a}\frac{da}{dx}$ and $\frac{1}{b}\frac{db}{dx}$. Thus $\frac{1}{a}\frac{da}{dx} = {}^2/_3 \frac{1}{b}\frac{db}{dx}$ for the plaitpoint circumstances of a mixture taken as homogeneous.[1]) With these values the form reduces to a quantity which will certainly be positive, as even if $a_1 a_2 > a_{12}^2$, the value of $\frac{a_1 a_2 - a_{12}^2}{a^2}$ can probably never be larger than $\frac{4}{9}\frac{1}{x(1-x)}$, the minimum value of which is $\frac{16}{9}$.

If $\frac{1}{b}\frac{db}{dx} = \frac{1}{a}\frac{db}{dx}$, the sign of the form under discussion, depends on the value of $\frac{da}{dx}$ or $\frac{1}{b}\frac{db}{dx}$. If $\frac{1}{b}\frac{db}{dx} > \sqrt{\frac{16}{5}\frac{1}{x(1-x)}\frac{1}{a}}$, a negative value of the form is possible. So for mixtures, in which the components differ greatly in the size of the molecules, the case of fig. 11 occurs for minimum T_k, and this minimum value of T_k could not be realised. For mixtures, for which $\frac{1}{a}\frac{da}{dx} > \frac{1}{b}\frac{db}{dx}$, $\left(\frac{1}{b}\frac{db}{dx}\right)^2$ may be neglected with respect to $\frac{9}{4}\left(\frac{1}{a}\frac{da}{dx}\right)^4$, which is even perfectly allowable in the limiting case, for which $b_1 = b_2$, and $\frac{d^2\psi}{dx^2}$ will be negative,

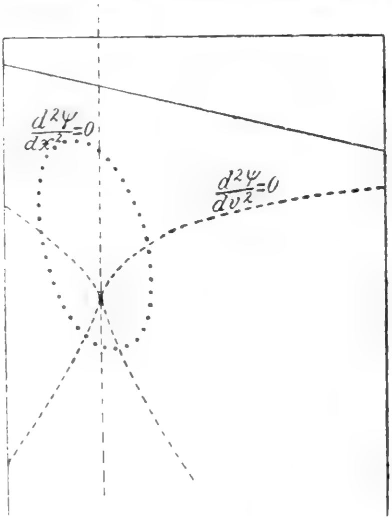

Fig. 11.

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[1]) In all the above calculations the equation of state has been applied with

when we put:

$$\frac{3}{4}\left(\frac{1}{a}\frac{da}{dx}\right) > \sqrt{\frac{1}{x(1-x)}}\,.$$

As minimum value for which this is the case, we should then have:

$$\frac{1}{a}\frac{da}{dx} > \frac{8}{3}$$

In all such cases, in which the critical circumstances of a mixture taken as homogeneous, fall in the region in which $\frac{d^2\psi}{dx^2} < 0$, these circumstances are not to be realised. Nor are they to be realised when $\frac{d^2\psi}{dx^2} > 0$, but then the spinodal curve passes at least at a small distance round this point, and the plaitpoint circumstances are not very different from these which would be the critical circumstances with an homogeneous substance. If $\frac{d^2\psi}{dx^2} < 0$, a considerable difference may be expected.

THE SPINODAL CURVE AND THE PLAITPOINTS WHEN $\frac{dT_k}{dx}$ IS POSITIVE.

Let us now again proceed to the discussion of the course of the spinodal curve and the plaitpoints; but now in the case that with increasing value of b the quantity T_k rises. Let T_{k_2} be much higher than T_{k_1}, and $\frac{a_2}{b_2} > \frac{a_1}{b_1}$. Now two cases are possible. The value of $\frac{d^2\psi}{dx^2}$ may be positive or negative in the critical points of every arbitrary mixture. For $x=0$, and in general for very small value of x, where $\frac{1}{x(1-x)}$ is very large, $\frac{d^2\psi}{dx^2}$ is certainly positive, however large the value of $\frac{d^2a}{dx^2} : a$ may be, and also for values of x differing little from 1. If $\frac{\frac{d^2a}{dx^2}}{a}$ is small, $\frac{d^2\psi}{dx^2}$ is positive in the critical points of all mixtures. But for large values of $\frac{d^2a}{dx^2} : a$ there are two values of x, between

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value of b not depending on v. Hence in this equation we get the factor $^2/_3$ for which, as we have already repeatedly observed, we should really substitute $\frac{5}{6}$.

which $\frac{d^2\psi}{dx^2}$ is negative in the critical points. If in this case we draw the line $\frac{d^2\psi}{dv^2}=0$ with a top, either at $x=0$, or at a small value of x, the curve $\frac{d^2\psi}{dx^2}=0$, which is chiefly restricted to the left side of the v,x-figure, lies partly outside the curve $\frac{d^2\psi}{dv^2}=0$, and on the small volumes. If we now apply the reasoning of p. 737 etc. also in this case, when we had the reversed state as far as $\frac{d^2\psi}{dv^2}=0$ is concerned, we conclude that for large values of x the spinodal curve does not move for away from $\frac{d^2\psi}{dv^2}=0$, but that it is forced back to smaller volumes for those values of x, where $\frac{d^2\psi}{dx^2}$ is negative, and draws again very near to $\frac{d^2\psi}{dv^2}=0$ with very small values of x. Naturally the course of the q-lines in connection with the course of the p-lines must indicate this.

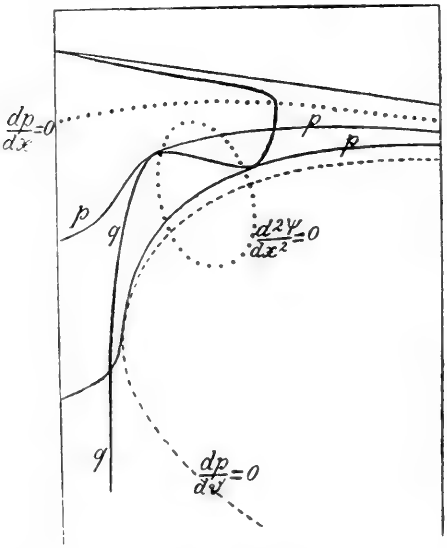


Fig. 12.

The course of the p-lines for this case must be derived from the right side of fig. 1, from which appears at the same time that the curve $\frac{d^2\psi}{dxdv}=0$ occurs, but with sensibly smaller volumes than those of $\frac{d^2\psi}{dv^2}=0$. And the course of the q-lines is then indicated by fig. 5 or perhaps sometimes by fig. 6. In fig. 12 a couple of p-lines have been drawn and a q-line which touches these p-lines, which lines yield, therefore, points for the spinodal curve. Here again three plaitpoints are to be expected: 1st. a realisable plaitpoint P_1 above the curve $\frac{d^2\psi}{dx^2}=0$, 2nd. a hidden plaitpoint P_2 on the left of $\frac{d^2\psi}{dx^2}=0$ and above $\frac{d^2\psi}{dv^2}=0$, and 3rd. the ordinary gas-liquid plaitpoint P_3 on the left of $\frac{d^2\psi}{dv^2}=0$, but shifted to the side of the small volumes. Now it is to be expected that the value of p in the first mentioned plaitpoint is smaller than in the last mentioned. For T_k strongly rising, the pressure strongly decreases when we pass along the curve $\frac{d^2\psi}{dv^2}$ to the right — and only if $\frac{d^2\psi}{dx^2}=0$ should strongly project above $\frac{d^2\psi}{dv^2}=0$ we should enter the region of high pressures. The hidden plaitpoint has, of course, far lower pressure than the two others. The value of x for the first mentioned plaitpoint is larger than that for the hidden plaitpoint. The gas-liquid plaitpoint has the smallest value of x. Proceeding along the spinodal curve we get a course of p, as has been previously drawn by me. (See These Proc. March 1905 p. 626). If T is made to increase, $\frac{d^2\psi}{dv^2}=0$ contracts. The top moves to the right, and reaches a position, in which $\frac{d^2\psi}{dx^2}$ is negative for the critical circumstances. But this means that the gas-liquid plaitpoint and the hidden plaitpoint have coincided already before. When they coincide we have again, as we observed p. 744 $\left(\frac{dv}{dx}\right)_p=\left(\frac{dv}{dx}\right)_q$, $\left(\frac{d^2v}{dx^2}\right)_p=\left(\frac{d^2v}{dx^2}\right)_q$ and $\left(\frac{d^3v}{dx^3}\right)_p=\left(\frac{d^3v}{dx^3}\right)_q$. After this coinciding we have again a simple plait with a simple plaitpoint. But the plaitpoint lies far more to the left than would be the case if the curve $\frac{d^2\psi}{dx^2}=0$ did not exist any longer, and it also has a much larger pressure. With further rise of T nothing of importance is to be expected. For neither the fact that $\frac{d^2\psi}{dx^2}=0$ lies quite outside $\frac{d^2\psi}{dv^2}=0$, nor that $\frac{d^2\psi}{dx^2}=0$ vanishes, gives rise to new phenomena, because this takes entirely place in the unstable region. If we now draw either the value of the plaitpoint temperature or of the plaitpoint pressure as function of x, and if we restrict ourselves to the realisable quantities, so excluding the hidden ones, this line separates into two detached parts. The right part begins at that value of x, in which the plaitpoint P_1 possesses a pressure large enough to show itself on the binodal curve of the plait whose plaitpoint is P_3, and passes then to $x=1$. The left part begins at $x=0$, and disappears before P_3 and P_2 coincide, namely, when P_3 lies on the binodal line, of which P_1 is then the plaitpoint.

That what we have called hidden plaitpoints, can never exhibit themselves, requires no explanation. That what in general we have called realisable plaitpoints, need not always show themselves, may indeed be assumed as known from the former thermodynamic considerations about the properties of the ψ-surface — but yet it calls for further elucidation now that we examine the properties of stability and of realisability by considering the relative position of the p- and the q-lines. We shall, however, only be able to give this elucidation, when by treating the rule to which I alluded in the beginning of this communication, we have also indicated the construction of the binodal curve.

To get a clear insight into the critical phenomena for the case that for mixtures between two definite values of x the critical point falls in the region in which $\frac{d^2\psi}{dx^2}$ is negative, we must again distinguish two cases; viz.: 1. the case that already at $T=T_{k_1}$ the curve $\frac{d^2\psi}{dx^2}$ partly projects above $\frac{d^2\psi}{dv^2}=0$, in which case already at $T=T_{k_1}$ the two plaitpoints P_1 and P_2 are found, and 2. the case that at $T=T_{k_1}$ the curve $\frac{d^2\psi}{dx^2}=0$, lies quite enclosed within $\frac{d^2\psi}{dv^2}=0$. In fig. 13 the second case is represented. Now if for values of $T>T_{k_1}$ the top of $\frac{dp}{dv}=0$ does fall within $\frac{d^2\psi}{dx^2}=0$ there must have been contact of the two curves at a lower T, and intersection at a higher T. As long as the two curves do not yet touch, the spinodal curve is little or not transformed, and no other plaitpoint is to be expected as yet than the ordinary gas-liquid plaitpoint which lies at smaller value of x than the top of $\frac{dp}{dv}=0$. If the two curves intersect, the plaitpoints P_1 and P_2 have appeared first as coinciding heterogeneous plaitpoints, later as two separate ones. Naturally the

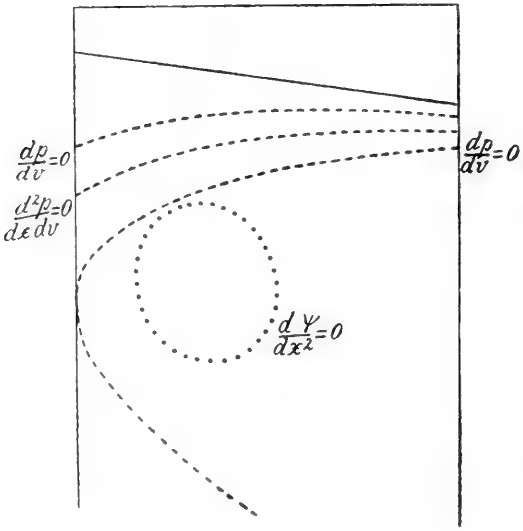


Fig. 13.

value of x for the two coinciding heterogeneous plaitpoints is larger than the value of x for the plaitpoint P_3. With further rise of the temperature, when $\frac{d^2\psi}{dx^2}=0$ rises further above $\frac{d^2\psi}{dv^2}=0$, the plaitpoints P_1 and P_2 move further apart. P_1 moves towards larger values of x, and P_2 (the hidden plaitpoints) to smaller value of x. And the two heterogeneous plaitpoints P_3 and P_2 coinciding at still higher value of T, there is a continuous series of values of x from $x=0$ up to $x=1$, for which plaitpoints occur. For every value of x only one. I have drawn (These Proc. VII, p. 626) the transformation of what I called there a principal plait and a branch plait. But this transformation refers, properly speaking, more to the binodal curve of such a complex plait than to the spinodal curve. If we then draw T_{pl} as function of x, such a line has a maximum and a minimum value, both lying above T_{k_1}. The minimum value at the origin of the double plaitpoint P_1 and P_2, and the maximum value at the disappearance of P_2 and P_3 in consequence of their coinciding. Also when P_{pl} is drawn as function of x, we get a similar curve. As in general $\frac{dp}{dx}=\frac{dp}{dx_T}+\left(\frac{dp}{dT}\right)_x\frac{dT}{dx}$, $\frac{dT_{pl}}{dx}$ will be $=0$, if $\frac{dP_{pl}}{dx}=0$, because $\left(\frac{dp}{dx}\right)_T$ is equal to 0 in a plaitpoint. But the value of P_{pl} as function of T_{pl} exhibits a more intricate form. As $T\frac{dP_{pl}}{dT}=T\left(\frac{dp}{dT}\right)_{v,x}+\frac{(-)}{\left(\frac{d^2v}{dx^2}\right)_{pT}}$, $\frac{dP_{pl}}{dT}$ is determined by the properties of the substance in the plaitpoint, e. g. by $\frac{d^2v}{dx^2}_{pT}$. This quantity is the same for double plaitpoint, and so $\frac{dP_{pl}}{dT}$ has two equal values in such a double plaitpoint. The plaitpoint curve has therefore two cusps in the case treated. The left branch extends from T_{k_1} to the temperature at which P_3 and P_2 coincide. The right branch begins at T_{k_2}, and runs then back to the temperature at which the double plaitpoint P_1 and P_2 originates. The middle branch gives the hidden plaitpoints. But here, too, we must again notice that not the whole outside branches can actually be realised, the splitting up into three phases when we draw near the cusps having a greater stability then the homogeneous plaitpoint phase. These are the phenomena observed by KUENEN for the mixtures of ethane and alcohols with greater values of b than that of ethane. Perhaps the change of

$\left(\frac{db}{dx}\right)$ may already account for the fact that the peculiar feature of this phenomenon disappears more and more when, retaining ethane, we choose an alcohol with larger value of b; so that the phenomena point to the fact that a normal plaitpoint line might be expected if we proceed in the series of the alcohols. As condition for $\frac{d^2\psi}{dx^2}$ being negative in the critical circumstances, we had:

$$\frac{1}{x(1-x)}+\frac{\left(\frac{db}{dx}\right)^2}{4b^2}-\frac{9}{8}\frac{\frac{d^2a}{dx^2}}{a}<0 \quad \text{(see p. 837)}$$

For in general it is to be expected that this value cannot so easily be realised for large value of $\frac{db}{dx}$ than e. g. for almost equal value of b_1 and b_2. That the mixture of ethane with methyl alcohol displayed quite different phenomena might already be expected on account of the fact that we have then a case for which with increasing value of b the value of T_k decreases. It is viz. almost sure that b is smaller for methyl alcohol than for ethane.

If for $T=T_{k_1}$ the curve $\frac{d^2\psi}{dx^2}=0$ should already partially project above $\frac{d^2\psi}{dv^2}=0$, this will bring about but little change in the phenomenon. Only the minimum value of T_{pl} will descend below T_{k_1} in the (T_{pl}, x)-figure. In the same way the left cusp will have to be drawn at lower value of T than T_{k_1}.

It is, therefore, required for the course of the plaitpoint phenomena, that $T_g > T_{k_1}$, and so according to the value of T_g (p. 830).

$$\frac{\frac{d^2a}{dx^2}}{b}\, x(1-x)\frac{(1-y_g)}{(1+y_g)^2}>\frac{8}{27}\frac{a_1}{b_1}.$$

In this inequality x, dependent on the value of $\frac{b_1}{b_2-b_1}$, lies between $\frac{1}{3}$ and $\frac{1}{2}$, and y_g between $\frac{1}{2}$ and 0. Let us write:

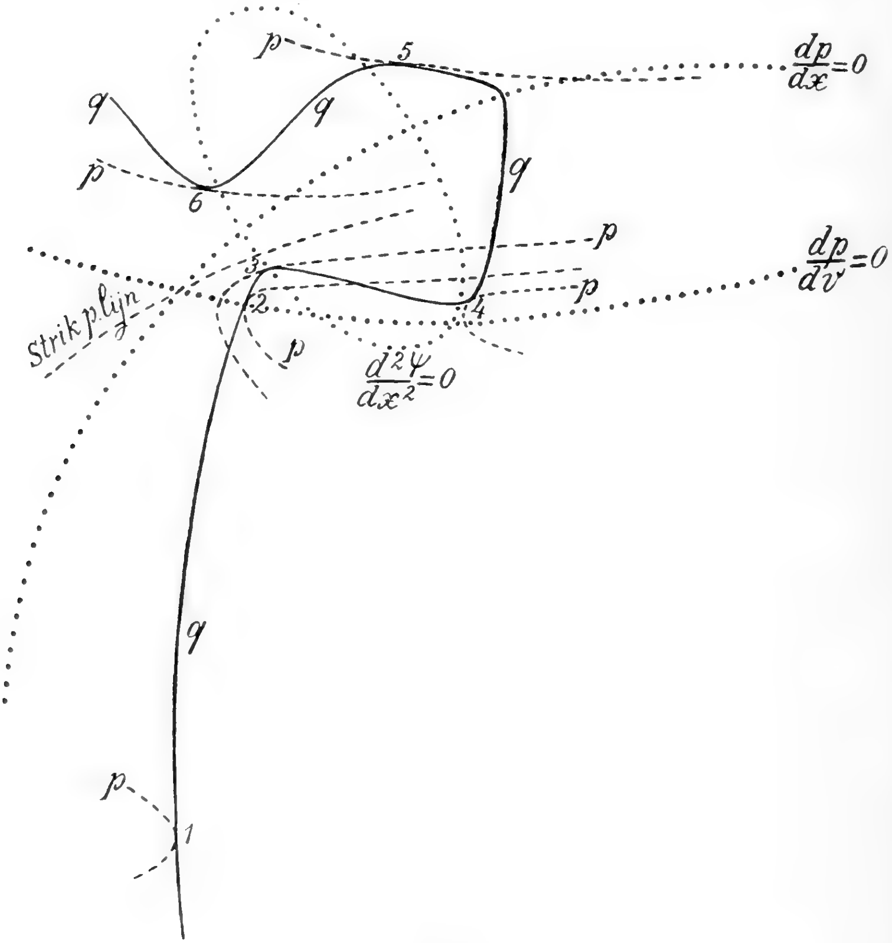
$$\frac{a_1+a_2-2a_{12}}{a_1}\, x(1-x)\frac{(1-y_g)}{(1+y_g)^2}>\frac{4}{27}\left\{1+\frac{x}{\frac{b_1}{b_2-b_1}}\right\}.$$

By successively increasing x from $\frac{1}{3}$ to $\frac{1}{2}$, and deriving the corresponding values y_g and $\frac{b_1}{b_2-b_1}$ from the table of p. 829, we can calculate the value which $\frac{a_1+a_2-2a_{12}}{a_1}$ must have at the least in order to satisfy this inequality. If we put $x=\frac{1}{3}$, to which $\frac{b_1}{b_2-b_1}=0$ corresponds, we see that only $a_1=0$ might be put. If x is made to increase, which implies that the ratio of the size of the molecules approaches 1, the value of $\frac{a_1+a_2-2a_{12}}{a_1}$ required to satisfy the inequality, decreases. For the limiting case $x=\frac{1}{2}$, $b_1=b_2$ and $y_g=0$, $\frac{a_1+a_2-2a_{12}}{a_1}$ must be $>\frac{16}{27}$ to enable us to put $T_g > T_{k_1}$.

But this value must be larger for b_1 smaller than b_2, and the larger as the difference between b_2 and b_1 increases. If this equality is not satisfied, so if $T_g < T_{k_1}$, we have a plaitpoint line of a perfectly normal shape. This is inter alia the case when for a low ratio between b_1 and b_2, also a not very high ratio between the critical temperatures is found. First, however, we should have to know how a_{12} depends on a_1 and a_2, before for given ratio of b_1 and b_2 we could indicate how large the ratio of $\frac{a_1}{b_1}$ and $\frac{a_2}{b_2}$ would have to be to justify us in expecting either the complicated or the simple shape of the plaitpoint line. Moreover, I repeat that it should be considered in how far numerical values occurring in the given equations, would have to be replaced by others on account of the only approximate validity of the equation of state.

From all this appears in how high a degree the properties of the function $\frac{d^2\psi}{dx^2}$ influence the shape of the plait, and so also the miscibility or non-miscibility in the liquid state, and that the influence of the properties of this function may be put on a level with that of the function $\frac{d^2\psi}{dv^2}$. We shall further demonstrate this by also examining the case that the curve $\frac{d^2\psi}{dx^2}=0$ exists, and intersects the curve $\frac{d^2\psi}{dx\,dv}=0$.

Let us now take a region of fig. 1 such that the line $\frac{d^2\psi}{dxdv}=0$ occurs on it, and that this line has the position as drawn in fig. 6. Then the liquid branch of $\frac{d^2\psi}{dv^2}=0$ lies on the right side of the region at larger volumes than those of $\frac{d^2\psi}{dxdv}=0$. These two curves might intersect on the left side. If now also the curve $\frac{d^2\psi}{dx^2}=0$ occurs, which will be the case if the temperature is low enough, and if this curve intersects both $\frac{d^2\psi}{dxdv}=0$ and $\frac{d^2\psi}{dv^2}=0$, we have the shape of the q-lines as drawn in fig. 6, and there will again be formed a complex plait, whose shape and properties we shall have to examine.



Strik-p-lijn = loop-p-line.
Fig. 14.

That intersection may take place of $\frac{d^2\psi}{dx^2}=0$ with $\frac{d^2\psi}{dxdv}=0$, has been proved on pages 834 and 835.

We saw before that one q-line may possess 2 or 4 points of contact with p-lines, but now we have a case in which the number of points of contact can rise to 6. In fig. 14 has been drawn: 1. the curve $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$, 2. the loop-p-line, 3. a q-line to which horizontal tangents may be drawn in 4 points, and a vertical tangent in 1 point and 4 portions of 6 p-lines touching the q-line. The pressure in point 1 is much larger than in 2, rises then, has a maximum in 3, descends again and reaches in 4 its lowest value. The greatest pressure is found in point 5, and in 6 the pressure has been drawn lower than in 5, but it may be higher than in point 1. Consult fig. 1 for the direction of the p-lines in the points of contact. These 6 points of contact are again points of the spinodal curve. So on the right there is again a portion of the spinodal curve which follows closely the line $\frac{dp}{dv}=0$ in its course, also on the left a portion that does not move far away from this line. But between these two portions the spinodal curve must have been strongly forced back towards smaller volumes to avoid the line $\frac{d^2\psi}{dx^2}=0$.

In the points where $\frac{dp}{dx}=0$ intersects the curve $\frac{d^2\psi}{dx^2}=0$ the spinodal curve touches this curve, because $\frac{d^2\psi}{dx^2}$ must be $=\frac{\left(\frac{d^2\psi}{dxdv}\right)^2}{\frac{d^2\psi}{dv^2}}$ for the points of the spinodal curve, and so it must remain in the region where $\frac{d^2\psi}{dx^2}$ is positive, except when $\frac{d^2\psi}{dxdv}=0$. It may then even be doubted if $v>b$ is found for all the points of the spinodal curve.

Values of $v<b$ would mean that the left part and the right part of the liquid branch of the spinodal line would remain separated from each other; and this would imply for the miscibility or non-miscibility of the components that at the temperatures for which this is the case, even infinitely large pressure would be insufficient to bring about mixing. Already in my Théorie Moléculaire I raised this problem, and I showed, that if b is a linear function of x, cases

are conceivable in which the spinodal line could intersect the line $v=b$ twice, but that if $\frac{d^2b}{dx^2}$ has positive value, as is really to be expected, intersection will never take place. But if we acknowledge again that the knowledge of the equation of state is insufficient for very small volumes it follows that we had better not pronounce the solution of this question too decisively.

If the spinodal line is closed on the side of the small volumes, then a realisable plaitpoint will be found there, while there must be a hidden plaitpoint in the neighbourhood of the points 2 and 3. If the temperature is raised, the line $\frac{d^2\psi}{dx^2}=0$, as it now also intersects the line $\frac{d^2\psi}{dxdv}=0$, can contract to above $\frac{d^2\psi}{dv^2}=0$, before disappearing. If it has sufficiently ascended above $\frac{d^2\psi}{dv^2}=0$, the spinodal line will get a point where it splits 1) up, at which 2 new plaitpoints (homogeneous ones) are formed. So at this splitting point $\frac{d^2v}{dx^2_p}=0$ and $\frac{d^2v}{dx^2_q}=0$. This furnishes an indication as to the place where this splitting point will lie. That the q-line below $\frac{d^2\psi}{dxdv}=0$ must have a point of inflection, has been shown before (p. 736), where we derived a series of points of inflection of the q-lines passing through the point in which $\frac{d^2\psi}{dx^2}=0$ has the greatest volume. We have also previously (p. 628) derived a series of points of inflection of the p-lines starting from the point where $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$ intersect, and passing through the point where $\frac{dp}{dx}=0$ has the minimum volume. From this we conclude that the double plaitpoint can only occur when the line $\frac{dp}{dx}=0$ is intersected by $\frac{d^2\psi}{dx^2}=0$ pretty far to the left of the point with minimum volume, and so not far to the right of the asymptote of the line $\frac{dp}{dx}=0$.

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1) This splitting point I had already in view in my Théorie Moléculaire (Cont. II p. 42 and 43) where I indicate the temperature at which the detached plait (longitudinal plait) leaves the v,x-diagram, when it has not contracted to a single point.

I may remark in passing that VAN DER LEE's observations for water and phenol illustrate the case discussed here, and that through the existence of a maximum pressure the properties of the vapour-liquid binodal line give evidence either of the occurrence of the asymptote of the line $\frac{dp}{dx}=0$ in the v,x-diagram, or of its lying not far to the left. So there are 4 plaitpoints after the appearance of this double plaitpoint. So two serve as plaitpoints of the plait which is detaching itself and they are both realisable according to our nomenclature and when detachment has taken place, both can actually be realised. They serve then as plaitpoints of what must properly be called a *longitudinal plait.* The two other plaitpoints, viz. the hidden plaitpoint which we placed in the neighbourhood of the points 2 and 3 above, and the lowest of the newly formed plaitpoints then form a couple of heterogeneous plaitpoints, which do not show themselves on the binodal curve of the vapour-liquid plait and will soon coincide and then disappear. From this moment the binodal lines of the two plaits are quite separated and behave independently of each other. The vapour-liquid plait is then simple and perfectly normal. But also the longitudinal plait may then be considered as a normal one.

(*To be continued.*)

Waterstaat. — "*Velocities of the current in an open Panama canal.*"

By Dr. C. LELY.

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

§ 1. After an elaborate investigation the American Government has resolved on the execution of a project of a Panamacanal at high level, *viz.* at a height of 85 feet (25.9 M.) above the mean sea level. It will have three flights of locks.

Against this project of the minority of the Board of Consulting Engineers of 1905 there was a counterproject of the majority which favoured a canal at sea-level or rather a canal with one pair of locks. This canal would have been provided with one pair of locks in order to separate the Atlantic Ocean from the Pacific, but for the rest it would have been in open communication with these seas on both sides of the locks.

As a matter of fact this canal would not have been an open canal, therefore, like the Suez Canal, but a canal in which in most cases, if not in all, lockage would be necessary. A canal, therefore, which probably would have resembled more closely to the lockcanal proposed for Suez but not executed and strongly opposed, than to the present open Suez-Canal.

The question therefore presents itself whether the Panama-Canal, like the Suez-Canal might not have been made *open* and *without sluices.*

The technical commission of the International Congress of Paris in 1879 deemed a lock near the Panama-terminal an absolute necessity, because it was supposed that, without it the tidal motion of the Pacific would cause currents in the canal of a velocity of 2 to 2.50 M. per second [1]).

On the other hand the Board of Consulting Engineers of 1905 rightly judged that the necessity of such a lock was not established but, owing to lack of time, it was not able to investigate the matter [2]).

On page 56 of the report we find as follows:

"The question of the necessity of a tidal lock at the Panama end "of the canal has been raised by engineers of repute, but the limited "time available to the Board has not permitted the full consideration "of this question which is desirable. It is probable that in the "absence of a tidal lock the tidal currents during extreme spring "oscillations would reach five miles per hour. "(2.24 M. per second)" "While it might be possible to devise facilities which would permit "ships of large size to enter or leave the canal during the existence

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[1]) This opinion clashed with that of the original projectors Messrs Wijse and Reclus. In a statement made by the latter at the meeting of the Technical Commission of May 19, 1879 he explains that the inclination of the high and low waterlines in the Panama-Canal will be about the same as on the Suez-Canal, as a consequence whereof velocities of the current might be expected in the Panama-Canal which would not exceed very appreciably those of the Suez-Canal. The latter, as far as they are due solely to the tides, usually do not exceed 0.90 M. per second; under the influence of wind they may increase to 1.30 or 1.35 M.

[2]) At the time of the meeting of the Consulting Board competent experts were still of opinion that a lock at the Pacific-terminal would be necessary. Such appears clearly from the letter of Mr. T. P. Shonts Chairman of the Isthmian Canal Commission received by the Board at the beginning of its labours. In this letter occur the following lines:

"A disadvantage which the two plans have in common is that the rapid develop-"ments of naval architecture make it difficult to determine the proper dimensions "of the lock chambers. It is to be considered, however, that up to the present "time such developments has not been greatly hampered by deficient depth in the "harbors of the world, and that development here after will have that obstruction "to contend with. Moreover, it is not possible to dispense with locks entirely. Even "with the sea-level canal a tide lock will be required at the Panama end".

"of such currents, the Board has considered it advisable to contem-"plate and estimate for twin tidal locks located near Sosa Hill 'even though the period during which they would be needed would "probably be confined to a part of each spring tide."

It would require a special investigation, however, to know whether in a canal provided with locks, those locks would have to be used only during part of the spring tides.

For, the oscillations of the sea above and below the mean level executed in a period of three hours are on an average ± 1.23 M. at neap tide and ± 2.53 M. at spring time. This being so it seems probable enough that, both in the interest of navigation and to prevent eventual damages which might be caused by the closing of the lockgates against a strong current, lockage of the ships would be preferred to passing the lock with gates open. For, assuming the total profile of the locks to be equal to the profile of the canal, observations made in the Suez-Canal justify us in evaluating the velocity of the current at 0.70 to 0.90 M. at mean neap tide and at 1.00 to 1.30 M. at mean spring tide.

At all events, each time after the gates having been closed the passing of the lock with gates open would not be possible before the sea had again reached its mean level. As a consequence, at each tide requiring the closing of the gates, the period during which passing of the lock with open gates would be possible, would be less than three of the six hours included between two returns of the sea to its mean level.

Howsoever this be and leaving out of consideration the question to what degree a lock in a sea level canal will be an obstacle to navigation, it appears at all events that the necessity af such a lock has remained an unsolved question when in 1905 the projects of a Panamacanal were examined. The cause thereof lies in the uncertainty about the velocity of the currents which will occur in an open canal, particularly as a consequence of the tidal motion of the Pacific.

In addition to the motion caused by the tides, great velocities of the current may occur in a sea level-canal, with or without tidal lock, at the time of high floods of the Chagres and other rivers, if the water of these rivers must be carried off by the canal. In contradistinction to the project of 1879 such would have been the case in the sea-level canal according to the project of the Board of Consulting Engineers.

The Board comes to the conclusion that in a sea level canal with tidal lock currents will thus be caused reaching a maximum velocity of 1.18 M. per second. (2.64 miles per hour). The Board is of opinion that such a velocity will be no hindrance to navigation.

These same velocities will occur in an open canal as well as in a sea-level canal with tidal lock, at least if in both cases the water of the rivers must be carried off by the canal. They occur very rarely however and need not necessarily lead to an increase of the maximum velocities caused by the tidal motion.

§ 2. The reasons which led the technical commission of the Congress of Paris in 1879 to expect currents with a velocity of 2—2,50 M. per second in an open canal, are twofold. In the first place, the commission gave some examples of currents with a velocity of 2—3,50 M. per second observed on the lower course of rivers where similar differences exist between high and low-water as on the Panama canal on the Side of the Pacific.[1])

In the second place the commission published a memorandum of Mr. KLEITZ, one of its members, containing some summary calculations in regard to the velocities which must be expected in an open canal.[2])

It is evident that on the lower end of a river with a great amplitude of the tide very considerable velocities of the current *may* occur; but it does not follow that equal velocities *will* occur in an open Panama-canal. This will be the case only if the remaining circumstances which have a decisive influence on the velocity are about the same in the two cases. Now it is evident that the velocity of the current caused by the tidal motion of the water will be no less dependent on the depth and in particular on the mean depth for the whole of the width, than on the amplitude of the tide and this irrespective of the question whether we have to do with a river or with an open canal of relatively great length. In other words the velocity of the current will depend as well on the proportion of the amplitude to the mean depth as on each of these quantities separately. Furthermore it is easily seen that in a river these velocities will depend in a great measure not only on the discharge but also on the changes of width and depth and on the inclination of the bottom near its mouth. In fact, the examples communicated by the commission show clearly that the velocity must be dependent in a high measure on other causes besides the amplitude of the tides. For among the examples of the commission we find the Rivière de l'Odet with an amplitude of the tides of 5 M. and

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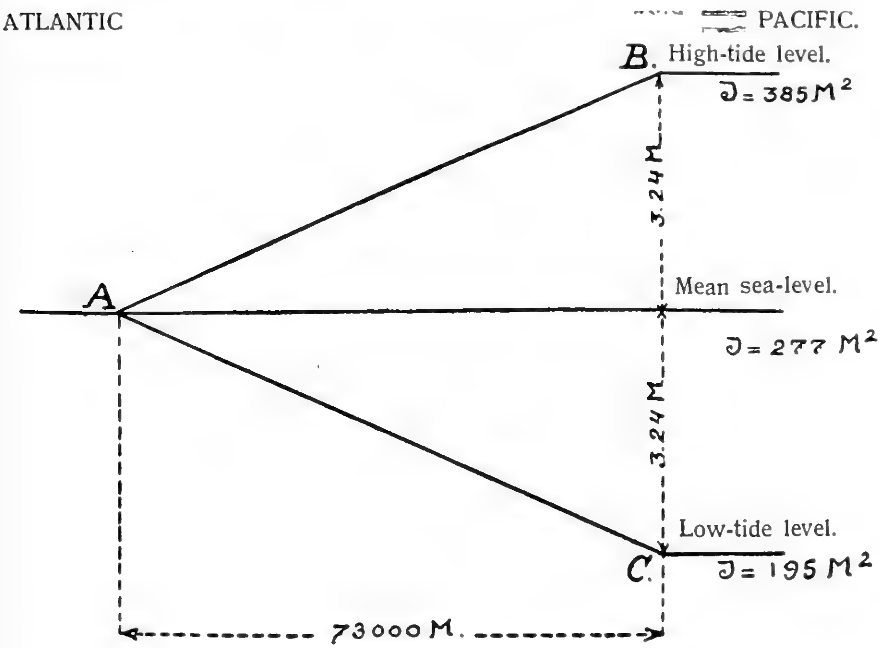
[1]) See: Congrès international d'études du canal interocéanique. Compte rendu des séances. Paris 1879 page 362.

[2]) Ib. p. 384 and Pl. IV fig. 6.

velocity of the high water flow of 3.50 M. and furthermore La Charente with an amplitude of the tides of 6.35 M. and a velocity of the high-water flow of 2 M.

As regards the calculation of Mr. KLEITZ, it is as follows:



According to the above figure the area of the wet section of the canal on the side of the Pacific was adopted to be 385 M.² at high-water and 195 M.² at low water.

The difference between the mass of water in the canal at high and low tide is then taken for the volume of the prism A B C.

$$\text{therefore} = 73000 \times \frac{385 - 195}{2} \text{ M}^3 = 6.935.000 \text{ M}^3.$$

As the interval between high and low tide is about six hours, the change of the mass of water per second is found to be 321 M³ on an average. The mean wet section of the canal on the side of the Pacific being $^1/_2$ (385 + 195) M², that is 290 M², Mr. KLEITZ derives for the velocity of the inflow during the whole period of high tide or for the outflow during the whole period of low tide

$$\frac{321}{290} = 1.11 \text{ M.}$$

Furthermore, assuming that the most rapid change of the mass of the water will occur about at the time at which the sea-level is equal to the mean level and besides, that this most rapid change is equal to double the mean change, the maximum inflow is put at $2 \times 321 = 642$ M³.

As the wet section of the canal at the mean level is about 277 M², we find $\frac{642}{272} = 2.32$ M. per second for the maximum velocity.

It is easily seen that these calculations are valueless. For the fact has been wholly overlooked that a certain time must elapse before some rise or fall at the mouth of the canal on the Pacific will make itself felt over the whole length of the canal. If therefore, shortly after ebb, the level in the canal near its mouth begins to rise and, shortly afterwards, the first inflow takes place, the level of the canal further inland will still be falling and the water will there be flowing out as a consequence. Similarly when shortly after the moment of high tide on the sea, the level of the canal near its mouth begins to fall and shortly afterwards outflow sets in, the level further inland will still be rising and there the inflow will not yet have ceased.

Moreover the in- and outflow of the canal on the side of the Atlantic has been left wholly out of consideration. They will certainly not be small but will not take place at the same moments as the in- and outflow on the side of the Pacific. We may see that the difference in time, before mentioned, will not be insignificant but will have a great importance, by considering that, on the Suez-canal, the propagation of the high tide takes place with a velocity of about 10 M. p. second. Assuming the same velocity for the Panama-canal the propagation of the tidal motion over the whole of the length of the canal will require about 2 hours. As a consequence the currents near the two terminals of the canal will have different directions during a great part of the tide.

The incorrectness of the reasons for the conclusion of the congress of 1879, according to which a lock is to be considered an absolute necessity seems to have attracted little attention at that time, and consequently the canal was originally executed with the intention of building a sluice on the side of the Pacific.

FERDINAND DE LESSEPS, who always considered it a great advantage that the Suez-canal was executed without locks, probably never favoured this lock in the project of the Panama-canal. This led him in May 1886 to address himself to the French Academy of Sciences, requesting it to institute an investigation about the influence of the tidal motion of the Pacific and the Atlantic on the motion of the water in an open Panama-canal.

The commission charged with this investigation reported on the matter in the meeting of 31 May 1887. This commission consisted of the members of the section of Geography and Navigation and besides of the members DAUBRÉE, FAVÉ LALANNE, DE JONQUIÈRES and BOUSSINESQ and the reporter BOUQUET DE LA GRIJE.

This report, though short, contains the results of extensive computations, which led the commission to the following highly remarkable and important conclusion.

"que, dans aucun cas, les courants dus à la dénivellation ne pour-
"ront depasser 2½ *noeud"* (±1.29 *M. par seconde*) *"et que cette vitesse,*
"qui ne peut être atteinte tous les ans que pendant quelques heures,
"ne parait pas de nature à gêner la navigation des bateaux à vapeur
"dans le canal que l'on creuse actuellement à Panama".

This conclusion was accepted by the Academy and the question concerning the possibility of an open Panama-canal without locks was placed in quite another light than that in which it appeared after the congress of 1879.

Owing to particular circumstances, this conclusion of the French Academy of Sciences has attracted comparatively little attention. For in the same year that this conclusion was reached, the original project of a sea-level canal with lock had to be given up and to be replaced by a canal with several locks. It was the beginning of the sufferings of the Panama-canal.

Since then the principal consideration has always been to limit the excavations to the utmost. For this purpose the hilly country required a canal at high level, consequently several locks.

§ 3. Therefore, if we wish to answer the question whether an open Panama-canal without sluices is possible, we have to inquire in the first place, whether the report of the French Academy of Sciences, of 1887 is based on sound foundations.

What were these foundations?

In accordance with observations at the tide-gauge at Panama the differences between high and low water, in other words, the amplitudes of the tides at the mouth of the Panama-canal were adopted to amount to:

at neap tide, on an average	2.46 M.
,, spring ,, ,, ,, ,,	5.06 M.
,, ,, ,, maximum in March or Sept.	6.76 M.

The commission now calculates the velocity of the current for this maximum difference in height of the tides on the Pacific of 6.76 M., neglecting the usually small tidal oscillation in the Atlantic and further starting from the following suppositions:

1. that experience shows that on a canal communicating on the one side with a sea of variable level, on the other side with a sea of constant level, the amplitude of the tidal curve diminishes uniformly from one sea to the other and further that the retardation of the tide is proportional to the distance, that therefore:

if $Y =$ half the amplitude of the tides of the Pacific,
$l =$ length of the canal,
$\omega =$ velocity of propagation of the tides,

the level y, with respect to the mean canal- or sea-level, at a distance x from the Pacific, will be:

$$y = - Y\left(1 - \frac{x}{l}\right) \cos.\left(2\,t - \frac{x}{\omega}\right)$$

2. that, in accordance with what has been observed on similar canals, particularly on the Suez-canal between Suez and the Bitter-Lakes, the velocity of propagation of the tide can be represented by the well known formula:

$$\omega = \sqrt{g\left(H + \frac{3}{2}y\right)} \pm Kv$$

where:

$H =$ depth of the canal below mean sea-level,
$v =$ velocity of the current,
$K =$ constant (0.4 at flood-time, 1.2 at ebb);

3. that, from the levels which have been derived by means of the suppositions 1. and 2. for any moment and for two mutually not too distant places, the velocity of the current for that moment may be computed by applying the formula:

$$v = 56{,}86 \sqrt{Ri} - 0.07.$$

By means of these suppositions the velocity of the currents have been computed for places at 9, 27, 45 and 63 K.M. from the Pacific, assuming a tide of the amplitude of 6.76 M. The results are as follows [1]:

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[1] The length of the canal which according to the project made at that time, would amount to 72 K.M. has been put at 76 K.M. in the calculations to allow for the curves. The bottomwidth was put at 21 M, the depth at 11.50 M. below mean sea-level at Panama, and 9 M. at Colon, the slopes at 1 horizontal on 1 vertical.

Time elapsed since low tide on the Pacific.	Distances from the Pacific.			
	9 K.M.	27 K.M.	45 K.M.	63 K.M.
Moon-hours.	Velocities of the current in M. per second.			
0	— 0.95	— 1.00	— 0.77	— 0.69
½	— 0.81	— 0.90	— 0.93	— 0.72
1	— 0.60	— 0.84	— 0.87	— 0.83
1½	— 0.13	— 0.75	— 0.82	— 0.85
2	+ 0.35	— 0.59	— 0.75	— 0.86
2½	+ 0.67	— 0.34	— 0.63	— 0.81
3	+ 0.84	+ 0.35	— 0.42	— 0.73
3½	+ 0.93	+ 0.63	+ 0.08	— 0.61
4	+ 0.98	+ 0.78	+ 0.43	— 0.41
4½	+ 1.02	+ 0.93	+ 0.80	0
5	+ 1.17	+ 1.06	+ 0.82	+ 0.51
5½	+ 1.16	+ 1.11	+ 0.86	+ 0.66
6	+ 1.09	+ 1.06	+ 0.98	+ 0.76
6½	+ 0.97	+ 1.01	+ 0.97	+ 0.85

+ = current *from* the Pacific *towards* the Atlantic
— = „ „ „ Atlantic „ „ Pacific

From these computations follows that the maximum velocity in the canal on the side of the Pacific, due exclusively to the tidal motion, will amount to 1.17 M. Supposing that there might be some difference between the mean sea level of the Atlantic and the Pacific and that this difference might amount to 0.50 M., the commission concludes that the maximum velocity might then increase to 1.26 M. The commission thus finally arrives at the conclusion referred to above.

§ 4. The two first suppositions on which the computations are based will probably not seriously deviate from the truth. For they are, at least partially, confirmed by what is observed on the Suez-canal.

The commission further points out, that the formula for the velocity of propagation of the tidal wave, which has been derived in the supposition that the amplitude of the tide is relatively small as compared with the depth of the water, leads to results which, for the Suez-canal, agree closely with the observations. For the formula leads to a velocity of propagation of 10.06 M., whereas we find 9.54 M. by observation.

Matters stand somewhat differently for the third supposition. The formula by which the velocities of the currents are computed is the well known formula for permanent uniform motion. It is in the nature of the thing that such a motion cannot occur in a canal where a strong tidal motion takes place. But the question on which every thing depends is not so much this, whether the use of this formula leads to sufficiently correct velocities for any moment, as the following, whether the computed maximum velocities are not too small.

In reference to this question we may remark that in general the formula will lead to too small a value of the velocity during the period that change in level is accompanied by decrease of inclination; to too great a value where the change is accompanied by an increase of inclination.

If, taking this into consideration, we examine the parts of the canal K.M. 0—9 and K.M. 9—27, during the period of $4^1/_2$ to 6 hours after low tide on the Pacific, we get as follows:

Time elapsed since low tide	Mean inclination K.M. 0—9	K.M. 9—27
4½ hours	0.000044	0.000040
5 „	0.000048	0.000046
5½ „	0.000048	0.000047
6 „	0.000044	0.000045

From these data it appears that, during the half hour preceding the epochs at which the velocities reach their maximum value at K.M. 9 and 27 the mean inclination for the part 0—9 as well as for the part 9—27 has been little variable but increasing.

From this it follows that by the application of the formula at these epochs we probably cannot have made any important error.

Meanwhile, in order to test the validity of the computations, we have still to inquire whether the computed velocities, taken in conjunction with the computed levels, satisfy the equation of continuity.

$$\frac{dI}{dt} = -I\frac{dv}{dx} - v\frac{dI}{dx}$$

where I represents the area, v the mean velocity of the wet section at the distance x from the Pacific, at the epoch t.

We can make out, approximately, in how far the computed levels and the velocities satisfy this condition by availing ourselves of the levels and velocities computed for each half hour and for the different distances from the Pacific. We thus find as follows:

A. For the differences in the discharge at 9 and 27 K.M. distance from the Pacific.

Moon-hours elapsed since low tide on the Pacific.	Area *I*		Velocity *v*		Dis-charge *Iv*		Per half hour in part 9—27		Excess of *in*flow over *out*flow in half an hour
	9	27	9	27	9	27	*in* flow	*out* flow	
	M².	M².	M.	M.	M³.	M³.	M³.	M³.	M³.
4½	450	388	1.02	0.93	459	361			
							914000	713000	+201000
5	475	407	1.17	1.06	556	431			
							1.013000	807000	+206000
5½	491	420	1.16	1.11	570	466			
							1.002000	828000	+174000
6	498	428	1.09	1.06	543	454			

B. For the change of the mass of water contained in part 9—27.

Moon-hours elapsed since low tide on the Pacific.	Area *I*		Change of area during half an hour.		Mean change for part 9—27.	Change of mass per half hour for part 9—27.
	9	27	9	27		
	M².	M².	M².	M².	M².	M³.
4½	450	388				
			+ 25	+ 19	+ 22	+ 396000
5	475	407				
			+ 16	+ 13	+ 14^5	+ 261000
5½	491	420				
			+ 7	+ 8	+ 7^5	+ 135000
6	498	428				

Comparing the last columns of the tables A and B we get the following differences for part 9—27:

from $4^1/_2$ to 5 hours + 195000 M^3, or on an average per sec. + 108 M^3.
,, 5 ,, $5^1/_2$,, + 55000 ,, ,, ,, ,, ,, ,, ,, + 31 ,,
,, $5^1/_2$,, 6 ,, — 39000 ,, ,, ,, ,, ,, ,, ,, — 22 ,,

It appears from this comparison, that by the computed velocities, taken in conjunction with the computed levels, the condition of continuity is not fully satisfied.

Therefore, assuming the levels to be correct, the velocities need some correction.

Suppose these corrections for the consecutive half hours to be

$$\text{for K.M. } 9 = \delta_1, \delta_2, \delta_3, \delta_4,$$
$$\text{for K.M. } 27 = \delta_1', \delta_2', \delta_3', \delta_4',$$

we find for the values of the corrections:

$$\delta_1 = +0.15\ M. \qquad \delta_1' = -0{,}13\ M.$$
$$\delta_2 = +0.12\ ,, \qquad \delta_2' = -0{,}10\ ,,$$
$$\delta_3 = -0.04\ ,, \qquad \delta_3' = +0{,}04\ ,,$$
$$\delta_4 = -0{,}01\ ,, \qquad \delta_4' = +0{,}01\ ,,$$

Therefore, applying the corrections, for the velocities themselves:

	at K.M. 9	at K.M. 27
at $4^1/_2$ hours	1,17 M.	0,80 M.
,, 5 ,,	1,29 ,,	0,96 ,,
,, $5^1/_2$,,	1,12 ,,	1,15 ,.
,, 6 ,,	1,08 ,,	1,07 ,,

From these numbers it appears that we can satisfy the condition of continuity at least for the part 9—27, during the period between $4^1/_2$ and 6 hours after low tide, by relatively speaking slight modifications of the computed velocities.

It cannot be denied, however, that the circumstance of the condition of continuity not being necessarily satisfied in applying this method of computing the velocities, indicates that this method is uncertain to some extent; though it appears that the uncertainty, at least as regards the calculation of the maximum velocities, will be small.

Another reason of uncertainty in the computation of the velocities lies in the value assumed for the coefficient of the formula for uniform motion.

This value, 56,86, is not the result of a great number of observations made on rivers and canals of about the same inclination and depth as the Panama-canal, but of observations for rivers of considerably smaller depth.

We may of course test the validity of this coefficient, as well as, more generally, the validity of the formula itself, by comparing the velocities it yields for the Suez-canal with those really observed there. Of the observations which have been made about the velocities in that part of the canal which lies between the Bitter Lakes and Port-Thewfik, those of 23 July, and 8 en 22 August and 6 September 1892 have been published [1]).

These observations, however, are insufficient for a fair comparison.

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[1]) See: The Suez-canal according to the posthumous papers of I. F. W. Conrad arranged by R. A. van Sandick. Tijdschrift Kon. Instituut van Ingenieurs 1902—1903, p. 89 and 90.

They have been made for two parts of the canal each 200 M. in length and separated by only 4.9 K.M. One part was included in that division of the canal which at that time had been widened to a bottomwidth of 37 M. while the other, having a bottomwidth of only 22 M., was situated a little beyond the point of transition to the not yet widened canal. As a consequence the motion of the water on the whole of this part of the canal, 4.9 K.M. in length, cannot have been uniform [1]).

Moreover these observations are only relative to the velocities in the middle of the current, observed by means of floats down to a depth of 6 M. below the surface, whereas the velocity given by the formula represents the average velocity for the whole of the wet section. Meanwhile a comparison of these observations with the results obtained by the formula might still give some idea about the reliability of the formula.

The comparison of the observations referred to above with the results yielded by the formula, putting the coefficient at 56.86, lead to the following results:

OBSERVATIONS ON THE SUEZ-CANAL IN 1892.

Day and hour of the observation		Direction of the current.	Distance between the places of observation.	Mean difference of level between the places of observation.	Observed velocities. Averages during an hour in the		Computed mean velocity for the widened part. [2])
					widened part	unwidened part	
			K.M.	M.	M.	M.	M.
23 July	11—12 a.m.	flood	4.9	+ 0.12	+ 0.75	+ 0.97	+ 0.64
„ „	5—6 p.m.	ebb	4.9	— 0.14	— 0.84	— 1.11	— 0.58
8 Aug.	11—12 a.m.	flood	4.9	+ 0.09	+ 0.69	+ 0.87	+ 0.47
„ „	5—6 p.m.	ebb	4.9	— 0.11	— 0.80	— 0.93	— 0.57
22 „	6—7 a.m.	ebb	4.9	— 0.16	— 0.88	— 1.05	— 0.68
„ „	12—1 p.m.	flood	4.9	+ 0.07	+ 0.66	+ 0.82	+ 0.46
6 Sept.	11—12 a.m.	flood	4.9	+ 0.07	+ 0.66	+ 0.89	+ 0.47
„ „	5—6 p.m.	ebb	4.9	— 0.10	— 0.85	— 0.98	— 0.53

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[1]) The first part was the widened part of the canal between K.M. 149 and 149.2; the other the not widened part between K.M. 144.1 and 144.3. The transition of the widened to the not widened part was situated at K.M. 144.4.

[2]) As the part of the canal from K.M. 149 to 144.4 had been widened the observed difference of level is relative to the widened part.

From this table we derive for the proportion between the computed average velocity for the whole of the wet section to the velocities observed down to 6 M. in the middle of the widened part of the canal, the following values:

	at high water flow (from the Red Sea)	at ebb flow (towards the Red Sea)
	1.17	1.45
	1.47	1.40
	1.43	1.30
	1.40	1.61
Mean	1.37	1.44

The true value of this proportion for the case in which observation and computation agree, is unknown. But if we consider that the floats went down to only 6 M. below the surface, whereas the depth of the water at flood tide was over 8.50 M. and at ebb time over 7.50 M. and furthermore, that the canal had side slopes of 1 vertical on $2^1/_2$ horizontal, we conclude that at all events the velocity in the middle must have considerably exceeded the average velocity for the whole of the section. As far as can be ascertained therefore, the formula applied to the Suez-Canal leads to results which do not clash with the observation.

More conclusive information cannot be derived from a comparison of the computed velocities to the observed values. As long therefore as complete observations, made for the widened Suez canal, concerning the relation between the velocity of the current, the tidal motion and the dimentions of the section, have not furnished us with more reliable information about the value of the coefficient and about the question whether the formula applies fully to the case, we cannot avoid a relatively considerable uncertainty in the calculation of the maximum velocity.

§ 5. A closer examination is therefore required to decide in how far the velocity of the current in an open canal may cause a hindrance to navigation and whether this hindrance cannot be overcome.

In discussing this question we must consider, on the one hand that the computed velocities represent average velocities for the whole of the wet section and that therefore the absolute velocities in the middle of the canal will be more considerable; on the other hand, however, that the computed velocities are relative to the greatest possible differences in the height of the tide. The computed maximum velocities may occur therefore only on a couple of days every year. And on these days only during a few hours.

In how far a relatively rare velocity of the current offers difficulties to navigation is of course ascertained in the best way by a comparison to canals on which under similar conditions similar velocities occur. For such a comparison the Suez-canal offers the best conditions. For this canal several observations about the velocity of the current are known. Published observations, however, cannot lay claim to completeness, at least not for the present purpose. In the first place because they have not been frequent enough to justify the belief that among them will have occurred these rare cases which by an unfavourable coincidence of circumstances, must have given rise to exceptionally great velocities. In the second place because the measurements are, as a rule, relative to absolute velocities in the middle of the canal and not to the average velocity for the whole of the wet section.

Moreover, in comparing the Panama-canal to the Suez-canal we have to consider that the dimensions of the former will be much more considerable than those of the latter as originally executed. Consequently such velocities as have caused no difficulties for the Suez-canal will cause them still less for the Panama-canal.

For the Suez-canal between the Bitter Lakes and Suez originally had a bottomwidth of 22 M. and a depth of 8 M. below mean springtide low water, with which dimensions corresponds a cross section of 330 M^2. On the other hand the sea level Panama-canal would get a bottomwidth of about 45.7 M. (150 feet) and a depth of about 12.2 M. (40 feet) corresponding with a cross section of 855 M^2.

Observations, made during the period 1871—1876, have brought to light the following facts about the velocities of the current in the Suez-canal between the Bitter Lakes and Suez. [1])

"The maximum velocity of the high water flow, running North-"ward, amounts to 0.80 to 0.90 M. at the springtides of the months "of May and November, to 1.15—1.35 M. p. s. in the months of "January and February.

"The maximum velocity of the ebb flow running Southward amounts "to 0.75—0.80 M. at the springtides of the months of May and Novem-"ber, to 1.20—1.25 M. p. s. in the months of July and August.

"Along Port-Thewfik in the canal south of the main channel

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[1]) *Vide* the paper of Mr. J. F. W. CONRAD pp. 89 and 90.

"towards Suez, bottomwidth 80 M., the velocity of the high water "flow at springtide is 0.60 to 0.70 M., at neaptide 0.45 to 0.50 M., "in the winter-season with strong South wind 1.00 to 1.20 M. p. s. "The velocity of the ebb flow at springtide is 0.55 to 0.60 M. In "the summer with strong North wind 0.90 M. p. s.

"Outside the mouth of the canal at Port-Thewfik no velocity of "the current has been observed."

The observations of 23 July 1892 made under circumstances which, as regards the flow, were certainly not unfavourable, led already to velocities which, at flood tide, ranged from 0.95—1.03 M. and were in the mean 0.97 M. at flood tide and 1.11 M. at ebb.

Mr. Dauzats, chief engineer of the Suez-canal, speaking at the meetings of the Technical subcommission of the International Congress for the Panama canal in 1879, stated in regard to the sidings of the Suez-canal, as follows [1]:

"Dans les canaux où le courant est faible, et là où n'existe aucun courant, il suffit de faire les gares d'un seul côté; mais dès que la vitesse atteint 0.75 ou 1.50 M, il faut les établir des deux côtés et en face l'une de l'autre".

By this statement we are certainly justified in concluding that the said engineer, founding his opinion on his experience of the Suez-canal, deemed allowable velocities of the current of 1.50 M. The small original bottomwidth of the Suez-canal of 22 M., however, caused difficulties for the simultaneous navigation in both directions.

The following communications of Mr. E. Quellennec, consulting engineer of the Suez-canal company, proves that these velocities of the current offer no difficulties even for the big ships which at present navigate the Suez-canal. These communications to the Board of Consulting Engineers of 1905 are as follows:

"In the Suez section the velocity of the current very often exceeds 0.60 meter per second, and reaches at times 1.35 Meters per second.

"In the latter case the ships do not steer very well with the "current running in; however the navigation is never interrupted "on account of the current. In the Port Said section ships can "moor with a current running in either direction; in the Suez "section they always moor with the current running out". [2])

The canal between the Bitter Lakes and the Red Sea has at present a width of about 37 M., but a widening of the cross section

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[1]) See: Congrès international etc 1879, p. 361.

[2]) See: Report of the Board of Consulting Engineers for the Panama-canal, Washington 1906, p. 176.

to 45 M. width and 10.5 M. depth is being executed. After this widening, navigation will certainly experience still less difficulty than at present. Meanwhile, and this point deserves attention, the velocity of the current after the completion of the widening for the whole of the canal between Suez and the Bitter Lakes, will not be lessened but increased. For, owing to the surface of the two Bitter Lakes, which is about 23800 H.A., the widening will only cause insignificant modifications in the level of these Lakes. Consequently the fall of the water between the Red Sea and the Bitter Lakes will be nearly unaltered after the widening both at high — and low water. Under these circumstances the enlargement of the cross section will necessarily cause increased velocity of the current.

The mere consideration of the maximum velocity which may occur during a few hours every year, and even then only on the side of the Pacific, is evidently inadequate for reaching a true estimate about the question whether the velocities of the current in an open Panama-canal without lock will offer difficulties of any importance for navigation. We have to pay regard in the first place to the velocities which will regularly occur on the whole length of the canal at mean spring-tide and mean neaptide.

These velocities may be derived with some approximation from those found by the French Academy for a maximum difference in tide of 6.76 M.[1]), at least if we suppose that these velocities will not considerably deviate from the truth.

We thus find for the *maximum velocities*

at K.M.	9	27	45	63
at mean neap tide :	0.70 M.	0.67 M.	0.59 M.	0.51 M.
,, ,, spring ,,	1.01 ,,	0.96 ,,	0.85 ,,	0.74 ,,

The following diagrams show the velocities of the current, for the interval of from 9 to 63 K.M. distance to the Pacific, at mean spring tide and mean neap tide, 0 to 6 Moon-hours after ebb on the Pacific. They were derived from the calculations of the French Academy of Sciences.

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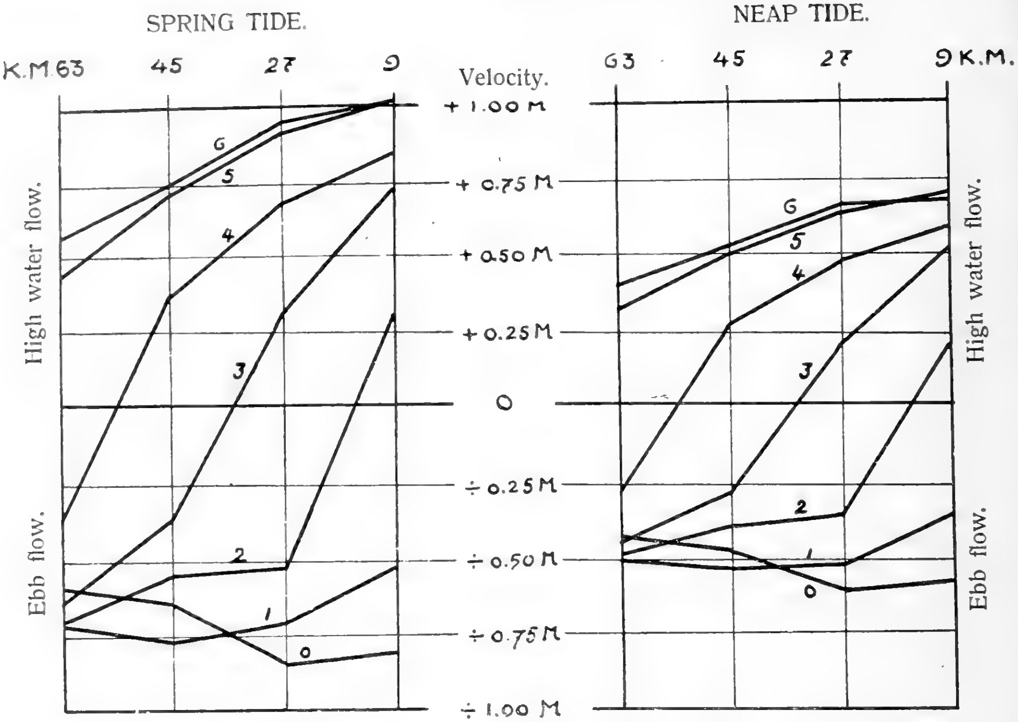
[1]) The approximation neglects the differences of the velocities of propagation of the tide for different amplitudes. We thus obtain for the velocity v', at an arbitrary place, the amplitude being y', the following value, which is expressed in terms of the velocity v for an amplitude y:

$$(v' + 0.07) = (v + 0.07)\sqrt{\frac{y'}{y}}$$



The figures inscribed in the diagram represent the hours elapsed since low tide in the Pacific.
+ = current *from* the Pacific towards the Atlantic
÷ = „ „ „ Atlantic „ „ Pacific.

§ 6. From the preceding considerations we may conclude that, as far as we can judge by direct computation of the velocities, to be expected in an open Panama canal, there is reason to think that these velocities will indeed be *somewhat*, but not considerably greater than those on the Suez-canal between the Bitter Lakes and the Red Sea.

Meanwhile we ought not to forget, that both in these computations and in our knowledge about the velocities which occur on the Suez-canal there remains some or rather considerable uncertainty. This uncertainty might only be diminished by more complete observations than have been published as yet concerning the relation between velocity of the current, tidal motion and dimensions of the cross-section of the Suez-canal.

We shall be enabled to get at a just estimate therefore about the question whether an open Panama-canal without lock is possible, only by following a way different from that of a comparison of the computed velocities with those observed on the Suez-canal. This way may consist in trying to get at a direct knowledge of the *differences* of the velocities on the two canals by a comparison of the circumstances which will occur on the two. Afterwards the circumstance that, on the Suez-canal the velocity of the current offers no difficulty, in conjunction with the probable value of the velocity of this canal, will help us in deciding whether these differences are of such a nature as to produce undoubted difficulties on the Panama-canal.

In making this comparison it will be permissible to assume that the violent winds occurring in the Suez-canal, which cause velocities of the current 0.30 to 0.50 M. in excess of those due to the tidal motions, are not to be expected on the Panama-canal near the Pacific.

First, however, we have to inquire whether an open canal cannot be executed in such a way that for that part where the current will be greatest the difficulties caused by such great velocities can be removed. It is evident that this would be possible only by giving a very great width to the canal. This is practically impossible for that part of the canal which intersects mountainous country, but it is well feasible for that part of the canal which extends from the Pacific to the Culebra mountain, that is to near Pedro-Miguel, a part which for the greater part intersects low country.

If to this part of the canal, where just the greatest velocities will occur, a bottomwidth is given of for instance 500 feet (about 150 M.) instead of 150 feet (45.7 M.) no difficulties will be experienced from any presumable velocity of the current.

Such a widening of the canal on the side of the Pacific would however increase the inclination and the velocity of the current in the remaining part, at least if no particular measures are taken to prevent such increase.

These measures would necessarily consist in making a reservoir or lake in open communication with the widened part of the canal. This reservoir or lake would have to be of such an area that it would be capable of retaining the water which, during the rise of the level, it would receive from the widened part in excess of what would be discharged by the unwidened part. During the fall of the level it would restore this surplus to the widened part.

From the nature of the thing this arrangement is theoretically possible. Whether it be practically possible depends on the surface which a determinate widening would entail.

A lake of somewhat over 800 H.A., such as is represented on Plate I, is feasible in the low country bordering on the canal near its mouth on the Pacific.

Starting from this area it is possible to determine the degree of widening which may be given to the part near the Pacific in such a way that, under given circumstances, for instance at spring tide, no change will occur in the gradient of the high and low water lines, nor in the velocity of the current in the remaining part of the canal.

As soon as the amplitude of the tides exceeds that of springtide the inclination and the velocity of the current will be somewhat increased for the wider part, somewhat diminished for the remaining part, as compared with what they would be without the widening of the first part and without the addition of a lake. In the case of a smaller amplitude of the tides the reverse will occur.

Owing to the situation of the ground the junction of the widened canal with the lake must be made at a distance of about 12 K.M. from the Pacific terminal of the canal. Not before 3 K.M. farther however, that is not before 15 K.M. from the sea, the surface of the lake reaches a considerable breadth. Therefore if the inclination of the high and low water lines remains nearly unchanged and if, according to the most recent project, the length of the canal is fixed at about 80 K.M., the amplitude of the tide in the lake may reach $(5.06 - 15 \times 0.0632)$ M. = ± **4.10** M.

With such an amplitude a mass of water may be received, in the interval between high and low water, of $800 \times 10.000 \times 4.10$ M^3. $= 32,800,000$ M^3.

Assuming, as an approximation, that this mass is received within a period of six hours, we find that *on an average* 1500 M^3. will be received per second.

The surplus width of the part of the canal near the Pacific must be determined in such a way, therefore, that *on an average* 1500 M^3. may be displaced — without increase of the velocity of the current — in excess of what might be displaced if the width remained normal.

It is not well possible, without elaborate computation, to fix accurately the surplus width necessary for the purpose. But it is easily seen that this *surplus* width must be about 100 M. so that a bottom-width of 150 M. might be given to the widened part extending from the entrance of the canal to the junction with the lake. Corresponding therewith the width at the spring tide level would be about 250 M. At K.M. 64 this width might gradually be reduced to the normal width.

It will be possible therefore to remove eventual difficulties offered by considerable velocity of the current on the part of the canal nearest the Pacific, by increasing the bottomwidth of this part. (16 K. M. in length).

Now let us consider how the case stands for the remaining part of the canal, 64 K. M. in length.

On this part the inclination of the high and low water lines will amount to 3.16 cM. at mean springtide and to 1.52 cM. at mean neaptide.

On the Suez-canal the inclination of the high and low water lines between the Bitter Lakes and the Red Sea amounts to 2.52 cM. per. K. M. at mean spring tide and to 1.48 cM. at mean neaptide.

Under the influence of the direction and force of the wind, the height of the tides on the Suez-canal may be increased or diminished by about 0.25—0,33 M.

As a consequence the inclination of the high and low water lines may be increased by about 1 cM. per K. M.

As the distance of the Bitter Lakes to the Red Sea is about 28 K.M., this already enables us to conclude that the velocities of the current in an open Panama-canal, for the first 28 K. M. on the side of the Atlantic, cannot greatly differ from those which occur on the Suez-canal (See Plate II).

If therefore — leaving out of consideration the absolute value of the velocities — we may assume that the velocity of the current will offer no difficulties on the Suez-canal even when it will have been widened, then it follows that on an open Panama-canal, for about the distance of 28 K. M. from the Atlantic, no difficulties will be met with on account of the velocity of the current.

Finally as to the middle part of the canal extending for about 36 K. M. between K. M. 28 and K. M. 64 from the Atlantic.

For this part the *differences* between the velocities of the current, occurring therein, with those occurring in the preceding 28 K. M., may be computed with sufficient accuracy by means of the equation of continuity.

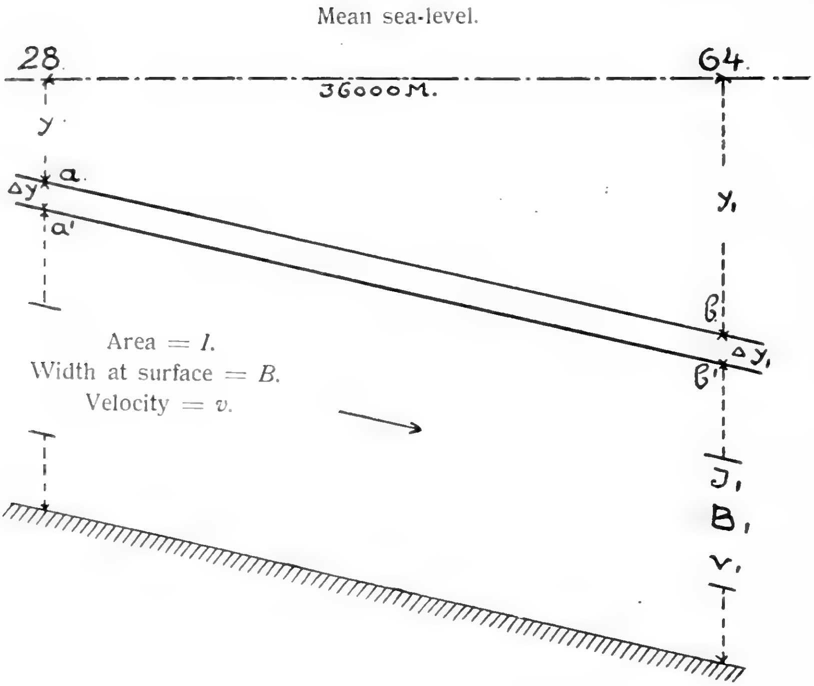
For, let *ab* be the canal's surface for this part, at the epoch *t*, a little before low water, at the distance of 64 K. M. from the Atlantic. Similarly let *a′b′* be the canal's surface a second later, then necessarily

$$-\frac{(B+B_1)}{2} \times 36000 \times \frac{\Delta y + \Delta y_1}{2} = Iv - I_1 v_1$$

from which:

$$(v_1 - v) = \frac{36000\,(B+B_1)\,(\Delta y + \Delta y_1)}{4\,I_1} + v\,\frac{I - I_1}{I_1}$$

Now the quantities $I, I_1, B, B_1, \Delta y$ and Δy_1, are known for the epoch *t*, at least if we admit that — as is the case on the Suez-canal — the high- and lowwaterlines for the part 28—64 K.M. are



nearly straight lines, and further that the velocity of propagation of the tides is known with sufficient accuracy, likewise owing to observations made on the Suez-canal. Therefore we will be able to determine the difference of the velocities at 64 and 28 K.M. distance from the Atlantic, for the epochs at which $\frac{I-I_1}{I_1}$ is a small quantity. This will be the case near the moment of low water.

For the difference of the velocities v_1 and v, during the half hour preceding the moment of lowwater at K.M. 64, during which half hour the velocity of the current will be maximum at that point, we find as follows for spring-tide. We assume that between the distances 28 K.M. and 64 K.M. (from the Atlantic) there is a retardation of the tides of just one hour :

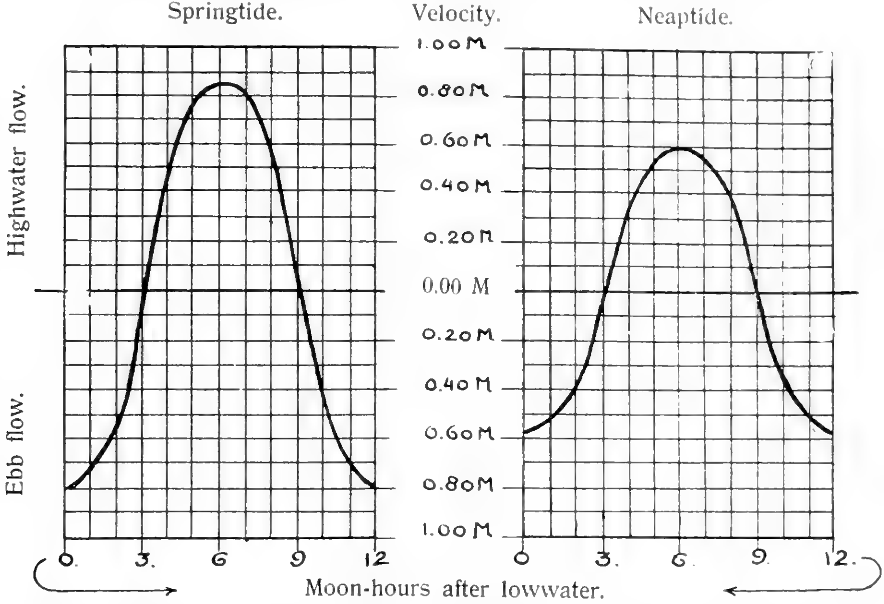
at $^1/_2$ hour before lowwater : $(v_1-v) = 0.32 \text{ M.} + 0.02\, v$
,, lowwater : $(v_1-v) = 0.12 \text{ M.} + 0.015\, v.$

From these figures it appears, that during the half hour before lowwater at K.M. 64 the *differences* of the velocities of the current are only to a small extent dependent on the value of the velocity v. These differences, therefore, may be determined with sufficient precision, even if the velocity v is only approximatively known.

By observations made on the Suez-canal during the period 1871—

1876 the velocity-curve for a place near the Red Sea is known both for springtide and for neaptide. It has been represented in the following figures. [1])

Mean velocity-curves at the entrance of the Suez-canal.



The above velocity curves probably do not represent the mean velocities but the velocities in the middle of the canal. They have been derived from measurements made every hour partly by means of floats partly by means of the current meter of Woltmann.

It deserves attention, however, that at the time of these observations the Suez-canal had still only a depth of 8 M. below low water and a bottomwidth of 22 M. The section of the canal is now being increased to a bottomwidth of 45 M. and a depth of 10,5 M. below low water. The velocities in the widened canal may perhaps exceed by 20 percent those observed on the canal during the period 1871—1876.[2])

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[1]) These curves are borrowed from the Etude du régime de la Marée dans le canal du Suez par M. Bourdelles, in the Annales des Ponts et Chaussées of 1898. They occur originally in a Note sur le régime des eaux dans le canal maritime de Suez et à ses embouchures in 1884 by Lemasson Chief Engineer of the canal-works.

[2]) For the original cross section of 8 M. depth below low water, 22 M. bottomwidth and slopes of 1 vertical on 2 horizontal we have:

Area $I = 304$ M^2; wet circumference $O = 57.9$ M., consequently $R = 5.25$ M. For the future cross section of 10.5 M. depth, 45 M. bottomwidth and slopes of 1 vertical on $2\frac{1}{2}$ horizontal, we will have: $I = 749$ M^2., $O = 101.5$ M. therefore $R = 7.37$ M. Now $\sqrt{\frac{7.37}{5.25}} = 1.20$.

If, in consideration of this fact, we substitute in the second member of the formula, for v the values observed in the period 1871—1876 increased by 20 percent, we finally find

$$\tfrac{1}{2} \text{ hour before low water } (v_1 - v) = 0.33 \text{ M.}$$
$$\text{at} \quad ,, \quad ,, \quad (v_1 - v) = 0.13 \text{ M.}$$

The differences 0.33 and 0.13 M. represent the differences of the simultaneous velocities, not those of the maximum velocities at the distances of 64 and 28 K.M. from the Atlantic.

At the moment that the velocity reaches its maximum at K.M. 64, the velocity at K.M. 28, where the tides set in about an hour later, will still be below the maximum at that place. According to the observations on the Suez-canal we may assume that, at the epochs mentioned, the velocities of the current at K.M. 28 will at least be about 0.15 M. and 0.05 M. below the maximum of that place. Hence we may conclude that the maximum velocities at K.M. 64 and 28 will certainly not differ 0.18 M, and probably not much over 0.08 M. We are sufficiently justified therefore in assuming that the velocity at K.M. 64 may be about 0.15 M. in excess of that of K.M. 28.

As appears from what has been stated before the difference is inferior to the increase of the velocity of the current on the Suez-canal under the influence of the wind, which may amount to 0.30—0.50 M. It cannot, therefore, cause any serious difficulty.

§ 7. For an open Panama-canal executed as follows:

From the Atlantic to K. M. 64 having the same normal cross section as that of the project for the sea-level canal;

from K. M. 64 to K. M. 68, which is the place where the canal will be connected with a lake gradually widening;

from K. M. 68 to the Pacific at K. M. 80 having bottomwidth of 400 to 500 feet;

the following conclusions in regard to the velocities of the current at springtide may be accepted:

On the first 28 K. M. of such an open canal, velocities of the current will occur at springtide which, on an average, will be about equal to those, which will take place at spring tide and with a moderate wind on the Suez-canal between the Bitter Lakes and the Red Sea as soon as the widening of this canal will be complete.

On the subsequent 36 K. M. of such an open canal the maximum velocities at springtide will exceed those on the preceding part by

about 0.15 M. They will not exceed however those on the Suez-canal with a strong wind.

For the last 16 K. M. of such an open canal the maximum velocities at springtide may be somewhat more considerable. On account however of the great width, which may be given to this part they will cause no serious difficulty.

Therefore, if we assume, as we have good reason to do, that even at spring tide and with wind the velocities of the current on the Suez-canal offer no serious difficulty to navigation we may conclude that on a Panama-canal of the above description also navigation will experience no difficulties on account of the velocities of the current.

Therefore, *if we leave out of consideration* the question whether an open Panama-canal without tidal lock is to be preferred either to a sea-level canal with such a lock, as proposed by the Board of Consulting Engineers, or to a summit level canal with three locks, as is now in course of execution, we may conclude, in the main in conformity with the conclusion of the French Academy of Sciences of 1887, but for different reasons:

That the velocities of the current due to tidal motion in an open Panama-canal without tidal lock will be no obstruction to navigation.

Zoology. — "*On the formation of red blood-corpuscles in the placenta of the flying maki* (*Galeopithecus*). By Prof. A. A. W. Hubrecht.

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

At the meeting of November 26, 1898, I made a communication on the formation of blood in the placenta of Tarsius and other mammals, which was later completed by a more extensive paper, containing many illustrations (Ueber die Entwicklung der Placenta von Tarsius und Tupaja, nebst Bemerkungen über deren Bedeutung als hämatopoietische Organe; Report 4th Intern. Congress of Zoology, Cambridge 1898). The facts observed by me and the interpretation founded on them, have not until now been generally accepted, and in a recent very extensive discussion of the position of the problem concerning the origin of the red blood-corpuscles in the 14th volume of the "Ergebnisse der Anatomie und Entwicklungsgeschichte" (Wiesbaden 1905), by F. Weidenreich, the author, when mentioning my views, emits the supposition that I mixed up phagocytic and haematopoietic processes.

This conclusion was not based on a renewed and critical examination of the material, studied by me. I have regretted this, since I have pointed out clearly and repeatedly that the numerous preparations at Utrecht concerning this and other embryological problems are always available for comparative and critical work, also for those who do not share my views. Moreover it appears from the literature, mentioned in WEIDENREICH's paper, that the more extensive and illustrated article, quoted above, has remained unknown to him.

All this would not have induced me to return to this subject once more, were it not for the fact that during the last months I have become acquainted with the placentation-phenomena of a totally different mammal in which these phenomena have never yet been studied, namely Galeopithecus volans, which, like Tarsius, Nycticebus, Tupaja and Manis, was collected by me in the Indian Archipelago in 1890—1891 as extensively as possible for embryological purposes. During the first origin of the placenta of this rare and in many respects primitive mammal [1]), phenomena are observed which elucidate the process of blood-formation in the placenta in such an uncommonly clear manner that in this case it will be difficult to deny the evidence.

The formation of blood in the placenta of Galeopithecus may be said to take place according to a much simpler plan than in Tarsius, although the principal outlines remain the same and here also the non-nucleate haemoglobine-carrying blood-corpuscles must be regarded not as modified cells but as nuclear derivatives. Likewise the placenta of Galeopithecus bears testimony that not only the maternal mucosa but also the embryonic trophoblast takes part in the blood-formation, while the thus formed blood-corpuscles — also those that are furnished by embryonic tissue — circulate in the maternal blood-vessels only.

In Galeopithecus the process is simpler especially in this respect that here no megalokaryocytes play a part in the formation of blood, so that it is less easy — as WEIDENREICH did — to regard blood-corpuscles that are set free (such as we notice it in Tarsius, when the big lobed nuclei of these megalokaryocytes disintegrate) as being on the contrary devoured in that moment by phagocytosis! [2])

The haematopoiesis is started in Galeopithecus in the following manner. At about the same time that the young germinal vesicle, which has just gone through the two-layered gastrulation stage (gastrulation by delamination [3])), has attached itself to the surface of the strongly folded and swollen maternal mucous membrane, this mucous

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[1]) W. LECHE is inclined (Ueber die Säugethiergattung Galeopithecus, Svenska Akad. Handl. Bd. 21, N°. 11, 1886) to see in Galeopithecus a form which must be placed in the neighbourhood of the ancestral form of the bat.

[2]) Sectional series of Tarsius of a later date give a still clearer image than those which served for my figures of 1898.

[3]) See on this point Anatomischer Anzeiger Bd. 26, 353.

membrane reacts in the manner, well-known in other mammals (Tarsius, hedgehog, rabbit, bat,. etc.) by perceptible changes in the uterine glands in the vicinity of this place of attachment and by the formation of so-called trophospongia-tissue, consisting of a modification of the interglandular connective tissue, to which are added proliferations of uterine and glandular epithelium.

As the final product of these preliminary phenomena we now see that a part of the maternal mucosa where the germinal vesicle has coalesced with the mucosa, presents a more compact proliferation, while nearer the periphery the uterine glands, by strong dilatation of their lumen, differ clearly from the other uterine glands, as this is also the case in Tarsius, Lepus and other mammals during early pregnancy. The dilated glands may be followed up to their mouth; this mouth, however, no longer connects the glandular lumen with the uterine lumen, since in this place the embryonic trophoblast has disturbed the connection and covers the mouths of the glands.

This trophoblast now also shows unmistakable signs of cell-proliferation, although it does not at once attack and destroy the maternal epithelium, as in the hedgehog, Tarsius, Tupaja, etc. but rather finds itself facing this maternal epithelium in full proliferation, in the manner stated by me also for Sorex [1]). Instead of being closely adjacent, however, spaces are left open from the beginning between trophoblast and trophospongia, which spaces are partly mutually connected and partly are subdivided into smaller compartments by trophoblastic villi, attaching themselves to the trophospongia-tissue. In this manner the free surface of the trophoblast, facing the embryo, obtains a knobbed appearance. [2])

Already in early developmental stages, when there is as yet no question of the folding off of the embryo and long before blood-carrying allantoic villi have become interlocked with these trophoblastic villi for the further completion of the placenta, we find in the spaces between trophoblast and trophospongia numerous blood-corpuscles of which we can not say that they have been carried thither by maternal vessels exclusively, although there can be no doubt that a connection between these spaces and the maternal vascular system is established at an early date. In the manner, indicated above, these spaces communicate also with the uterine glands which are here dilated. And in these glands as well as in

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[1]) Quarterly Journal of Microscopical Science, vol. 35.

[2]) Certain modifications which I observed when the germinal vesicle develops in a uterus which is still in the puerperal stage, may be left out of account here.

the interglandular tissue and in the cells, lining the just mentioned spaces, phenomena take place which force us to the conclusion *that a great number of these blood-corpuscles originate in loco.* When we follow these phenomena up to their earliest appearance, we find that in the dilated glands in many places compact cell-heaps are formed, which sometimes lie quite loose in the gland, but in other cases are still found in direct connection with the cell-lining of the gland. We must assume that this latter condition represents the original one and that consequently we have here an epithelial proliferation by which new cell-material is carried into the region of the future placenta.

The final product of these lumps of tissue, which in early stages appear so distinctly as cell-heaps, is an agglomerate of non-nucleated blood-corpuscles. The gradual transition of the nucleate cells into the blood-discs may be followed step by step by successively comparing preparations of the youngest and subsequent stages: often in one preparation all transitions are found together. It then appears that the conclusions I drew for Tarsius and Tupaja in 1898 are confirmed here, viz. that the blood-discs are produced by gradual transitions from the modified nuclei of the above-mentioned cell-heaps and that in this process transitional stages are generally found, comparable to what I called "haematogonia" in the above-quoted paper. They resemble polynuclear leucocytes from which they may be distinguished, however (also according to MAXIMOW and SIEGENBEEK VAN HEUKELOM; see report of the meeting of the Amsterdam Academy of Nov. 26, 1898), by certain characteristics. This phenomenon has been more fully investigated by POLJAKOFF, who also regards the non-nucleate corpuscles as nuclear derivatives and not as cells, deprived of their nuclei. In his paper [1]) numerous illustrations are given of stages corresponding to my haematogonia. It appears from the literature, mentioned by POLJAKOFF that my paper of 1898, preceding his publication, was unknown to him: the concordant results which we have obtained at an earlier date, are confirmed in a striking manner by the phenomena seen in Galeopithecus.

But blood-corpuscles are also produced by other sources besides these epithelial glandular proliferations. Between the dilated glands we find in Galeopithecus in the trophospongia-tissue very conspicuous groups of large cells with a big, but circular nucleus. They show a tendency to lie together in nests, which nests are more or less kept together by elongated cells, forming a spurious wall which distantly remind us of an endothelium.

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[1]) Biologie der Zelle. In Arch. f. Anat. u. Phys. Abth. 1901. Pl. I and II.

These cells also are gradually dissolved into blood-corpuscles: as the uterus grows and the trophospongia passes through its successive developmental stages, they disappear: the blood-corpuscles which owe their existence to them, fall into the above-mentioned spaces, from whence they are taken up in the further circulation. The intermediate stages that can be observed in this way of blood-formation, are in fact an increase of nuclei by amitosis, as was also described by POLJAKOFF and later a gradual formation from these nuclear derivates of non-nucleated blood-discs.

To these two processes of blood-formation in the placenta of Galeopithecus a third must be added in which not the mother is the active agent, as in the two former cases, but the embryonic trophoblast. Of this trophoblast we described above how it forms the bottom of the cavities into which the newly-formed blood-corpuscles are discharged, and how it coalesces with the maternal trophospongia to such an extent that for many cells, which here are closely adjacent, it is impossible to determine whether they take their origin in the mother or in the trophoblast of the germinal vesicle.

Yet in regard to the wall of the cavities, which separates them from the lumen of the uterus, there can be no doubt that we have here trophoblastic tissue only. About the active proliferation of this trophoblast tissue there is no doubt, no more than about the question whether the numerous parts of this trophoblast that project into the cavities, partake in the haematopoiesis. As soon as these parts are examined with strong powers it is quite evident that here the nuclei of the trophoblast cells undergo similar modifications as were described above and that the final product of these modifications are again red non-nucleated blood-corpuscles which are added to those already present and originating from the mother. Now these corpuscles are, in the same way as I observed ten years ago in Tarsius and Tupaja, *set free into the maternal circulation and carried along by it.*

On the theoretical significance of the fact that the germinal vesicle takes an active and important part in increasing the number of units for the transport of oxygen in the maternal blood, I will not expatiate here.

And for the histological details of the formation of the bloodplates, resp. non-nucleated blood-corpuscles from an originally normal cell-nucleus, I refer to the coloured figures of pl. I and II of POLJAKOFF's paper in the 1901 volume of the Arch. f. Anat. u. Phys. (Anat. Abth.). With his illustrations I can identify everything I have observed in Galeopithecus. While in a very few cases there seems to be a possibility that the blood-corpuscle owes its existence to a change of the nucleus *in its entirety*, in the vast majority of cases a distinct amitotic disintegration is observed, the number of fragments varying, but generally lying between three and five. As the already modified nucleus dissolves into these fragments the comparability with polynuclear leucocytes seems more obvious, and the colour as a rule approaches more and more to that which the blood-corpuscles themselves assume in the artificially fixed preparation. The same fact was stated by me also for Tarsius in 1898 and figured on Pl. 14 figs. 91—96.

Finally I point out, since my results and those of POLJAKOFF agree in so many respects, that also RETTERER in the volume for 1901 of the Journal de l'Anatomie et de la Physiologie (Structure, développement et fonction des ganglions lymphatiques, p. 700) has obtained similar results and is inclined to assume a still closer genetic relationship between polynuclear leucocytes and haematogonia when he declares that the leucocytes, liberated from lymphatic glands "finissent par se convertir, dans la lymphe ou le sang, en hématies grâce à la transformation hémoglobique *de leur noyau . . .*"

Thus my observations on Galeopitheous form a link in the chain, which begins with HEINRICH MÜLLER in 1845 (Zeitschrift für rationelle Medicin vol. 3. p. 260) was then continued and upheld by WHARTON JONES (Phil. Trans. 1846, p. 65 and 71) and HUXLEY (Lessons in Elementary Physiology, 1866, p. 63) and which, since in 1898 Tarsius added another link, has with increasing weight bound up the question of the origin of the non-nucleated blood-corpuscles in mammals to the conception that these elements in the mammalian body are not equivalent with cells, but must be regarded as nuclear derivatives.

(May 24, 1907).

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