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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 26 April 1907. Dl. XV.)

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VOLUME IX

(— 1ST PART —)

JOHANNES MÜLLER :—: AMSTERDAM
: DECEMBER 1906 :

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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).

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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 $\frac{de}{v\varepsilon}$ when $v =$ valency of the metal and $\varepsilon =$ 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.

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

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

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

or

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

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:

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

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

$$\Delta = \frac{RT}{v\varepsilon} \ln \frac{K}{C} \quad \dots\dots\dots\dots \quad (5)$$

Mr. VAN LAAR already pointed out that this equation, already derived by him in the same way is identical with that derived by NERNST $\Delta = \frac{R\,T}{v\,\varepsilon} \ln \frac{P}{p}$, 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	$Au^{\cdot\cdot\cdot}$	» 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.

A. SMITS. "On the

A. SMITS. "On the course of the P,T-curves for constant concentration for the equilibrium solid-fluid."

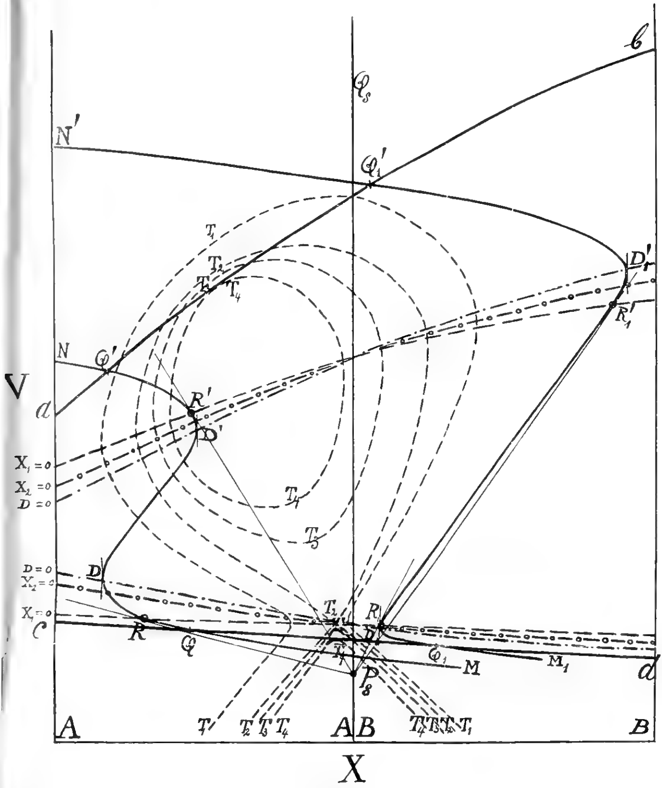

Fig. 1

$X_1 = \frac{d^2\psi}{dx^2} \cdot V_{xl}$

$X_2 = \frac{d^2\psi}{dx^2_l} \cdot W_l$

$D = \frac{d^2\psi}{dx^2}$

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 $M_1 Q_1 D_1 R_1 R_1' D_1' Q_1' N'$. 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:

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

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])

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

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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 cd 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 $\frac{\partial^2\psi}{\partial v^2{}_f}\,.\,V_{sf} = 0$.

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

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

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

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 *A B* is intermediate, we cut now that branch of the three phase line of the compound, which has a maximum.

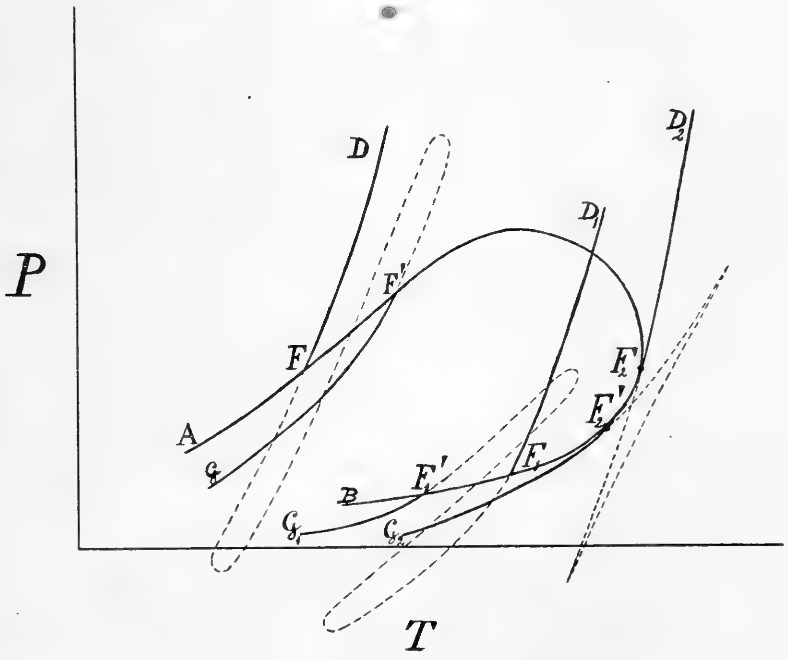

Fig. 2.

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 *F D*, 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 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*.

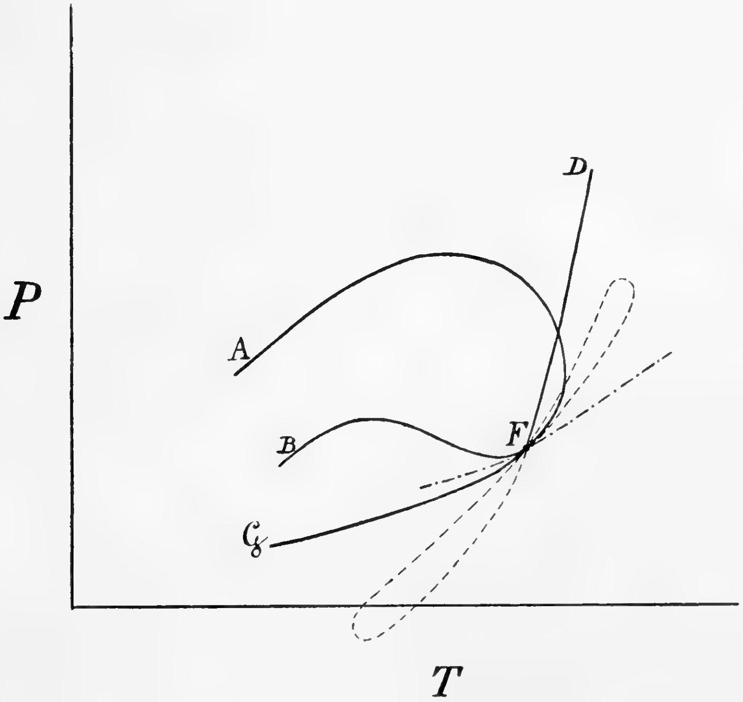

Fig. 3.

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

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

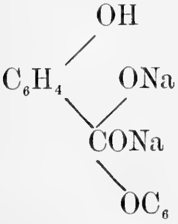
[2]) In this point the direction of the three-phase line is given by $T\frac{dp}{dT}=\frac{r}{v_d-v_l}$.

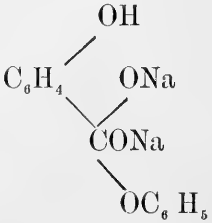
Chemistry. — *"The formation of salicylic acid from sodium phenolate."* By Dr. J. Moll van Charante. (Communicated by Prof. A. P. N. Franchimont).

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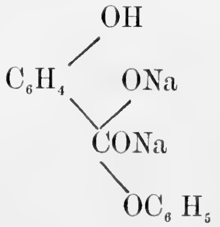
[1] B. B. (1905) 38 p. 714.

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.



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 th			
		M.p.	Mol. weight.	Equiv. Vole. (in the solid state.)	Sym
1	1-2-Nitro-Aniline.	72°	138	95.70	Rhomb
2	1-4-Nitro-Aniline.	146°	138	96.03	Mon.
3	1-2-4-Dinitro-Aniline.	182°	183	113.30	Mon.
4	1-2-4-6-Trinitro-Aniline.	190°	228	129.39	Mon.
5	1-4-Nitro-Diethyl-A.*)	78°	194	162.07	Mon.
6	1-2-4-Dinitro-Methyl-A.	178°	197	125.24	Mon.
7	1-2-4-Dinitro-Ethyl-A.	114°	211	145.41	Tricl
8	1-2-4-Dinitro-Dimethyl-A.	87°	211	142.95	Rhom
9	1-2-4-6-Trinitro-Dimethyl-A.	154°	256	165.05	Rhomb
10	1-2-4-Dinitro-Methyl-Ethyl-A.	59°	225	157.45	Tricl
11	1-2-4-Dinitro-Diethyl-A.	80°	239	173.94	Rhom
12	1-2-4-, + 1-3-4-Dinitro-Diethyl-A. (Double compound.)	59°	478	½(361.02)	Mon.
13	1-2-4-6-Trinitro-Diethyl-A.	164°	284	192.41	Mon.
14	1-2-4-Dinitro-Ethyl-n-Propyl-A.	55°	253	189.13	Rhom
15	1-2-4-6-Trinitro-Ethyl-Isopropyl-A.	109°	298	211.80	Tricl
16	1-2-4-Dinitro-Isopropyl-A.	95°	225	153.79	Tricl
17	1-2-4-Dinitro Dipropyl-A.	40°	267	202.50	Rhom
18	1-2-4-6-Trinitro-Dipropyl-A.	138°	312	227.23	Tric
19	1-2-4-Dinitro-Isobutyl-A.	80°	239	172.70	Mon
20	1-2-4-6-Trinitro-Isobutyl-A	95°	284	196.53	Rhom
21	1-2-4-Dinitro-Diïsobutyl-A.	112°	295	250.21	Mon
22	1-2-4-Dinitro-Allyl-A.	76°	223	157.93	Tric
23	1-2-4-Dinitro-Methyl-Phenyl-A.	166°	273	194.16	Mon
24	1-2-4-Dinitro Ethyl-Phenyl-A.	95°	287	210.48	Mon
25	1-2-4-Dinitro-Benzyl-A.	116°	273	187.50	Tric
26	1-2-4-Dinitro-Methyl-Benzyl-A.	144°	287	204.41	Mon
27	1-2-4-Dinitro-Ethyl-Benzyl-A.	73°	301	219.87	Mon
28	1-2-4-Dinitro-Phenyl-Benzyl-A.	168°	349	250.00	Mon
29	1-2-4-6-Trinitro-Ethyl-Nitraniline.	96°	301	183.09	Mon
30	1-2-4-6-Trinitro-Isopropyl-Nitraniline.	108°	315	201.53	Mon
31	1-2-3-4-6-Tetranitro-Methyl-Nitraniline.	146°	332	189.71	Mo

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

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

y:	Axial-Elements:	Topic Parameters:	No.
pyr.	$a : b : c = 1.3667 : 1 : 1.1585.$	$\chi : \psi : \omega = 5.3635 : 3.9245 : 4.5465$	1
m.	$a : b : c = 2.0350 : 1 : 1.4220; \quad \beta = 88°10'$	$\chi : \psi : \omega = 6.5406 : 3.2141 : 4.5704$	2
m.	$a : b : c = 1.9826 : 1 : 1.4088; \quad \beta = 85° 1\frac{1}{2}'$	$\chi : \psi : \omega = 6.8206 : 3.4403 : 4.8467$	3
m.	$a : b : c = 1.6560 : 1 : 1.5208; \quad \beta = 80°47\frac{1}{2}'$	$\chi : \psi : \omega = 5.9313 : 3.8149 : 5.7975$	4
m.	$a : b : c = 1.0342 : 1 : 0.9894; \quad \beta = 80°34'$	$\chi : \psi : \omega = 5.6210 : 5.4351 : 5.3775$	5
m.	$a : b : c = 1.2286 : 1 : 0.9707; \quad \beta = 83°28'$	$\chi : \psi : \omega = 5.8090 : 4.7281 : 4.5897$	6
ac.	$a : b : c = 1.2251 : 1 ; 0.9745$ $\alpha = 33°25\frac{1}{2}' \quad \beta = 83°22' \quad \gamma = 75°41'.$	$\chi : \psi : \omega = 6.2321 : 5.0871 : 4.9880$	7
pyr.	$a : b : c = 1.2154 : 1 : 1.0803.$	$\chi : \psi : \omega = 5.8035 : 4.7750 : 5.1583$	8
fen.	$a : b : c = 1.2936 : 1 : 1.3831.$	$\chi : \psi : \omega = 5.8455 : 4.5184 : 6.2493$	9
ac.	$a : b : c = 1.1497 : 1 : 1.6639.$ $\alpha = 75°46' \quad \beta = 92°33' \quad \gamma = 68°57'$	$\chi : \psi : \omega = 5.1900 : 4.5140 : 7.5106$	10
pyr.	$a : b : c = 1.2045 : 1 : 1.1513.$	$\chi : \psi : \omega = 6.0294 : 5.0058 : 5.7631$	11
m.	$a : b : e = 1.3435 : 1 : 1.3013; \quad \beta = 86°39'$	$\chi : \psi : \omega = 6.3064 : 4.6940 : 6.1083$	12
m.	$a : b : c = 1.1750 : 1 : 0.9462; \quad \beta = 86°28'$	$\chi : \psi : \omega = 6.5523 : 5.5762 : 5.2763$	13
pyr.	$a : b : c = 1.0535 : 1 : 0.9227.$	$\chi : \psi : \omega = 6.1045 : 5.7946 : 5.3466$	14
ac.	$a : b : c = 2.0162 : 1 .$ $\alpha = 75°0' \quad \beta = 99°17' \quad \gamma = 111°16\frac{1}{2}'$	———	15
ac.	$a : b : c = 1.1527 : 1 : 1.5790.$ $\alpha = 118°43' \quad \beta = 104°33' \quad \gamma = 85°12\frac{1}{2}'$	$\chi : \psi : \omega = 5.3440 : 4.6360 : 7.3201$	16
pyr.	$a : b : c = 1.0191 : 1 : 0.9246.$	$\chi : \psi : \omega = 6.1042 : 5.9890 : 6.5382$	17
ac.	$a : b : c = 1.3327 : 1 : 0.9055$ $\alpha = 119°46' \quad \beta = 111°0' \quad \gamma = 102°35'$	$\chi : \psi : \omega = 8.1556 : 6.1197 : 5.5414$	18
m.	$a : b : c = 0.7104 : 1 : 0.3591; \quad \beta = 85°34\frac{1}{2}'$	$\chi : \psi : \omega = 6.1870 : 8.7092 : 3.2145$	19
pyr.	$a : b : c = 0.7325 : 1 : 0.3470.$	$\chi : \psi : \omega = 6.7231 : 9.1782 : 3.1849$	20
m.	$a : b : c = 1.0717 : 1 : 0.9124; \quad \beta = 63°5\frac{1}{2}'$	$\chi : \psi : \omega = 7.0686 : 6.5960 : 6.0181$	21
ac.	$a : b : c = 1.0251 : 1 : 0.9632$ $\alpha = 71°16\frac{1}{2}' \quad \beta = 111°0' \quad \gamma = 116°40'$	$\chi : \psi : \omega = 5.9480 : 5.8024 : 5.5890$	22
m.	$a : b : c = 1.1518 : 1 : 1.6968; \quad \beta = 86°1'$	$\chi : \psi : \omega = 5.3389 : 4.6341 : 7.8650$	23
m.	$a : b : c = 0.4933 : 1 : 0.6586; \quad \beta = 78°6\frac{1}{4}'$	$\chi : \psi : \omega = 4.2994 : 8.7156 : 5.7401$	24
ac.	$a : b : c = 1.0385 : 1 : 0.8586$ $\alpha = 107°57' \quad \beta = 139°47' \quad \gamma = 78°23'$	$\chi : \psi : \omega = 7.2444 : 6.9757 : 5.9891$	25
m.	$a : b : c = 1.5086 : 1 : 1.3276; \quad \beta = 71°40'$	$\chi : \psi : \omega = 7.1735 : 4.7551 : 6.3129$	26
m.	$a : b : c = 1.7258 : 1 : 1.3087; \quad \beta = 84°5'$	$\chi : \psi : \omega = 6.9531 : 4.6084 : 6.0310$	27
m.	$a : b : c = 1.1373 : 1 : 1.3645; \quad \beta = 64°21\frac{1}{2}'$	$\chi : \psi : \omega = 6.4059 : 5.7640 : 7.6856$	28
m.	$a : b = 1.4187 : 1 . \quad \beta = 86°23\frac{1}{4}'$	———	29
m.	$a : b : c = 1.3924 : 1 : 0.9568; \quad \beta = 78°33'$	$\chi : \psi : \omega = 7.3676 : 5.2913 : 5.2743$	30
m.	$a : b : c = 1.6686 : 1 : 1.4712; \quad \beta = 76°37'$	$\chi : \psi : \omega = 7.1730 : 4.2987 : 6.3243$	31

hese 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: $C_6H_3 . \underset{(1)}{(NO_2)} . \underset{(2)}{Br} . \underset{(3)}{Br}$; 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.

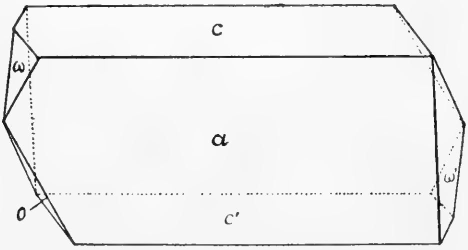

Fig. 1.

Triclino-pinacoidal.

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

$A = 90°30'$ $\alpha = 90°45^2/_3{}'$

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

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

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°16½′	—
$a : c = (100) : (001) =$*	69 23	—
$a : o = (100) : (1\bar{1}\bar{1}) =$*	65 11	
$c : o = (00\bar{1}) : (1\bar{1}\bar{1}) =$*	75 47⅓	—
$b : o = (0\bar{1}0) : (1\bar{1}\bar{1}) =$*	36 6	—
$a : \omega = (100) : (1\bar{1}1) =$	50 52	50°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 29⅔
$a : s = (\bar{1}00) : (\bar{1}\bar{1}\bar{1}) =$	49 59	50 49⅓
$b : s = (0\bar{1}0) : (\bar{1}\bar{1}\bar{1}) =$	45 48	45 52½
$c : s = (00\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	—	56 4
$o : s = (1\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	63 39	63 59⅔

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

The extinction on $\{100\}$ amounts to about 26½ 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: $C_6H_3 . (NO_2)_{(1)} . Br_{(2)} . Br_{(5)}$; 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.

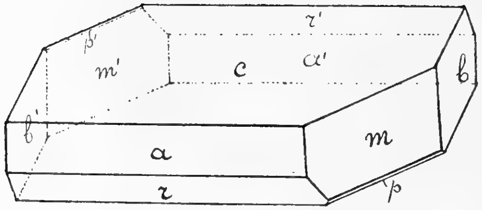

Fig. 2.

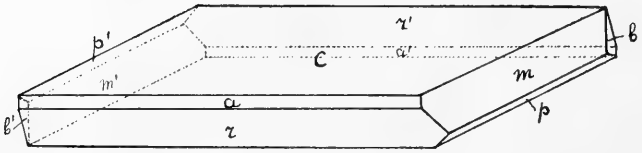

Fig. 3.

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

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 $\{\bar{15}\,.\,15\,.\,4\}$

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-derivatives ¹) 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.

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

$$A = 97^\circ 13^1/_2{}' \qquad \alpha = 97^\circ 36'$$
$$B = 113^\circ 30^1/_2{}' \qquad \beta = 113^\circ 37'$$
$$C = 90^\circ 38^1/_2{}' \qquad \gamma = 87^\circ 33'$$

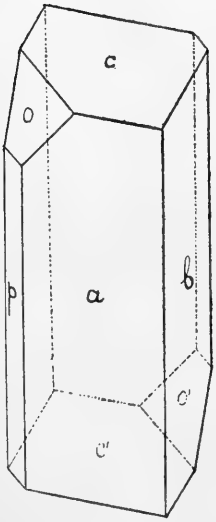

Fig. 4.

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:*
$a : b = (100) : (010) =^*$	$89^\circ 21^1/_2{}'$	—
$a : c = (100) : (001) =^*$	$66\ 29^1/_2{}'$	—
$b : c = (010) : (001) =^*$	$82\ 46^1/_2{}'$	—
$p : a = (1\bar{1}0) : (100) =^*$	$46\ 36$	—
$c : o = (001) : (1\bar{1}1) =^*$	$48\ 42$	—
$o : p = (1\bar{1}1) : (110) =$	$51\ 43$ (circa)	$52^\circ\ 1'$
$c : p = (001) : (\bar{1}10) =$	$100\ 29$ (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 $84^1/_2{}^\circ$ *lowers* the melting point of this substance. A mixture of $87\,^0/_0$ 1-2-4- and $13\,^0/_0$ 1-2-5-*Nitrodibromobenzene* melted at 56°. There seems, however, to be no question of an isomorphotropous mixing.

D. Nitro-2-6-Dibromobenzene.

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.

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

$$\beta = 83^\circ 24'.$$

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.

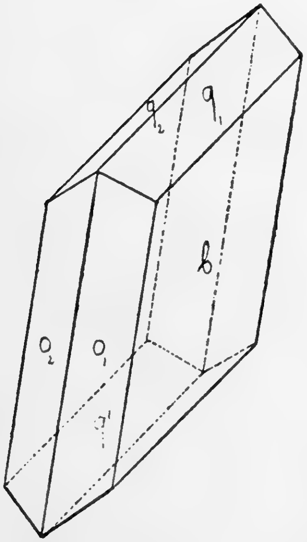

Fig._5.

	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: 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.
$\frac{0.04}{3}$ 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							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.	
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 » »	92	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: $\frac{1}{2}$ h. — $\frac{1}{2}$ h. — $\frac{1}{2}$h. — $\frac{1}{2}$ h. — 20 m. — 15m. — 10m.	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 prcipitinogen 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 =

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

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 =

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

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

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

So the equation (1) becomes:

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

or

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

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
$2^{h}\,15^{m}\,53^{s}.0$	$1297''.92$

h m s	Length of the chords ″
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: 2^h 34^m 44^s .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 „ „ „ $\alpha_{\text{☾}} = 157°42'47''.95$
(Hansen-Newcomb).
Declination „ „ „ „ „ „ $\delta_{\text{☾}} = 9°53'\ 3''.48$
(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

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

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	$\Delta\alpha_{\text{☾}-\odot}$	−3.20	$\Delta\delta_{\text{☾}-\odot}$	+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	$\Delta\alpha$ $(-\odot$	+0.49	$\Delta\delta$ $(-\odot$	+0.16	$\Delta\pi =$	— 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

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

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

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

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

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:

$$68.1(\Delta R+\Delta r)+56.2\Delta\alpha-25.2\Delta\delta=+489''.46-0.35(\Delta R-\Delta r)-12.9\Delta\pi$$

$$-81.6(\Delta R+\Delta r)+65.1\Delta\alpha-31.6\Delta\delta=+397''.87+0.24(\Delta R-\Delta r)+12.8\Delta\pi$$

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:

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

whence

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

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

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

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:

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

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%, 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 $C_1=-k_1T\;(log\,T-1)+((e_1)_0-T(s_1)_0),\ c_1=\dfrac{n_1}{\Sigma n_1}$ and $\theta_1=\dfrac{\partial\Theta}{\partial n_1}$; 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:

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

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 $\dfrac{\partial^2\omega}{\partial x^2}=0$, and ω becomes a *linear* function of x. But also $\dfrac{\partial^2 v}{\partial x^2}=0$, 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:

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

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 $\frac{\partial^2 \omega}{\partial x^2} = 0$. $\Big[$Otherwise evidently $\omega - x \frac{\partial \omega}{\partial x} = \omega_1 - {}^1/_2 x^2 \left(\frac{\partial^2 \omega}{\partial x^2}\right)_1 - {}^1/_3\, x^3 \left(\frac{\partial^3 \omega}{\partial x^3}\right)_1 - \ldots\Big]$ In the same way $v - x \frac{\partial v}{\partial x} = v_1$, and we get:

$$\left.\begin{array}{l} \mu_1(x, p) = C_1 - \omega_1 + pv_1 + RT\,log\,(1 - x) \\ \mu_1(o, p_0) = C_1 - \omega_1 + p_0 v_1 \end{array}\right\},$$

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:

$$pv_1 + RT\,log\,(1 - x) = p_0 v_1,$$

hence

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

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:

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

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 $\frac{RT}{34\, v_1}$ 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° $= 23{,}87 \times \frac{1{,}015}{1{,}19} = \underline{20{,}36}$ 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 $\gamma' = \frac{\gamma}{1001{,}4}$:

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

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

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

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):

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

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:

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

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 $\frac{\partial v}{\partial x}$].

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 $X_{\alpha_1 \alpha_2 \dots \alpha_p}$ 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

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

where for each of the terms of the second member the indicatrix $(\alpha_{q_1} \alpha_{q_2} \dots \alpha_{q_p} \alpha_{q_{p+1}})$ has the same sense as $(\alpha_1 \alpha_2 \dots \alpha_{p+1})$. 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 $u_1 \dots u_{p+1}$ 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 ${}^pX$:

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

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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 ${}^{p}X$, 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:

$$du_1 \ldots du_{p+1} \left| \begin{array}{l|ccc} & \dfrac{\partial^2 x_1}{\partial u_1 \partial u_{p+1}} & \ldots\ldots & \dfrac{\partial^2 x_p}{\partial u_1 \partial u_{p+1}} \\ & \dfrac{\partial x_1}{\partial u_2} & \ldots\ldots\ldots & \dfrac{\partial x_p}{\partial u_2} \\ & \vdots & & \vdots \\ & \dfrac{\partial x_1}{\partial u_p} & \ldots\ldots\ldots & \dfrac{\partial x_p}{\partial u_p} \\ \hline X_{123\ldots p} & & & \end{array} \right|$$

$$\text{and } du_1 \ldots du_{p+1} \left| \begin{array}{l|ccc} X_{123\ldots p} & & & \\ \hline & \dfrac{\partial x_1}{\partial u_2} & \ldots\ldots\ldots & \dfrac{\partial x_p}{\partial u_2} \\ & \vdots & & \vdots \\ & \dfrac{\partial x_1}{\partial u_p} & \ldots\ldots\ldots & \dfrac{\partial x_p}{\partial u_p} \\ & \dfrac{\partial^2 x_1}{\partial u_1 \partial u_{p+1}} & \ldots\ldots & \dfrac{\partial^2 x_p}{\partial u_1 \partial u_{p+1}} \end{array} \right|,$$

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

$$X_{123\ldots p} \left| \begin{array}{cccc} \pm 1 & \dfrac{\partial x_1}{\partial u_1} du_1 & \ldots\ldots & \dfrac{\partial x_p}{\partial u_1} du_1 \\ \vdots & \vdots & & \vdots \\ \pm 1 & \dfrac{\partial x_1}{\partial u_{p+1}} du_{p+1} & \ldots & \dfrac{\partial x_p}{\partial u_{p+1}} du_{p+1} \end{array} \right|$$

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 $u_1\, u_2 \dots u_{p+1}$ and if we integrate $X_{123\dots p}$ successively over the components of the elements of boundary according to the curved C_p''s we find:

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

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

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

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

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 ${}^pX$ 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 ${}^pX$ 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 ${}^pX$. For the component vectors of ${}^{p-1}Z$ we find:

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

The particularity may appear that one of the derivatives becomes 0. If the first derivative of an ${}^mX$ 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 ${}^pX$ 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 ${}^pX$ over a closed S_{p+1}, then we can substitute for the addition given by an S_{p+1} element the integral of ${}^pX$ 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 ${}^pX$. Let us find its component $X_{12 \dots p}$.

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

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

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

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

and

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

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 $\overline{\overset{2}{\nabla}}$ of the general ${}^{p+1}V$, so it is the general S_n integral of the $\overline{\overset{2}{\nabla}}$ 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 $\overline{\overset{1}{\nabla}}$ of the general ${}^{p-1}V$, so it is the general S_n integral of the $\overline{\overset{\scriptscriptstyle 1}{\nabla}}$ 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:

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

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

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 $\nabla = \overline{\nabla}^{2}/$, 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 ∇ 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.

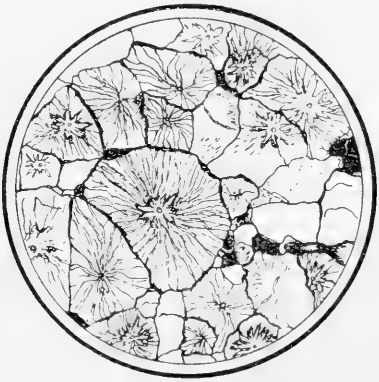

Fig. 2.
Phytosterol,
fused and solidified by cooling.

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.

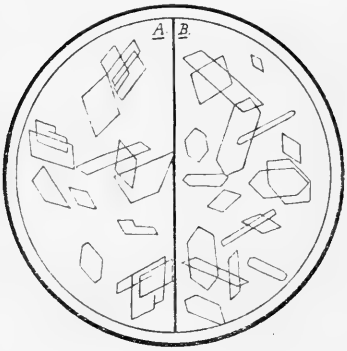

Fig. 3.
Phytosterol and Cholesterol from 95% Alcohol.

§ 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 melting-point 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).

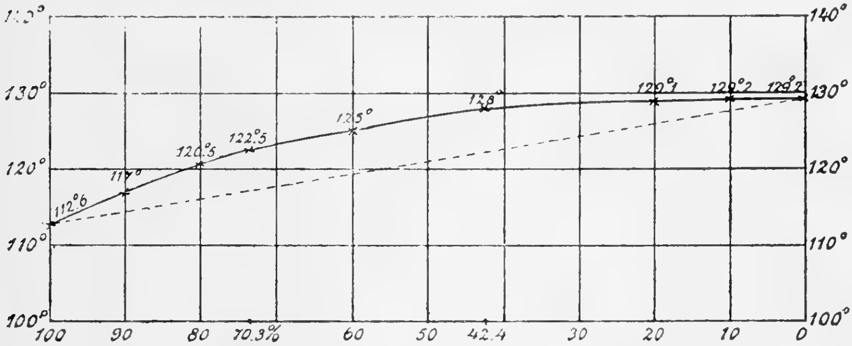

Fig. 4.
Cholesterol-, and Phytosterol-Acetate.

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 °/₀ cholesterol-acetate to 0 °/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 °/₀. The results are the most accurate when the quantity of phytosterol-ester[1]) amounts to 2°/₀—40°/₀. 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 °/₀ Chol. Acet. + 10 °/₀ 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°/₀, the meltingpoint is practically not altered; when it is 2°/₀ 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 ⊥ 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 ⊥ 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; *α-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. Génève (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

$$V_{Bi} = 21,064 \quad \text{and} \quad V_{Fe_2O_3} = 32,06,$$

and with the aid of the given relations and the values for α 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.

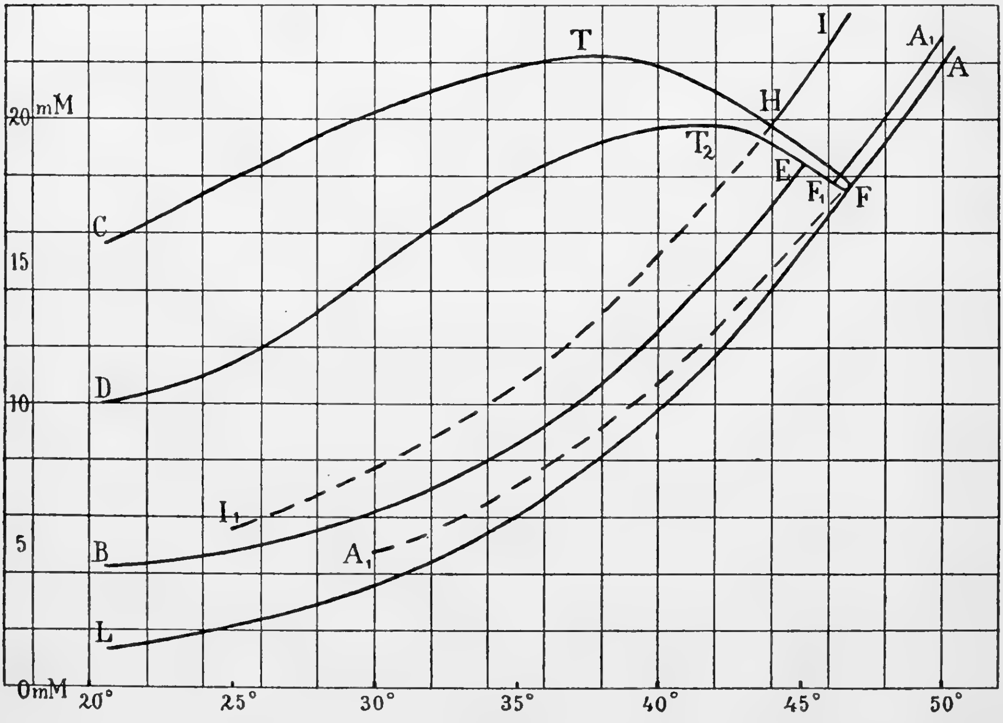

Fig. 1.

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

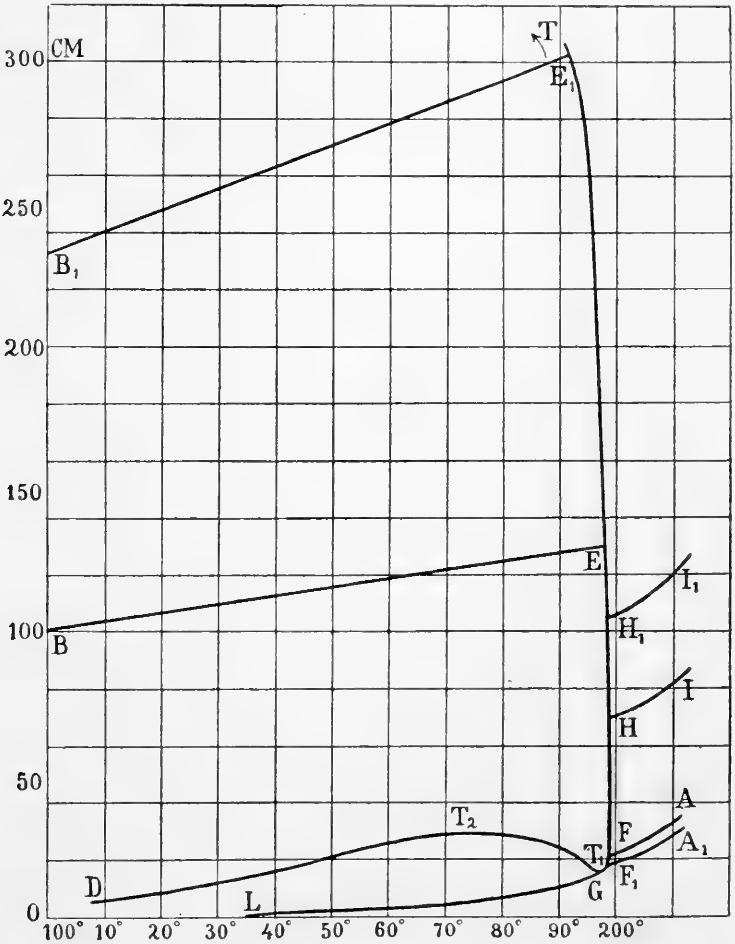

Fig. 2.

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_1t-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.

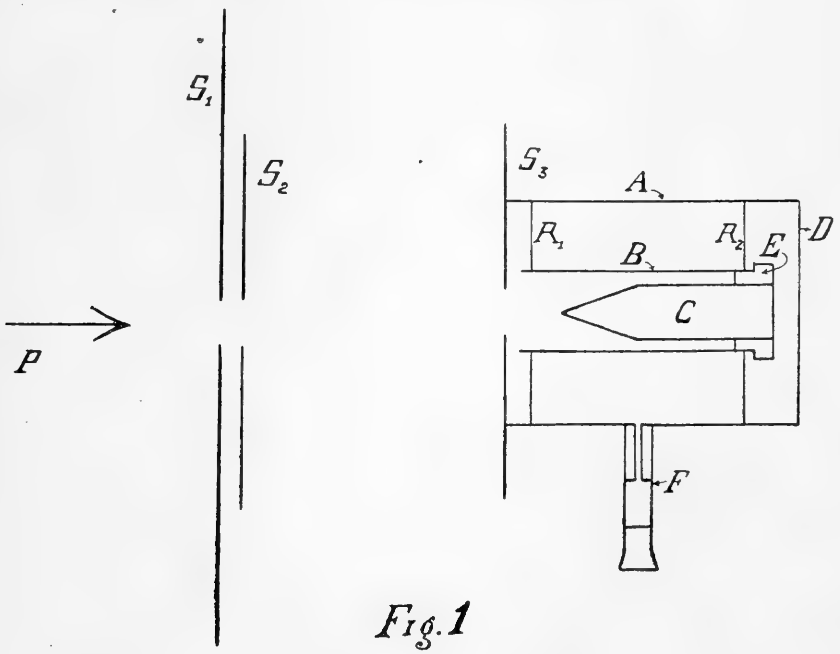

Fig. 1

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 rays¹).

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.

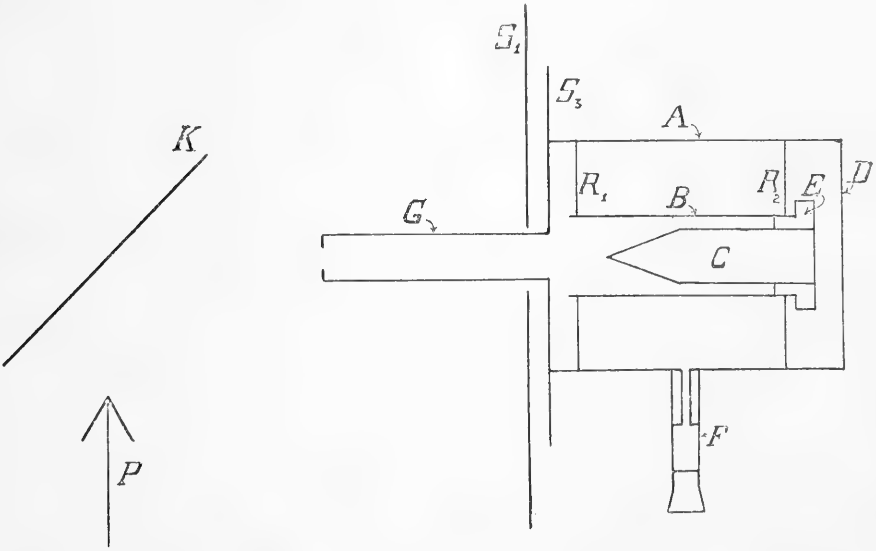

Fig. 2

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°/₀, 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°/₀ of formic acid, whilst pure triformin requires 78.4°/₀. The deficiency points to the presence of fully 10°/₀ 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 $10^0/_0$ of diformin.

Afterwards, when $100^0/_0$ 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.

$$n^d_{18} = 1.4412.$$

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.

$$Sp.\ gr._{12^\circ} = 0{,}6907 \qquad n_{D_{12^\circ}} = 1.3919.$$

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 $Sp.gr._{20} = 0.6603$, $nD_{20} = 1.3734$.; EYKMAN (R. **14**, (1881) 187) $Sp.gr._{14} = 0.6652$ $nD_{14} = 1.37725$.

[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 $X_{pqr...}$ a vector with indicatrix *opqr....* 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 $X_{pqr...}$ the indicatrix *pqr...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 ${}_2^1X$, 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 ${}_0^1X$, i. e. a first derivative (gradient) of a scalar distribution φ, we must have:

$$X_u=-\frac{\partial\varphi}{A\partial u}\ ,\quad X_v=-\frac{\partial\varphi}{B\partial v}\ ,\quad X_w=-\frac{\partial\varphi}{C\partial w}$$

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 ${}_0^1X$, 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]).

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

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

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 ${}^{1}_{0}X$ 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):

$$\int \varphi \frac{\partial \psi}{\partial \nu} dO - \int \varphi \bigtriangledown^2 \psi . d\tau = \int \psi \frac{\partial \varphi}{\partial \nu} dO - \int \psi \bigtriangledown^2 \varphi . d\tau$$

$$\left(= \int S \{grad.\ \varphi,\ grad.\ \psi\}\ dt. \right).$$

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

$$\int \varphi \,.\, \bigtriangledown^2 \psi \,.\, d\tau = \int \psi \,.\, \bigtriangledown^2 \varphi \,.\, d\tau,$$

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:

$$4\pi \,.\, \varphi_P = \int (-1 + coth\, r) \bigtriangledown^2 \varphi \,.\, d\tau.$$

So, if we put $-1 + coth\, r \equiv F_1(r)$, we have:

$$ {}^{1}_{0}X = \overline{\bigtriangledown_1} \int \frac{\overline{\bigtriangledown_2}\, {}^{1}_{0}X}{4\pi} F_1(r)\, d\tau. \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

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:

$$d\,(Hdh) = dh\, ds\, X \sin \textsc{f}.$$

So we have but to take $\dfrac{\Sigma}{dh}$ 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 $2 \cos \varphi \dfrac{\cosh r}{\sinh^3 r}$, 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 $= \dfrac{\cosh r}{\sinh^2 r}$, 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:

$$\operatorname{cosech} r - \tfrac{1}{2} r \operatorname{sech}^2 \tfrac{1}{2} r \equiv F_2(r),$$

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 ${}^{1}_{2}X$, 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:

$$ {}^{1}_{2}X = \overset{2}{\nabla} \int \frac{\overset{1}{\nabla}\, {}^{1}_{2}X}{4\pi} F_2(r)\, d\tau, \quad \ldots\ldots \quad (II) $$

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:

$$ \int \frac{\overset{2}{\nabla}\, X}{4\pi} F_1(r)\, d\tau + \int \frac{\overset{1}{\nabla}\, X}{4\pi} F_2(r)\, d\tau. $$

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

$\left(\text{i. e. a system such that } ds = \dfrac{\sqrt{dx^2 + dy^2 + dz^2}}{1 - \dfrac{x^2 + y^2 + z^2}{4}}\right)$

$$\nabla^2 u = -\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right),$$

but as ∇^2 of a vector distribution with components X, Y and Z, we find for the x-component X_{∇^2}:

$$X_{\nabla^2} = -\left(2X + \frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 X}{\partial y^2} + \frac{\partial^2 X}{\partial z^2}\right).$$

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:

$$ {}^{1}_{0}X = \overline{\overset{1}{\nabla}} \int \frac{\overline{\overset{2}{\nabla}}\, {}^{1}_{0}X}{2\pi}\, l\, coth\, \tfrac{1}{2} r\, d\tau, $$

$$ {}^{1}_{0}X = \overline{\overset{1}{\nabla}} \int \frac{\overline{\overset{2}{\nabla}}\, {}^{1}_{0}X}{2\pi}\, F_1\,(r)\, d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (I) $$

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:

$$-\frac{dU}{dr} = \coth r.$$

$$U = l \operatorname{cosech} r.$$

And we find for an arbitrary ${}^{1}_{2}X$:

$${}^{1}_{2}X = \overline{\nabla}^{2} \int \frac{\overline{\nabla}^{1}\, {}^{1}_{2}X}{2\pi}\, l \operatorname{cosech} r\, d\tau,$$

$${}^{1}_{2}X = \overline{\nabla}^{2} \int \frac{\overline{\nabla}^{1}\, {}^{1}_{2}X}{2\pi}\, F_2(r)\, d\tau. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (II)$$

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 $\bigtriangledown^2$.

We consider the hyperbolical Sp_3 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:

$$\tfrac{1}{2}\int \delta \Sigma \left(\frac{\partial u}{\partial x}\right)^2 d\tau = \int \Sigma \frac{\partial u}{\partial x} \cdot \frac{\partial \delta u}{\partial x} \cdot d\tau = \int u \cdot \frac{\partial . \delta u}{\partial \nu} \cdot dO - \int u \bigtriangledown^2 \delta u \cdot d\tau,$$

so that, as $\bigtriangledown^2 \delta u$ 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 $\frac{sin\ \varphi}{sinh\ r}$ (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

$$ {}^{1}_{0}X = \overline{\overset{1}{\nabla}} \int \frac{\overline{\overset{2}{\nabla}}\ {}^{1}_{0}X}{2\pi}\, l\ coth\ \tfrac{1}{2}\ r\ d\tau, $$

$$ {}^{1}_{2}X = \overline{\overset{2}{\nabla}} \int \frac{\overline{\overset{1}{\nabla}}\ {}^{1}_{2}X}{2\pi}\, l\ coth\ \tfrac{1}{2}\ r\ d\tau. $$

And from this ensues that also the general vector distribution X having under given rotation and divergency a minimum energy is equal to:

$$ X_{div.} + X_{rot.} = \overline{\overset{1}{\nabla}} \int \frac{\overline{\overset{2}{\nabla}} X}{2\pi}\, l\ coth\ \tfrac{1}{2}\ r\ d\tau + \overline{\overset{2}{\nabla}} \int \frac{\overline{\overset{1}{\nabla}} X}{2\pi}\, l\ coth\ \tfrac{1}{2}\ r\ d\tau. $$

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 ${}_2^1X$, 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 ${}_0^1X$, 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 ${}_0^1X$, 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.):

$$\int \varphi \frac{\partial \psi}{\partial \nu} \cdot dO_{n-1} - \int \varphi \nabla^2 \psi \cdot d\boldsymbol{\tau}_n = \int \psi \frac{\partial \varphi}{\partial \nu} \cdot dO_{n-1} - \int \psi \nabla^2 \varphi \cdot d\boldsymbol{\tau}_n$$

$$\left(= \int S(\nabla \dot{\varphi}, \nabla \psi) \cdot d\boldsymbol{\tau}_n \right).$$

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

$$\int \varphi \cdot \nabla^2 \psi \cdot d\boldsymbol{\tau}_n = \int \psi \cdot \nabla^2 \varphi \cdot d\boldsymbol{\tau}_n,$$

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:

$$k_n\, \varphi_P = \int w_n(r) \cdot \nabla^2 \varphi \cdot d\boldsymbol{\tau}_n.$$

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 ${}^1_0X$:

$$ {}^1_0X = \overline{\nabla}^{1} \int \frac{\overline{\nabla}^{2}\ {}^1_0X}{k_n} F_1(r)\, d\boldsymbol{\tau}\,; \qquad \ldots\ldots \qquad (I)$$

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 F with the direction of force:

$$d\Sigma = dh \,.\, X\, ds \sin F,$$

whilst we can easily find as necessary and sufficient condition for H:

$$d(Hdh) = dh \,.\, ds \,.\, X \sin F\,;$$

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 ${}_2^1X$ is obtained as integral of the vectors V of its vortex elements, in other words:

$$ {}_2^1X = \overset{2}{\nabla} \int \frac{\overset{1}{\nabla}\, {}_2^1X}{k_n} F_2(r)\, d\tau, \quad . \quad . \quad . \quad . \quad . \quad (II)$$

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:

$$\int \frac{\overset{2}{\nabla}\, X}{k_n} F_1(r)\, d\tau + \int \frac{\overset{1}{\nabla}\, X}{k_n} F_2(r)\, d\tau.$$

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: $H\beta'$ 5414, $H\gamma'$ 4542, $H\delta'$ 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 2^d^ type stars which approach to the 1^st^ type) are nearest to us and therefore have a smaller radiating power than the more yellow and redder stars of the 2^d^ type. "Researches 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 distance¹). 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		Typical star	n	$\tau_{4.0}$	$q_{4.0}$	$\pi_{4.0}$	L for $q=0''.10$	$2\tau/q$
MAURY	Dr. Cat.							
				″	″	″		
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 $\pi_{0.0}$			Derived from q $\pi_{0.0}$
II—IV	0″.0255	(6)	I—III	0″.021
IV—VI	0 .106	(5)	IV—V	0 .054
VII—VIII	0 .153	(10)	VI—VIII	0 .094
IX—XI	0 .226[1])	(6)	IX—XII	0 .21
XII—XIII	0 .442	(2)		
XIV	0 .567	(5)	XIII—XIV	0 .33
XV	0 .151	(8)	XV	0 .14
XVI	0 .171	(3)	XVI—XX	0 .096
XVII—XVIII	0 .115	(3)		

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 wave-lengths) as both are caused by the higher temperature. The general absorption by an atmosphere is also largest for the smaller wave-lengths, 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.

$$3 \log H + 4 \log P - 6 \log \alpha = const. + 3 \log \lambda - 2 \log \delta$$

$$m - {}^{10}/_{3} \log P + 5 \log \alpha = m_r$$

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)
Orion type

o Persei	0.61
η Orionis	2.51
δ Orionis	0.60
β Lyrae	7.85
α Virginis	0.33
V Puppis	34.2

Group VI—VIII (A)
Sirius type

β Aurigae	0.56
ζ Ursae	(3.41) 1)
Algol	0.72
α Androm.	0.36 2)
α_2 Gemin.	0.002

Group XII—XIV *a* (F—G)
Solar type

α Aurigae	0.185
χ Draconis	0.120
(W Sagittarii	0.005)
(X Sagittarii	0.001)
ι Pegasi	0.117
η Pegasi	0.234

Group XII—XIV *ac*

α Ursae min.	0.00001
ζ Geminorum	0.0023
η Aquilae	0.0029
δ Cephei	0.0031

Group XV (K)

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 rangyrang* 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_2 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 $K\,h\,d$ or $K\,h\,c$.

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 (𝔖 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 ℌ (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 𝔖 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^0. 14 '94 and N^0. 83, Pl. VIII). The hydrogen that might escape from the packing at ℌ 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^0. 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^0. 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

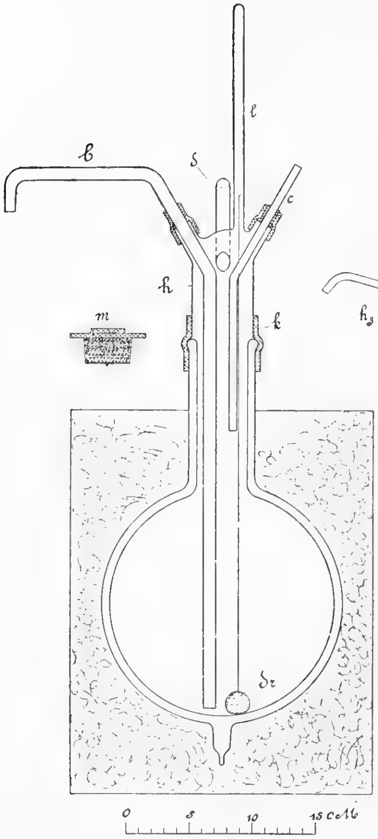

Fig. 1

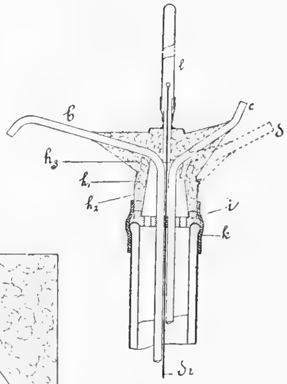

Fig. 2.

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 $\mathfrak{S}$ and to one or to both gasholders. When liquid hydrogen separates, the compressor $\mathfrak{S}$ 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 $\mathfrak{N}ha$, 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'_8 and d''_8 and further along K_o (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.

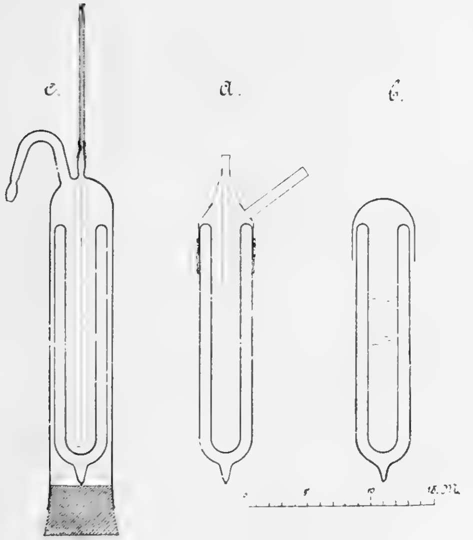

Fig. 3

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.

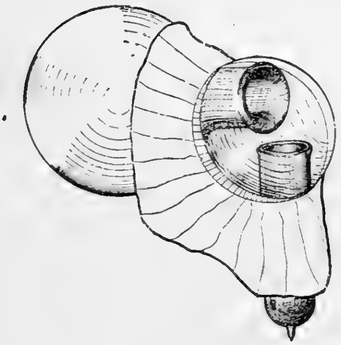

Fig. 4

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 ℜ*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 ℜ*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 ℌ and *Kf* at the dotted connection *Kf* stores the gas, which might contain minute impurities, in the separate reservoir ℜ*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 ℜ*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.

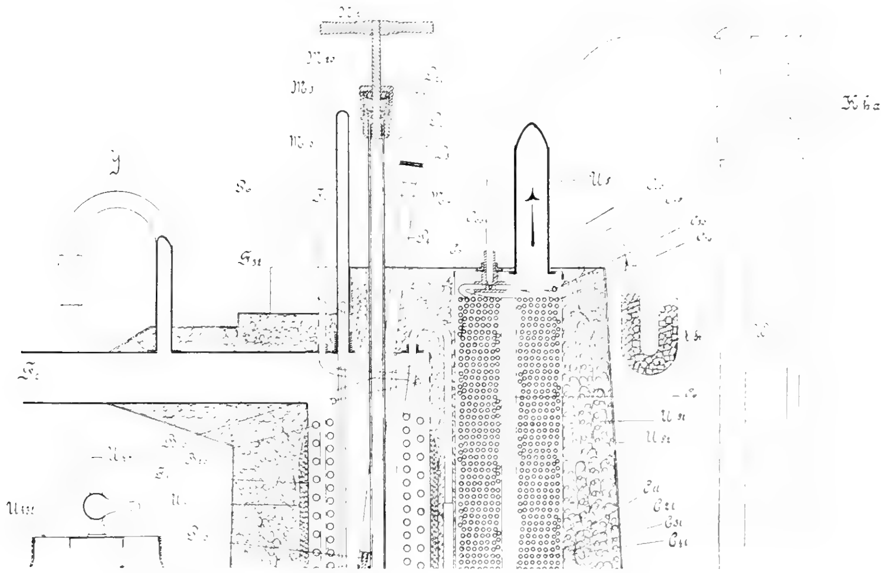
The cock Km is turned so that some more bottles of known capacity are collected of the blown- off gas than, according to the analysis, would be formed by the impurities present in the gas. In this way the purity of the hydrogen is brought to $^1/_{20}\,^0/_0$. It is led along Kl to the gasholders, and 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.

H. KAMERLINGH ONNES. 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. Pl. I.



H. KAMERLINGH ONNES. **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.** Pl I.

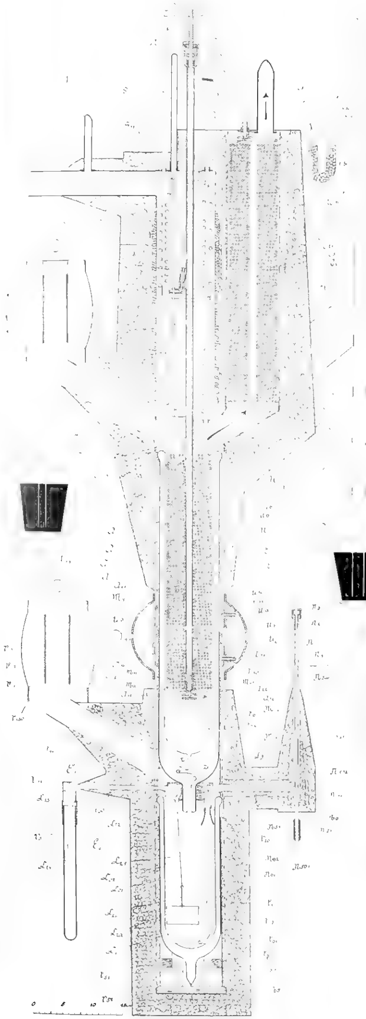


Fig. 2.

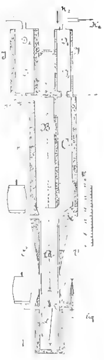


Fig. 1.

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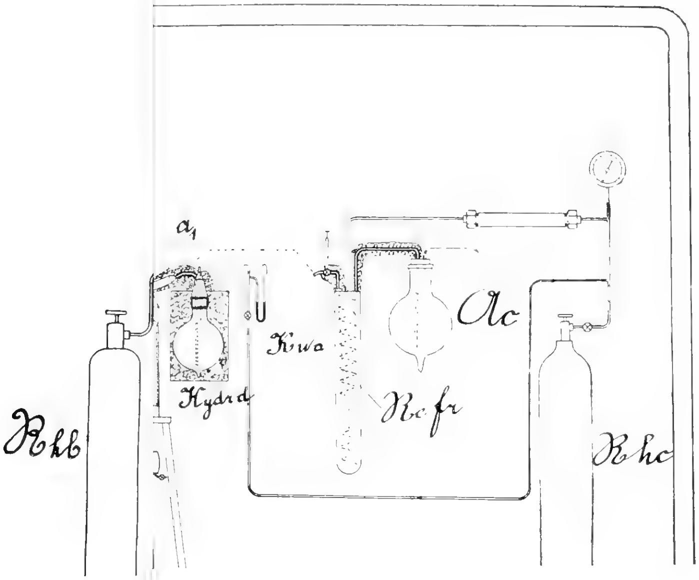
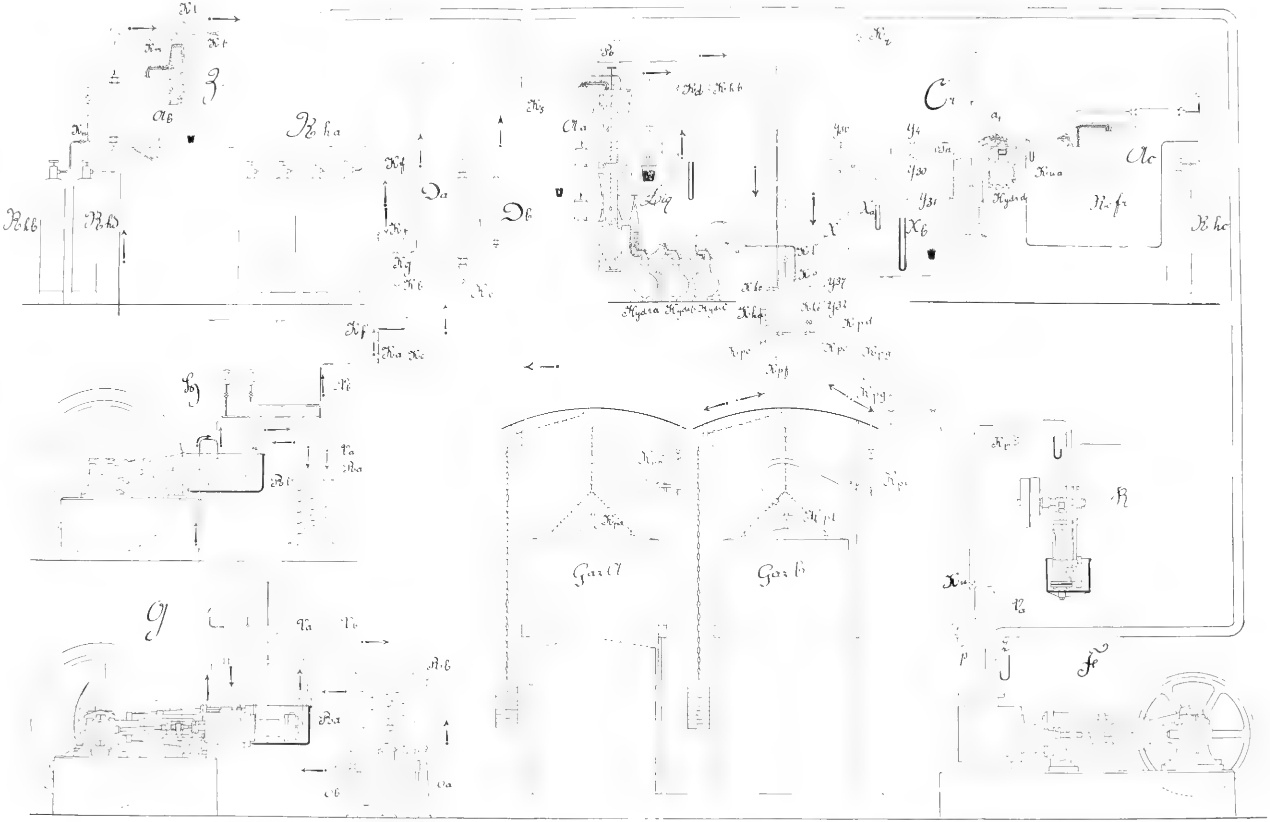
Pl. II.



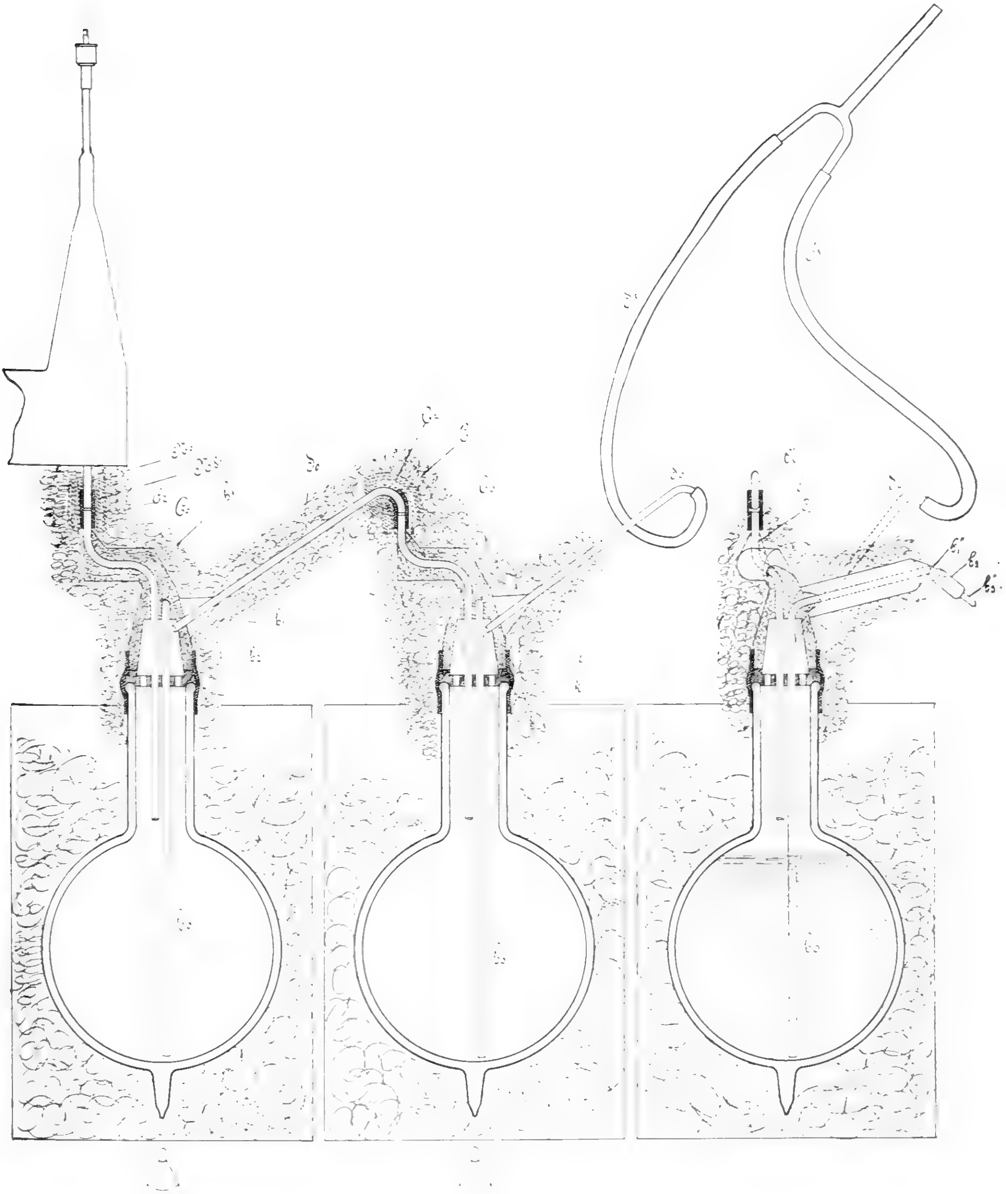
H. KAMERLINGH ONNES. Methods and apparatus used in the cryogenic laboratory at Leiden. X. How to obtain baths of constant and uniform temperature by means of liquid hydrogen.

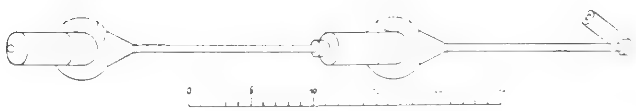
Pl. II.

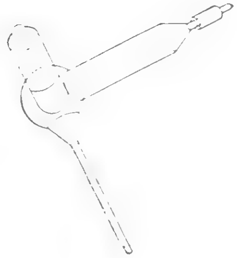


H. KAMERLINGH ONNES. Methods and apparatus used in the cryogenic laboratory at Leiden. X. How to obtain baths of constant and uniform temperature by means of liquid hydrogen.

Pl. III.

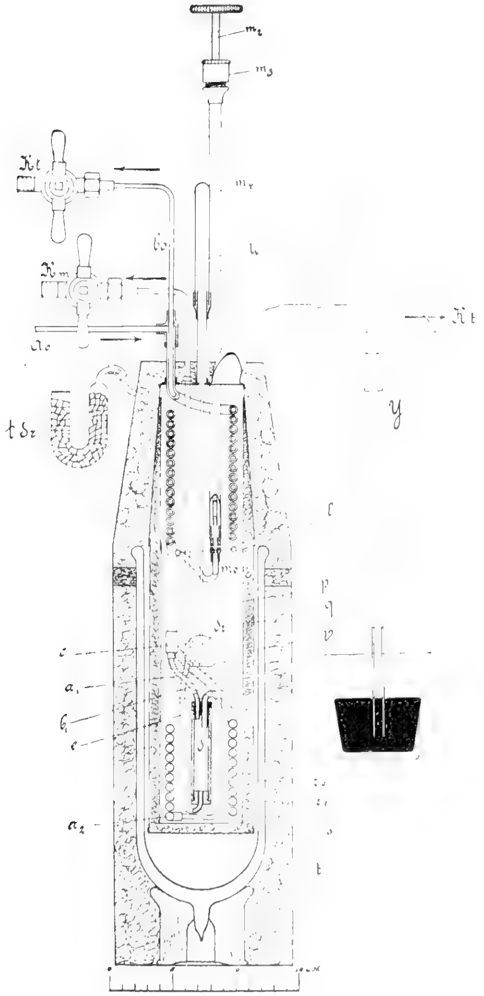






H. KAMERLINGH ONNES. Methods and apparatus used in the cryogenic laboratory at Leiden. XI. The purification of hydrogen for the cycle.

Pl. IV.

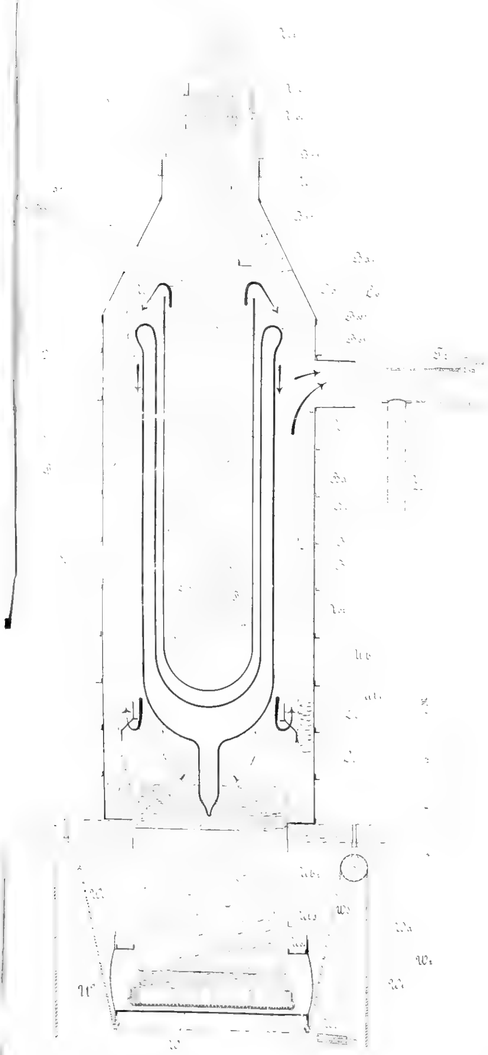


INGH ONNES. Methods and apparatus used in the cryogenic laboratory at Leiden.
Cryostat especially for temperatures from − 252° to − 259°.

Pl. V

KAMERLINGH ONNES. Methods and apparatus used in the cryogenic laboratory at Leiden.
XII Cryostat especially for temperatures from −252° to −259°.

Pl. V.



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 $\mathfrak{S}$ 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_3

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

AMERLINGH 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.

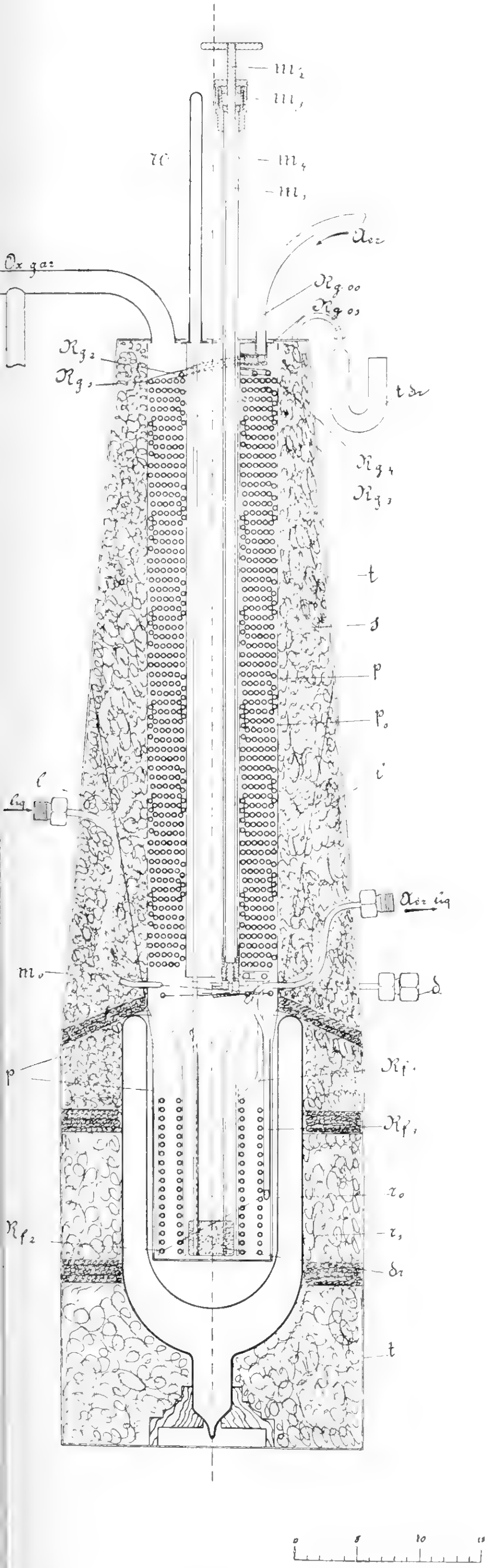


Fig. 1.

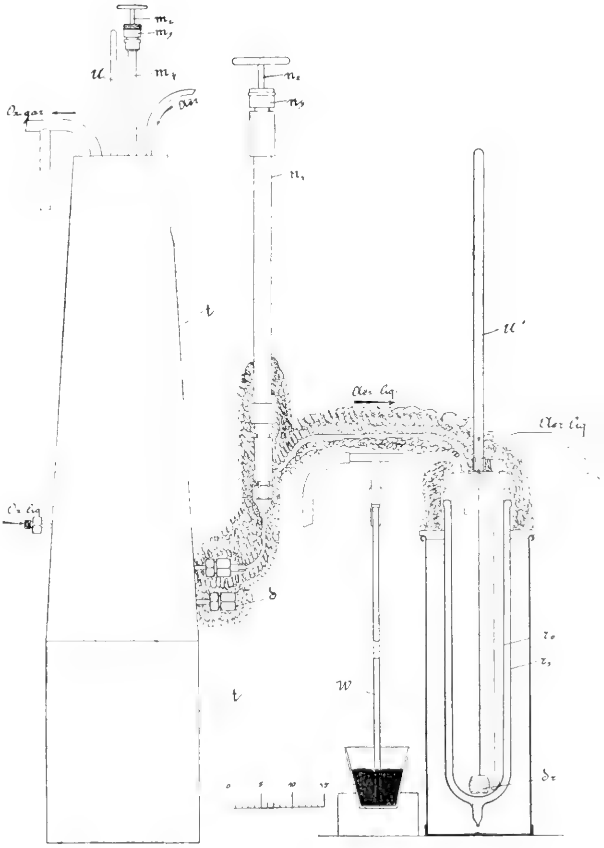


Fig. 2.

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. N⁰. 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. N⁰. 27, May '96 and N⁰. 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.

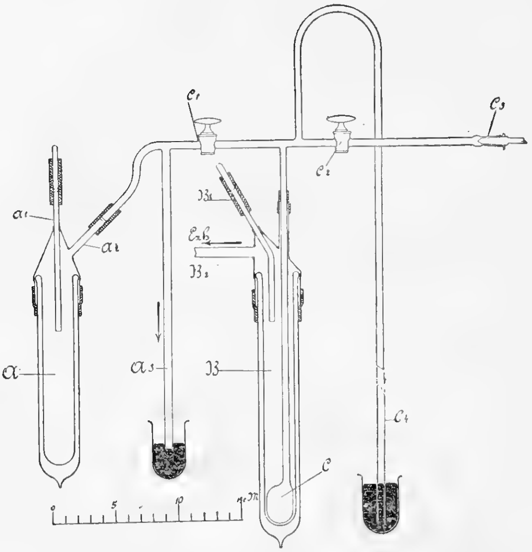

Fig. 5.

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-element¹), a gold- and a platinum-resistance thermometer²)

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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.

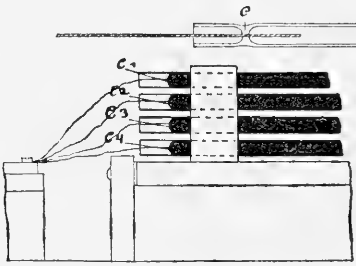

Fig. 2 and 3.

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.

Rheostat. S. and H. No. 15938.

Galvanometer deflections.

Commutators		$R'_w = 50+2+1+1.$ $R''_w = 7700.$			$R'_w = 50+2+1+1$ $R''_w = 7200.$		
elem.	galv.	left	zero	right	left	zero	right
			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 $P_3 + Q_2$.

Rheostat S. and H. No. 15689.

Galvanometer deflections.

$R'_c = 50 + 1.$ $R''_c = 3600.$			$R'_c = 50 + 1.$ $R''_c = 3800.$		
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.

Rheostat No. 17161.

Galvanometer deflections.

comm.	$R'_1 = 8000.$			$R'_1 = 8004.$		
Galv.	left	zero	right	left	zero	right
		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. β $R'_w = +0.001\ \Omega$	corr. β $R'_c = +0.001\ \Omega$	
corr. γ $R'_w = +0.0080\ \Omega$	corr. γ $R'_c = -0.00015\ \Omega$	corr. γ $R'_1 = -2.4\ \Omega$
corr. δ $R''_w = +179\ \Omega$	corr. δ $R''_c = +149\ \Omega$	corr. δ $R'_1 = +0.654\ \Omega$
	$R'''_c = 50.3163\ \Omega$	
	barom.hght.45°N.B.=76.21cM. corr. ε $R'''_c = -0.0373\ \Omega$	
	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.	Commutators 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 $P_3 + Q_2$.

$R_c' = 50+0.5+$ $+0.2+0.1+$ $+0.1$ $R''_c = 5500$	$R'_c = 50+0.5+$ $+0.2+0.1+$ $+0.1$ $R''_c = 5300$

Rheostat S. and H. No. 15689.

Galvanometer deflections.

left	zero	right	left	zero	right
	41.08			41.63	
38.82			38.45		
	41.22			41.81	
		39.84			41.50
	41.35			42.02	
42.37			41.80		
	41.49			42.15	
		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. $2^h 24'$	$E_c = 6.4075$ 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°. 94f.

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:

$$E = a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + e\left(\frac{t}{100}\right)^5 + f\left(\frac{t}{100}\right)^7 \quad . \; . \; . \quad (A)$$

and

$$E = a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + e\left(\frac{t}{100}\right)^4 + f\left(\frac{t}{100}\right)^5 \quad . \; . \; . \quad (B)$$

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 (*B*IV) which would represent as well as possible the temperature range from 0° to — 217°, two equations (*B*I and *B*III) which would moreover show a not too large deviation at — 253°, for one of which (*B*III) a large deviation was allowed at — 217°, while for the other (*B*I) the deviations are distributed more equally over all temperatures, and lastly an equation (*B*II) 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):

$$\left.\begin{array}{ll} a_4 = +\ 4.32044 & e_4 = +\ 0,011197 \\ b_4 = +\ 0,388466 & f_4 = -\ 0,0044638 \\ c_4 = -\ 0.024019 & \end{array}\right\} \quad . \quad . \quad . \quad . \quad (BIV)$$

If we only leave out of consideration — 259° we find for the coefficients of equation (B) the two following sets (comp. § 11):

$$\left.\begin{array}{ll} a_3 = +\ 4.33049 & e_3 = +\ 0,053261 \\ b_3 = +\ 0.436676 & f_3 = +\ 0,003898 \\ c_3 = +\ 0,048091 & \end{array}\right\} \quad . \quad . \quad . \quad (BIII)$$

and

$$\left.\begin{array}{ll} a_1 = +\ 4.35603 & e_1 = +\ 0,103459 \\ b_1 = +\ 0,531588 & f_1 = +\ 0,0118632 \\ c_1 = +\ 0,157678 & \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (BI)$$

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)

$$\left.\begin{array}{ll} a_2 = +\ 4.35905 & e_2 = +\ 0,111619 \\ b_2 = +\ 0,542848 & f_2 = +\ 0,0132130 \\ c_2 = +\ 0,172014 & \end{array}\right\} \quad . \quad . \quad . \quad (BII)$$

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 $-1641\,\mu$ per meter, while $-1687\,\mu$ 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.

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.

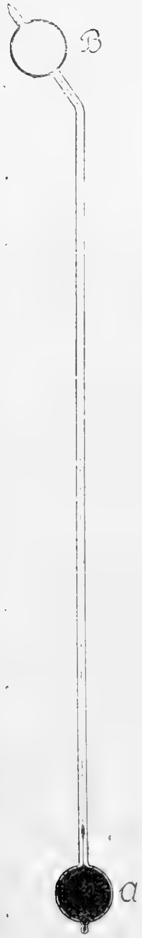

Fig. 1.

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_{160}	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	

[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	

$$W_t = W_c \left\{ 1 + 0{,}39097 \left(\frac{t}{100} \right) - 0{,}009862 \left(\frac{t}{100} \right)^2 \right\}.$$

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:

$$\frac{W_t}{W_0} = 1 + a \frac{t}{100} + b \left(\frac{t}{100} \right)^2 + c \left(\frac{t}{100} \right)^3 + d \left(\frac{10^2}{T} - \frac{10^2}{273{,}09} \right) \quad . \quad . \quad (A)$$

$$\frac{W_t}{W_0} = 1 + a \frac{t}{100} + b \left(\frac{t}{100} \right)^2 + c \left(\frac{t}{100} \right)^3 + d \left(\frac{10^2}{T} - \frac{10^2}{273{,}09} \right) + e \left[\frac{10^4}{T^2} - \frac{10^4}{(273{,}09)^2} \right] \quad . \quad (B)$$

$$\frac{W_t}{W_0} = 1 + a \frac{t}{100} + b \left(\frac{t}{100} \right)^2 + c \left(\frac{t}{100} \right)^3 + d \left(\frac{10^2}{T} - \frac{10^2}{273{,}09} \right) + e \left(\frac{10^6}{T^3} - \frac{10^6}{(273{,}09)^3} \right) \quad . \quad (C)$$

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	+ 0.011	— 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.	$W-R_A$	$W-R_{BI}$	$W-R_{BII}$
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 $\boldsymbol{\Omega}$ 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 $\boldsymbol{\Omega}$ 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

$$q_1 = u - u' \quad , \quad q_2 = v - v' \quad , \quad q_3 = w - w' \quad ,$$
$$q_4 = vw' - wv' \quad , \quad q_5 = wu' - uw' \quad , \quad q_6 = uv' - vu' \; ,$$

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 $\boldsymbol{\Omega}$ can also be represented by

$$E(q_1^2+q_2^2)+Dq_3^2+2Cq_3q_6+Bq_6^2+A(q_4^2+q_5^2)+2F(q_2q_4-q_1q_5)=0\,.\;.\;(2)$$

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

$$(AE-F^2)(x^2+y^2)+B(Ez^2-2Fz+A)=0, \quad . \quad . \quad (6)$$

$$D(x^2+y^2)+Ez^2-2Fz+A=0. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

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

$$D\,(x^2+y^2)+Ez^2-2\,Fz+A=0 \quad . \quad . \quad . \quad . \quad (9)$$

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

$$(D+E)\,(x^2+y^2)+2Ez^2-4Fz+(2A+B)=0 \quad . \quad . \quad (11)$$

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

$$l_0{}^2=\frac{p_6{}^2}{p_1{}^2+p_2{}^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

the angle λ between a ray and XOY by

$$tg^2\lambda=\frac{p_3{}^2}{p_1{}^2+p_2{}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

So the condition $l_0\,tang\,\lambda=a$ furnishes the complex

$$p_3p_6=a\,(p_1{}^2+p_2{}^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Here we have a simple example of a *symmetrical complex of revolution.*

The equation

$$p_3{}^2=a\,(p_1{}^2+p_2{}^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

determines a complex Ω whose rays form with the axis a constant angle, so they cut a circle lying at infinity.

The equation

$$a^2 p_3^2 = p_4^2 + p_5^2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

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

$$l^2 = \frac{p_4^2 + p_5^2 + p_6^2}{p_1^2 + p_2^2 + p_3^2} \quad . \; . \; . \; . \; . \; . \quad (17)$$

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

$$l_1^2 = \frac{(p_4^2 + p_5^2 + p_6^2) + 2c\,(p_1 p_5 - p_2 p_4) + c^2\,(p_1^2 + p_2^2)}{p_1^2 + p_2^2 + p_3^2}. \quad (18)$$

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

$$\{(\alpha_1 + \alpha_2)\, c^2 - \beta\}\,(p_1^2 + p_2^2) - \beta\, p_3^2 + (\alpha_1 + \alpha_2)\,(p_4^2 + p_5^2 + p_6^2) + \\ + 2\,(\alpha_1 - \alpha_2)\, c\,(p_1 p_5 - p_2 p_4) = 0. \; . \; . \; . \; . \; . \quad (19)$$

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

$$p_1 p_5 - p_2 p_4 = 0. \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

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

$$(BD - C^2)(x^2 + y^2) + AB = 0; \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

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 $O_1O_2O_3O_4$, 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*

$$A(D-E)y_1^{\,2}y_2^{\,2} + 2\{AB-(C-D)(C-E)\}y_1y_2y_3y_4 + B(D-E)y_3^{\,2}y_4^{\,2} = 0 \quad . \quad (23)$$

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

$$x_3\,x_4\,\{\,2A\,x_1\,x_2 + (D - E)\,x_3\,x_4\,\} = 0 \quad . \quad . \quad . \quad . \quad (24)$$

and

$$x_1\,x_2\,\{\,2B\,x_3\,x_4 + (D - E)\,x_1\,x_2\,\} = 0 \quad . \quad . \quad . \quad . \quad (25)$$

For a point $(0, y_2, 0, y_4)$ of the edge O_2O_4 the cone of the complex is represented by

$$A\,y_2^{\,2}\,x_1^{\,2} + 2\,(C - E)\,y_2\,y_4\,x_1\,x_3 + B\,y_4^{\,2}\,x_3^{\,2} = 0\,; \quad . \quad . \quad (26)$$

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:

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

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 $a_{12}=\sqrt{a_1a_2}$, while

$$(av-\beta\sqrt{a})^3\left[(1-2x)\,v-3x\,(1-x)\beta\right]+$$
$$+\sqrt{a}\,(v-b)^2\left[3(av-\beta\sqrt{a})\,(av-2\beta\sqrt{a})+\frac{a(v-b)\,(v-3b)}{x(1-x)}\right]=0\quad (2)$$

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:

$$\tau=4\omega\left[x(1-x)+(\varphi+x)^2\,(1-\omega)^2\right]\quad .\;\;.\;\;.\;\;.\quad (1a)$$

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

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

$$\Delta = \theta\,(\theta - 1) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; (3^a)$$

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:

$$\theta < \frac{\pi}{2\sqrt{\pi}-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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^e 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 $b_1 \lessgtr b_2$ 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 $b_1 \lessgtr b_2$. So the phenomeña 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.

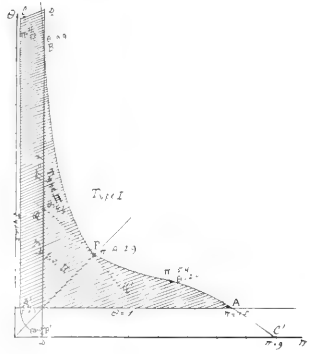
So after the above we arrive at the conclusion that in all cases in which a distinct longitudinal plait appears of the shape as in figs. 4^c or 6^c (so when the minimum D lies near R_2), the critical mixing point M of the three phases need not always lie on the longitudinal plait (see fig. 4^a), and 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.

nal plait).

J. J. VAN LAAR. „The shape of the spinodal and plaitpoint curves for binary mixtures of normal substances." Fourth communication: The longitudinal plait)



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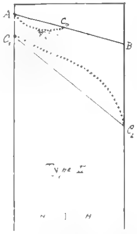
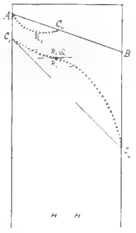
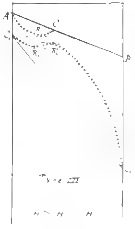
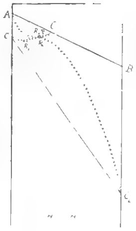
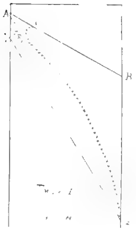


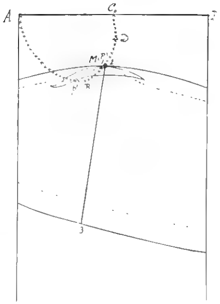
Fig 2a











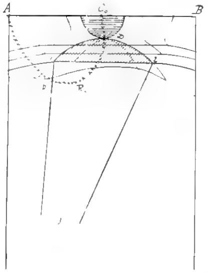


Fig 3a

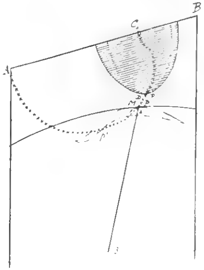


Fig 4a

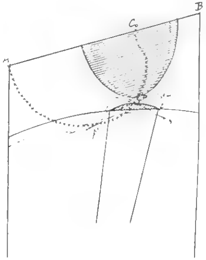
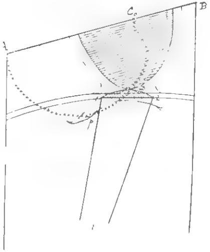


Fig 4b



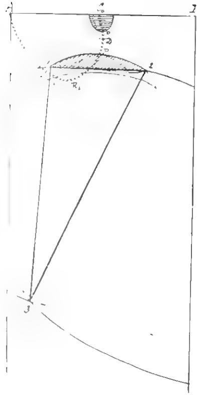


Fig 3b

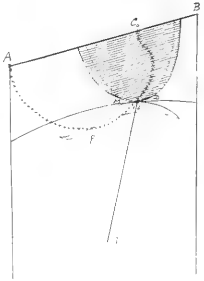


Fig 5a

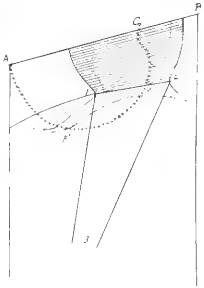
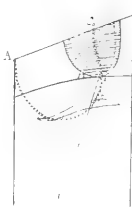
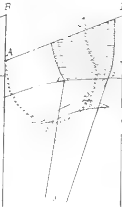
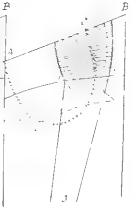


Fig 5b







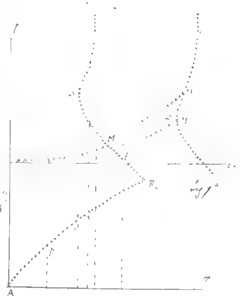


Fig 7

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).

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.

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.

---

[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 $\int_r^{\pi} \tfrac{1}{2}\,cot\,\tfrac{1}{2}\,r\,dr = -\,l\,sin\,\tfrac{1}{2}\,r \equiv F(r)$; so that for an arbitrary gradient distribution holds

$$ {}^{1}_{0}X = \overline{\nabla}^{1} \int \frac{\overline{\nabla}^{2}\, {}^{1}_{0}X}{2\pi} F(r)\, d\tau \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I) $$

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 ${}^{1}_{2}X$:

$$ {}^{1}_{2}X = \overline{\nabla}^{2} \int \frac{\overline{\nabla}^{1}\, {}^{1}_{2}X}{2\pi} F(r)\, d\tau . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II) $$

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 ²sphere 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:

$$ {}^{1}_{0}X = \overline{\nabla}^{1} \int \frac{\overline{\nabla}^{2}\; {}^{1}_{0}X}{4\pi} F_1 (r)\, d\tau. \quad . \quad . \quad , \quad . \quad . \quad . \qquad (I) $$

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:

$$ {}^{1}_{2}X=\overset{2}{\nabla}\int\frac{\overset{1}{\nabla}\,{}^{1}_{2}X}{4\pi}F_2(r)\,d\tau. \qquad \ldots\ldots \qquad (II)$$

And finally the arbitrary vector field X is the ∇ of the potential:

$$\int\frac{\overset{2}{\nabla}X}{4\pi}F_1(r)\,d\tau+\int\frac{\overset{1}{\nabla}X}{4\pi}F_2(r)\,d\tau.$$

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

$$\int_0^\pi \sin^h r\, dr = S_h:$$

$$\frac{(n-1)f(r)}{k_{n-1}} \sin^{n-1} r = -\sin^{n-2} r \cos r\, S_{n-2} - \sin^{n-4} r \cos r\, S_{n-4} \dots$$
$$\dots - \sin^2 r \cos r\, S_2 + \pi(1-\cos r)$$
(for n even)

$$= -\sin^{n-2} r \cos r\, S_{n-2} - \sin^{n-4} r \cos r\, S_{n-4} \dots$$
$$\dots - \sin r \cos r\, S_1 + 2r$$
(for n odd)

$$= \pi \cdot \frac{(n-1)(n-3)\dots}{(n-2)(n-4)\dots} \int_0^r \sin^{n-1} r\, dr = (n-1)\, S_{n-2} \int_0^r \sin^{n-1} r\, dr,$$
(for n even)

$$= 2 \cdot \frac{(n-1)(n-3)\dots}{(n-2)(n-4)\dots} \int_0^r \sin^{n-1} r\, dr = (n-1)\, S_{n-2} \int_0^r \sin^{n-1} r\, dr.$$
(for n odd)

If we write ξ_n for $2 \cdot \pi \cdot 2 \cdot \pi \cdot 2 \dots$, to n factors, we have

$$k_n = \frac{\xi_n}{(n-2)(n-4)\dots}, \text{ and } \frac{k_{n+1}}{k_n} = S_{n-1}.$$

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.

$$\frac{\cos\varphi}{\sin^{n-1}r}\cdot\frac{\frac{1}{2}S_{n-1}-\int\limits_{0}^{r}\sin^{n-1}r\,dr}{S_{n-1}}=\frac{\cos\varphi}{\sin^{n-1}r}\cdot\frac{\int\limits_{r}^{\frac{1}{2}\pi}\sin^{n-1}r\,dr}{S_{n-1}}.$$

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 (α) multiplied by $\frac{1}{2}$. We find on the half ^{n}sphere between P_1 and B:

$$\frac{1}{S_{n-1}}\cdot\frac{\cos\varphi}{\sin^{n-1}r}\int\limits_{r}^{\pi}\sin^{n-1}r\,dr.$$

On the half ^{n}sphere between P_2 and B:

$$-\frac{1}{S_{n-1}}\cdot\frac{\cos\varphi}{\sin^{n-1}r}\int\limits_{0}^{r}\sin^{n-1}r\,dr.$$

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:

$$\frac{1}{S_{n-1}}\cdot\frac{\cos\varphi}{\sin^{n-1}r}\cdot\int\limits_{r}^{\pi}\sin^{n-1}r\,dr\equiv\psi_n(r\,.)\cos\varphi.$$

III. For the potential of the fictitious "field of a single agens point" we find:

$$\int\limits_{r}^{\pi}\psi_n(r)\,dr\equiv F_1(r).$$

And for the arbitrary gradient distribution holds:

$${}_0^1X=\overline{\nabla^{1}}\int\frac{\overline{\nabla^{2}}\;{}_0^1X}{k_n}F_1(r)\,d\tau\quad.\;.\;.\;.\;\;.\;.\quad(I)$$

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:

$$\frac{d}{dr}\left\{\sin^{n-1}r\,.\,\frac{dF_1}{dr}\right\}=c\sin^{n-1}r\,.\quad.\quad.\quad.\quad.\quad.\qquad(H)$$

$$\sin^{n-1}r\,.\,\frac{dF_1}{dr}=c\int\sin^{n-1}r\,dr.$$

$$\frac{dF_1}{dr}=c\,.\,\frac{\int\sin^{n-1}r\,dr}{\sin^{n-1}r}.$$

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 ${}_1^2X$. 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:

$$ {}^{1}_{2}X = \overline{\nabla}^{2} \int \frac{\overline{\nabla}^{1}\, {}^{1}_{2}X}{k_n} F_2(r)\, d\tau \qquad \ldots\ldots \qquad (II)$$

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 $\overset{1}{_0}X$ we shall thus have to put the field of a divergency double point.

The Schering elementary potential $\int\limits_{r}^{\frac{1}{2}\pi} \frac{dr}{\sin^{n-1} r} \equiv v_n(r)$ 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 $\overset{1}{_0}X$ 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 (σ), deduced under F § II, multiplied by 2 :

$$\frac{\cos \varphi}{\sin^{n-1} r} \cdot \frac{\int_{r}^{1/2\pi} \sin^{n-1} r \, dr}{\frac{1}{2} S_{n-1}} \equiv \lambda_n (r) \cos \varphi .$$

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:

$$\int_{r}^{1/2\pi} \lambda_n (r) \, dr \equiv F_1 (r),$$

and for the arbitrary gradient distribution holds:

$${}^{1}_{0}X = \overline{\overset{1}{\nabla}} \int \frac{\overline{\overset{2}{\nabla}} \; {}^{1}_{0}X}{k_n} F_1 (r) \, d\tau \quad . \; . \; . \; . \; . \; . \; . \quad (I)$$

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:

$$\frac{dF_1}{dr} = - \frac{c}{\sin^{n-1} r} \int\limits_r^{1/2\pi} \sin^{n-1} r\, dr.$$

VI. In the usual way we deduce the ${}^2_1X$, which is planivector potential of the field E_2.

$$dh = c\varepsilon \sin^{n-2} r \sin^{n-2} \varphi.$$

Force in r-direction:

$$(n-1) \cos\varphi \left\{ \frac{2}{(n-1)S_{n-1}} + \frac{2 \cot r}{S_{n-1}} \cdot \frac{\int\limits_r^{1/2\pi} \sin^{n-1} r\, dr}{\sin^{n-1} r} \right\} \equiv (n-1) \cos\varphi \,.\, \mu_n(r).$$

$$\Sigma = \int\limits_0^{\varphi} (n-1) \cos\varphi \,.\, \mu_n(r) \,.\, c\varepsilon \sin^{n-2} r \sin^{n-2}\varphi \,.\, \sin r\, d\varphi =$$

$$= \mu_n(r) \,.\, c\varepsilon \sin^{n-1} r \sin^{n-1}\varphi.$$

$$H = \frac{\Sigma}{dh} = \mu_n(r) \sin r \sin\varphi \equiv \varkappa_n(r) \sin\varphi.$$

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:

$$\frac{U_1}{\cos\varphi} = \frac{1}{\cos^{2(n-2)}\tfrac{1}{2}r}\int_r^{\pi}\cos^{2(n-2)}\tfrac{1}{2}r\,\chi_n(r)\,dr +$$

$$+\frac{1}{\sin^{2(n-2)}\tfrac{1}{2}r}\int_{\pi-r}^{\pi}\cos^{2(n-2)}\tfrac{1}{2}r\,.\,\chi_n(r)\,dr.$$

2. a component U_2 through the radiusvector, according to the formula:

$$\frac{U_2}{\sin\varphi} = \frac{1}{\cos^{2(n-2)}\tfrac{1}{2}r}\int_r^{\pi}\cos^{2(n-2)}\tfrac{1}{2}r\,\chi_n(r)\,dr -$$

$$-\frac{1}{\sin^{2(n-2)}\tfrac{1}{2}r}\int_{\pi-r}^{\pi}\cos^{2(n-2)}\tfrac{1}{2}r\,.\,\chi_n(r)\,dr\,.$$

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:

$$\frac{\cos\varphi}{\sin^2 r}\,.\,\frac{\int_r^{\frac{1}{2}\pi}\sin^2 r\,dr}{\tfrac{1}{2}S_3} = \frac{2\cos\varphi}{\pi}\,.\,\left\{\frac{(\tfrac{1}{2}\pi - r)}{\sin^2 r} + \cot r\right\},$$

or if we put $\tfrac{1}{2}\pi - r = \gamma$:

$$\frac{2\cos\varphi}{\pi}\,.\,\left\{\frac{\gamma}{\sin^2 r} + \cot r\right\}.$$

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:

$$\sin\varphi = \pm\sin r, \quad \text{or} \quad \varphi = \begin{cases} r \\ \pi - r \end{cases}.$$

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	66
2	172	14	60
4	204	16	43
6	140	18	50
8	60	20	46
10	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	
$25\,\gamma$ 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%) 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.

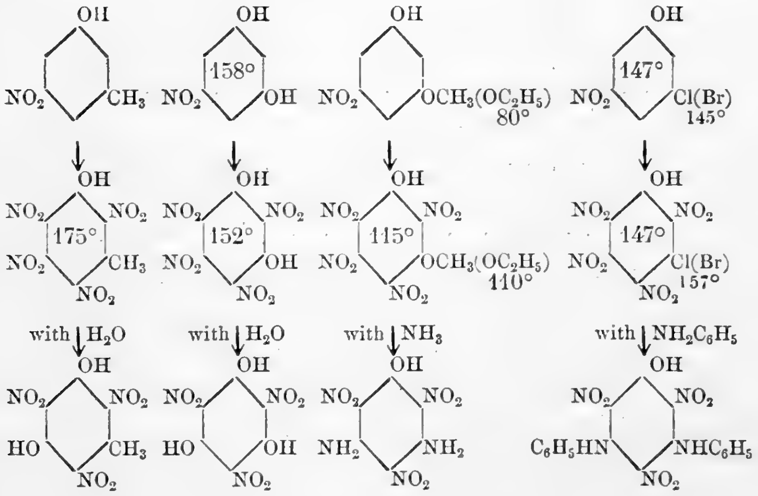
[2]) NEVILE en WINTHER Ber. **15**. 2986.

[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 $C_6H_3A_2B$ 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°/₀ 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	1.2893	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
Groningen } Sept. 1906, Laboratory of the University.

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.

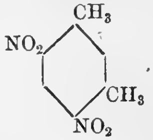
The investigation of the nitration of phthalic and isophthalic acid was taken up by us in order to determine the relative amount of the isomers simultaneously formed, as in the case of the mononitrophthalic acids only a rough approximation (by Miller) was known, whilst in the case of the mononitroisophthalic acids it had yet to be ascertained which isomers are formed there from.

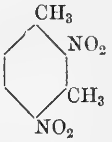
We commenced by preparing the five mononitro-acids derived from phtalic acid and isophthalic acid in a perfectly pure condition. In the case of the α- and β-nitrophthalic acids no difficulties were encountered, as the directions of Miller, save a few unimportant modifications, could be entirely followed. The acids were therefore obtained by nitration of phthalic acid and separation of the isomers.

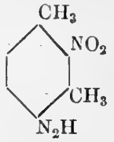
The *symmetric nitro-isophthalic acid* was prepared by nitration of isophthalic acid. It crystallises with 1 mol. of H_2O and melts at 255—256° whilst it is stated in the literature that it crystallises with $1^1/_2$ mol. of H_2O and melts at 248°. At first we hoped that the other two nitroisophthalic 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 %. 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

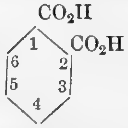
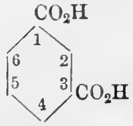
Quantitative nitration of phthalic acid. This was done with absolute nitric acid. It appeared that it proceeded very slowly even at 30°, and therefore the phthalic acid was left in contact with six times the quantity of nitric acid for three weeks. After dilution with water the acid was expelled by heating 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 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 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 of symmetric and 3.1 °/₀ of asymmetric nitroisophtalic acid.

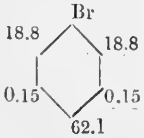
If we compare the above results with that of the nitration of benzoic acid where (at 30°) is formed 22.3 °/₀ ortho-, 76,5 °/₀ meta- and 1.2°/₀ paranitrobenzoic acid the following is noticed.

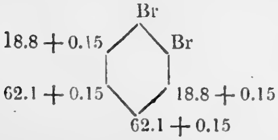
As in phthalic acid  the positions 3 and 6 are meta in regard to the one carboxyl and ortho in regard to the other and the positions 4 and 5 are also meta in regard to the one carboxyl but para in regard to the other it might be expected from my theories that the *α*-acid (the vicinal) is the main product 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	Zone	Deviation	n.	Curve
0°0	+0.56	5	+0.05	—9°0	+0.14	5	+0.26
—1 7	+0.35	4	+ 06	—10.2	+0.35	4	+ 32
—3.3	—0.17	6	+ 09	—13.2	+0.33	6	+ 57
—5.0	+0.50	5	+ 12	—15.0	+1.17	6	+ 79
—6.6	+0.22	4	+ 17	—18.2	+0.93	6	+1.32
—8.0	—0.05	5	+ 22				

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

$$\begin{array}{rrlrlrl} b' = +1 & 69200 & R + & 68100 & G + & 175800 & B \\ 0 & 1000 & R + & 1000 & G + & 1000 & B \\ -1 & 17{,}7 & R + & 15{,}7 & G + & 6{,}3 & B \end{array}$$

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.

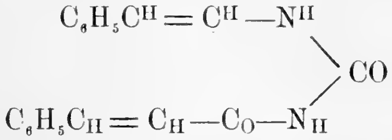
Chemistry. — *"Action of Potassium hypochlorite on Cinnamide".* By Dr. R. A. WEERMAN (Communicated by Prof. HOOGEWERFF).

(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 $C_6H_5CH = CH-NH-COOC_2H_5$. 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 5,78
pCt. C pCt. H 9,70 pCt. N
73,66 5,85
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 $e.e$, 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 $3^\circ 4'$, whereas the longitude of the ascending node, which therefore is also that of the fixed planes, is at present about $315\frac{1}{2}^\circ$.

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 $1^h24^m·5$; 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, $11^h2^m·3$ 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 $12^{h}9^{m}21^{s}$. 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	$8^{h}10^{m}$	$11^{h}54^{m}$	$3^{h}44^{m}$
„ 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^h59^m	9^h18^m	4^h19^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^h28^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 $12^h7^m15^s$ 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^h16^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^h19^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′′·786 and the sum of the diameters 2′′·374. 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′ = 38^{m}48^s East of Greenwich for the longitude of Hannover, this is = 6^h 16^m 12^s 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 10^h 47^m apparent time. On October 30, 1822, LUTHMER, of Hannover, witnessed an occultation of the fourth satellite by the third at 6^h 55^m 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^{h}55^m (Greenwich mean time). They are now only *just* free from contact. III  I, like an elongated star with little more than a black line between the components.

12^{h}00^m to 12^{h}04^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^{h}02^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 III ○○ II.

$13^{h}52^{m}$. 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 II ○○ III.

$14^{h}04^{m}$. 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).

$$\text{Ascending Node } 336^\circ 48' 23'' = \Omega,$$

$$\text{Inclination } \quad 2 \;\; 7\,17 = \mathrm{I},$$

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

$$\begin{array}{llll} \log R_{♃} = 0{\cdot}728527 & & \log R_{♁} = 0{\cdot}007179 \\ L_{♃} = \quad 141^\circ 23'\ 9''{\cdot}0 & & L_{♁} = 286^\circ 40'\ 3''{\cdot}5 \\ \beta \;\; = + \quad 0\ 52\ 26\ {\cdot}73 & & \Omega \;\; = 336\ 48\ 52\ {\cdot}0 \end{array}$$

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 $18^{u}{\cdot}5$ 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	+ $0,00^5$
»	1903 Jan. 14	II_n	III_n	0,11	0,344	—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	$10^s 26^\circ{\cdot}77$	$8^s, 22^\circ{\cdot}25$	$-15^r{\cdot}21$	$+0^r{\cdot}18$
IV	9 6·74	7 2·22	— 14·40	— 0·74
		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 $0{\cdot}92 = 16''{\cdot}9$. 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 $10^s 14^\circ{\cdot}37$, 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,	$10^{h}46^{m}{\cdot}9$	M.T.	Grw.	$0^{m}{\cdot}7$	earlier
inferior conjunction (mean of ingress and egress)	16 July	$5^{h}40^{m}{\cdot}0$	,,	,,	$0^{m}{\cdot}3$	,,
superior conjunction	17 July	$23^{h}54^{m}{\cdot}4$	,,	,,	$0^{m}{\cdot}7$	,,

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, $14^{h}4^{m}{\cdot}2$ M.T. Grw. = January 2, $2^{h}13^{m}{\cdot}55$ civil time of Paris; the error amounts to $0^{\circ}{\cdot}07$ or $0^{r}{\cdot}01$ linear measure only, an arc traversed by the satellite in $0^{m}{\cdot}5$.

(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 $18''{\cdot}37$. 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		0,708		0,560		0,420		6^{s}	0^{c}	6^{s}	0^{m}
					4		3		2		2				
	5	11	25	0,891		0,705		0,558		0,418			5	5	25
					10		8		7		4				
	10	11	20	0,881		0,697		0,551		0,414			10	5	20
					17		14		10		8				
	15	11	15	0,864		0,683		0,541		0,406			15	5	15
					23		18		15		11				
	20	11	10	0,841		0,665		0,526		0,395			20	5	10
					30		23		18		14				
	25	11	5	0,811		0,642		0,508		0,381			25	5	5
					36		29		23		17				
1	0	**11**	0	0,775		0,613		0,485		0,364		**7**	0	**5**	0
					42		33		26		20				
	5	10	25	0,733		0,580		0,459		0,344			5	4	25
					48		37		30		22				
	10	10	20	0,685		0,543		0,429		0,322			10	4	20
					53		42		33		25				
	15	10	15	0,632		0,501		0,396		0,297			15	4	15
					57		46		36		27				
	20	10	10	0,575		0,455		0,360		0,270			20	4	10
					62		49		39		29				
	25	10	5	0,513		0,406		0,321		0,241			25	4	5
					66		52		41		31				
2	0	**10**	0	0,447		0,354		0,280		0,210		**8**	0	**4**	0
					69		55		43		32				
	5	9	25	0,378		0,299		0,237		0,178			5	3	25
					72		57		45		34				
	10	9	20	0,306		0,242		0,192		0,144			10	3	20
					75		59		47		35				
	15	9	15	0,231		0,183		0,145		0,109			15	3	15
					76		60		48		36				
	20	9	10	0,155		0,123		0,097		0,073			20	3	10
					77		61		48		36				
	25	9	5	0,078		0,062		0,049		0,037			25	3	5
					78		62		49		37				
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 $\frac{x'-x}{u'-u}$ 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:

$$\cos^2 \theta = \frac{r}{r'} \cos^2 \theta' = \frac{r}{r'} - \frac{r}{r'} \sin^2 O' .$$

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″·37 in accordance with DAMOISEAU.

	Diameter		Radius
I	$1''{\cdot}07 =$	$0^{r}{\cdot}058$	$0^{r}{\cdot}029$
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* N°. 3764, (21 Jan. 1902).

Therefore;

	Sum of the diameters	Sum of the radii
I + II . .	$0^{r}{\cdot}110$	$0^{r}{\cdot}055$
I + III . .	0·143	0·0715
I + IV . .	0·134	0·067
II + III . .	0·137	0·0685
II + IV . .	0·128	0·064
III + IV . .	0·161	0·0805

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, 2me 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
	$1^{h}{\cdot}324$,	$1^{h}{\cdot}245$,	$1^{h}{\cdot}103$,	$2^{h}{\cdot}263$,	$1^{h}{\cdot}774$,	$3^{h}{\cdot}725$;
between the central occultation and the second contact:						
	$1^{h}{\cdot}204$,	$1^{h}{\cdot}161$,	$1^{h}{\cdot}059$,	$2^{h}{\cdot}190$,	$1^{h}{\cdot}767$,	$3^{h}{\cdot}725$,
therefore in all						
	$2^{h}{\cdot}528$,	$2^{h}{\cdot}406$,	$2^{h}{\cdot}162$,	$4^{h}{\cdot}453$,	$3^{h}{\cdot}541$,	$7^{h}{\cdot}450$,
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 $=496''{\cdot}0$, and took $18''{\cdot}37$ for Jupiter's semidiameter, so that, by division $r_{IV}=27{\cdot}00102834$. 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 $496''0 : 18''{\cdot}37$ is not 27·00102834 but 27·000544366. 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^h34^m,	3^h24^m,	$3^h\,3^m$,	6^h18^m,	$5^h\,0^m$,	10^h26^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 Delambre, 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:

II $+ 0^s\cdot005\,127\,374$,
III $+ 0\cdot029\,084\,25$,
IV $- 0\cdot092\,654\,834$,

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, $20''\cdot4451$ for the aberration and $8''\cdot57116$ 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, $u_{\rm I}$, $u_{\rm II}$, $u_{\rm III}$ and $u_{\rm IV}$ 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 $\pi_{\rm III}$ and $\pi_{\rm IV}$ the perijovia of III and IV; by Π the longitude of the ascending node of Jupiter's equator on its orbit; finally by $\varLambda_{\rm II}$, $\varLambda_{\rm III}$ and $\varLambda_{\rm IV}$ 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 $u_{\mathrm{I}}—u_{\mathrm{II}}$.

N°. 5, (amplitude 3°·07) gives the jovicentric latitude of I, necessary to find the second term of the geocentric latitude. The argument is $u_{\mathrm{I}}—\Delta_{\mathrm{I}}$.

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 $u_{\mathrm{II}}—u_{\mathrm{III}}$.

N°. 5, 6 and 7 serve for the latitude.

N°. 5, (amplitude 3°·05), has the argument $u_{\mathrm{II}}—\pi_{\mathrm{IV}}$;
N°. 6, („ 0 ·47), „ „ „ $u_{\mathrm{II}}—\Delta_{\mathrm{II}}$;
N°. 7. („ 0 ·03), „ „ „ $u_{\mathrm{II}}—\Delta_{\mathrm{III}}$.

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 $u_{\text{III}}—\pi_{\text{III}}$.

N°. 6, (amplitude 0°·04), has the argument $u_{\text{III}}—\pi_{\text{IV}}$, 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 $u_{\text{III}}—\pi$, $u_{\text{III}}—\varLambda_{\text{III}}$ and $u_{\text{III}}—\varLambda_{\text{IV}}$.

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 $u_{\text{IV}} — \pi_{\text{IV}}$.

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 $u_{\text{IV}}— \varLambda_{\text{IV}}$.

N° 7, (amplitude 0°·04), is a minute perturbation, caused by III; its argument is $u_{\text{IV}}—\varLambda_{\text{III}}$.

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.

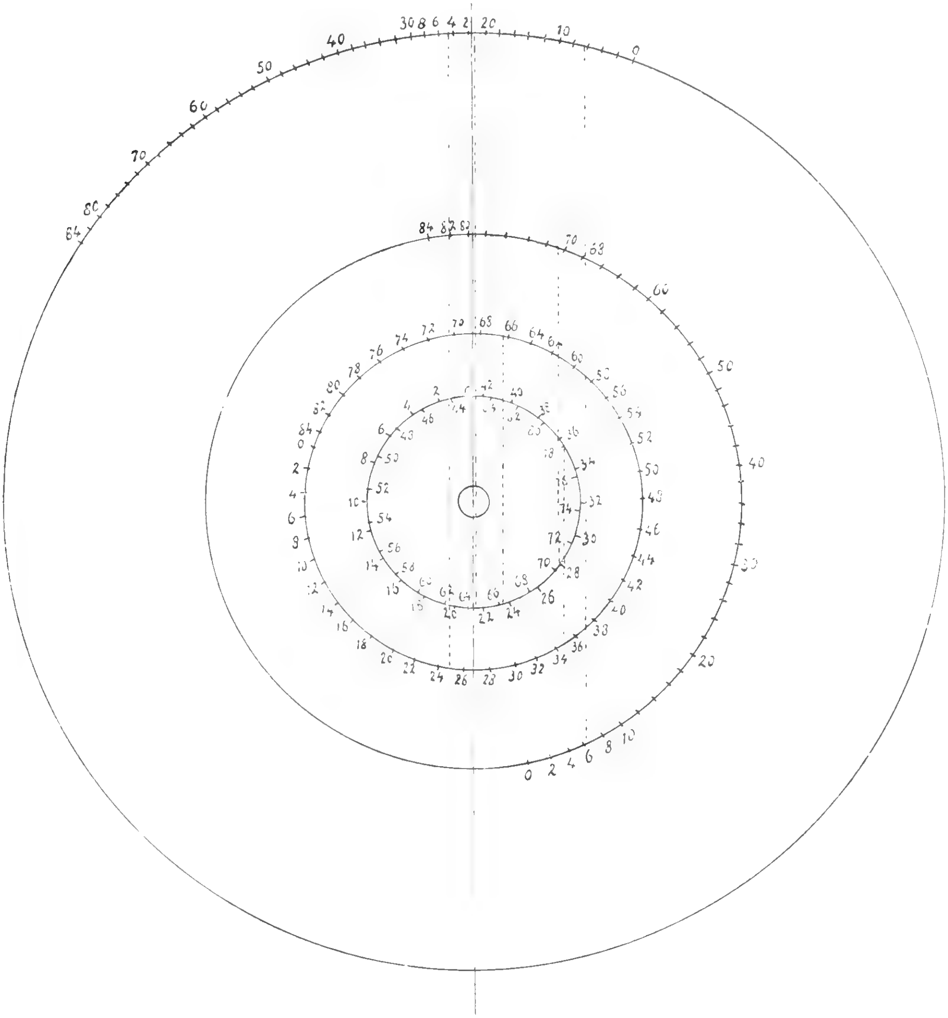
At the conjunction the elongations, counted along the orbit of Jupiter, are equal; they are to be found in the next column. If the elongation is +, the satellite, as seen by a northern observer, using a terrestrial telescope, will be to the left of the planet. Therefore if he uses an inverting telescope, 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 11^h 2^m.3 M. T. Greenwich = 11^h 11^m.65 M. T. Paris = 23^h 11^m.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 $5^{h}55^{m}$	31 May $17^{h}46^{m}$	I_n	II_n	$+2^{r}18$	$-0^{r}16$	$-0^{r}12^{5}$	$+0,03^{5}$	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	
14	9 » 5 6	8 » 16 57	IV_f	II_f	−9, 19	+0, 59	+0, 43	−0, 16	13	and II eclipsed ? 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: Occulted satellite	Occulting satellite	$x = x'$	Occulted satellite y	Occulting satellite y'	$y' - y$	Duration of central occultation	Visible at
24	17 June 9^{h}39^m	16 June 21^{h}30^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. Ko
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. K
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. Hamilto
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 Asi
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

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occultation of III_f by II_f,
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II			
4	5	6	7
3s 9°0	10s 2°8	0s 18°6	11s 28°
2,9	5 18,7	5 0,2	9 10,
2,1	0 16,5	9 8,9	1 2,
1,3	11 18,8	11 24,8	11 20,
15,3	3 26,8	2 22,5	10 1,
24,8	11 9,2	11 9,7	11 0,
6,2	2 11,8	2 11,8	2 11,
0,9	1,9	1,9	1,
17,2	5 19,7	4 15,9	11 24,

5 + 0°53
6 − 0,32
7 0,00
− IX + 0,05
+ 0,26

$x' = -2^r 00$ $y' = +0^r,04$

	III					
	Mean Longitᵉ	5	6	7	8	9
°0	0s 17°45	0s 7°7	2s 24°3	2s 2°0	8s 6°3	6s 26°4
,4	1 20,32	1 20,3	1 20,3	1 20,3	1 20,3	1 20,3
,7	0 25,16	25,2	25,2	25,2	25,2	25,2
,6	0,32	0,3	0,3	0.3	0,3	0,3
,7	3 3,25	2 23,5	5 10,1	4 17,8	10 22,1	9 12,2
1	− 0,13					
2	− 0,04					
4	+ 0,04					
5	+ 0,15					
6	+ 0,01					
	3 3,28					
-G	4 9,25					
de	10 24,03					

7 + 2°01
8 + 0,11
9 + 0,03
− IX − 0,11
+ 2,04

$x' = -9^r,01$ $y' = +0^r,055$

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Civil time at Paris,
Mean ,, ,, ,, ,
5 ,, ,, ,, Greenwich.

	Civil time at Paris	Mean time at Greenwich	n = near, f = far: Occulted satellite	n = near, f = far: Occulting satellite	$x = x'$	Occulted satellite y	Occulting satellite y'	$y' - y$	Duration of central occultation	visible at
[illegible]	5 July 8ʰ 2ᵐ 5	4 July 19ʰ 53ᵐ 2	II_f	III_n	+2°80	−0°17	−0°29	−0°12	7ᵐ	Sydney
[illegible]	5 » 17 58	5 » 5 49	I_n	III_n	−2,75	+0,15	+0,15	0,00	6	Cape
[illegible]	5 » 17 34	5 » 5 25	I_f	IV_n	−3,04	+0,14	+0,09	−0,05	7	Cape, Moscow
	5 » 21 54	5 » 9 45	III_n	IV_n	−4,85	+0,28	+0,16⁵	−0,11⁵	79	Washington
	7 » 7 37	6 » 19 28	I_f	II_n	−5,60	+0,30	+0,31	+0,01	8	Sydney
[illegible]	8 » 14 55	8 » 2 46	II_f	I_n	−4,82	+0,04	+0,11	+0,07	4	Madras
	8 » 18 44 8	8 » 6 35 5	III_f	I_n	−4,64	+0,26⁵	+0,25	−0,01⁵	8	Moscow
	9 » 20 13	9 » 8 4	III_f	II_n	+8,89	−0,50	−0,40	+0,10	11,5	Berlin, etc.
[illegible]	10 » 20 52	10 » 8 47	I_f	II_n	−5,53	+0,31	+0,30	−0,01	7	Utrecht
[illegible]	12 » 4 6 5	11 » 15 57	II_f	I_n	−1,97⁵	+0,04	+0,13	+0,09	4	Mt Hamilton
[illegible]	12 » 20 57	12 » 8 47	I_f	III_n	−1,95	+0,11	+0,13⁵	+0,02⁵	6	Utrecht
[illegible]	13 » 5 25	12 » 17 15	IV_f	III_n	−6,50	+0,35	+0,40	+0,05	10,5	Pacific
[illegible]	13 » [illegible]	13 » 8 30	IV_f	I_n	−0,27	+0,05	+0,05	0,00	6	☌♃
	14 » 0 12 5	13 » 12 3	IV_f	II_n	+1,20⁵	−0,01⁵	+0,01⁵	+0,03	4	IV eclipsed
[illegible]	14 » 10 8 5	13 » 21 59	I_f	II_n	−5,42	+0,29	+0,32	+0,03	7	Perth
[illegible]	15 » 17 17	15 » 5 7	II_f	I_n	−2,12	+0,04	+0,14	+0,10	4	Cape
	15 » 22 1	15 » 9 51	III_f	I_n	−5,27	+0,28	+0,30	+0,02	9	Berlin, etc.
[illegible]	17 » 23 11	17 » 11 2	I_f	II_n	−5,34	+0,29	+0,31⁵	+0,02⁵	6,5	Charkow
[illegible]	19 » [illegible]	18 » 18 21	II_f	I_n	−2,22	+0,06	+0,14	+0,08	4	Pacific
71	19 » 14 5	19 » 2 56	II_f	III_n	+3,77	−0,22	−0,15	+0,07	7	Central Asia
72	19 » 23 [illegible]	19 » 11 47	I_f	III_n	−1,13⁵	+0,05	+0,12	+0,07	6	Astrachan

Occultation of II_f by I_n, on July 15, 1908 at 17^h27^m civil time Paris.

	I: M. Longitᵉ	I: 1	I: 2	I: 3	I: 4	I: 5		II: M. Longitᵉ	II: 4	II: 5	II: 6	II: 7
1858	9ˢ 5°74	7ˢ27°5	1ˢ 0°8	0ˢ 1°4	0ˢ18°1	10ˢ20°9		8ˢ17°66	3ˢ 9°0	10ˢ 2°8	0ˢ18°6	11ˢ28°5
1880	6 9,80	0 13,2	11 8,4	0 0,8	2 5,9	7 24,6		4 3,87	10 2,9	5 18,7	5 0,2	9 10,6
—1830	0 6,20	11 22,6	3 8,9	11 28,6	10 4,2	10 20,7		2 2,03	2 2,1	0 16,5	0 8,9	1 2,3
July	3 21,51	5 13,4	0 15,0	5 28,4	4 2,7	3 21 5		11 18,83	8 1,3	11 18,8	11 24,8	11 20,1
July 1908	7 13,25	10 22,7	4 3 1	5 29,2	5 0,9	8 27,7		2 12,39	11 15,3	3 26,8	2 22,5	10 1,5
15ᵈ	10 28,85	0 12,6	0 1,2	0 13,8	11 19,6	10 28,8		11 9,25	11 24,8	11 9,2	11 9,7	11 0,3
17ʰ	4 24,14	0,6		0,7	2 12,3	4 24,1		1 11,81	1 6,2	2 11,8	2 11,8	2 11,8
27ᵐ	3,82				1,9	3,8		1,90	0,9	1,0	1 0	1,9
	11 10,06	11 5,9	4 4,3	6 13,7	7 4,7	0 24,4		4 5,35	0 17,2	5 19,7	4 15,9	11 24,5
1	— 1,06						1	— 0,52				
2	— 0,46						2	— 0,08		5 + 0°54		
4	+ 0,43						4	+ 0,60		6 — 0,32		
	11 9,27			5 + 1°27				4 5,35		7 0,00		
S−G	4 17,37			— IX + 0,05			S−G	4 17,37		IX + 0,06		
Amplitude	6 21,90			+ 1,32			Amplitude	11 17,98		+ 0,26		
			$x = -2°{,}26$	$y = +0°{,}11$					$x' = -2°{,}00$		$y' = +0°{,}04$	

$$2°{,}26 - 0{,}830 \angle t = -2°{,}00 + 0{,}691 \angle t$$
$$1{,}521 \angle t = +0°{,}26$$
$$\angle t = -0^h{,}172 = -10^m{,}3$$
$$x = -2°{,}12$$

Result 15 July at $17^h16^m{\cdot}7$ Civil time at Paris.
= 5 16 ·7 Mean ,, ,, ,, ,
= 5 7 35 ,, ,, ,, Greenwich

Due account has been taken of the fact that the number of bissextile days between 1858 and 1908 differs from that between 1830 and 1880. For between (1 January) 1830 and (1 January) 1880 we have 12 bissextile days, against 11 between (1 January) 1858 and (1 January) 1908. The difference has been allowed for by treating 1908 as if it were a *common* year in the line of *July*, which contains the motions for the months January to June (inclusive). For on the pages 201, 209, 217 and 225, which contain the motion of the four satellites for the several months, we find two tables, one headed "Années communes", the other headed "Années bissextiles".

The fifth line of this computation (July 1908) may be used for all the conjunctions of this month.

As a second example we will take the occultation of III_f by II_f, for which our drawing gave June 2, 1908, 12^h9^m3 civil time at Paris as a first approximation.

	II: Mean Longitᵉ	II: 1	II: 2	II: 3	II: 4	II: 5	II: 6	II: 7		III: Mean Longitᵉ	III: 5	III: 6	III: 7	III: 8	III: 9
1908 June	9ˢ 1°15	9ˢ25°6	4 0 6	4ˢ2°6	8ˢ1°6	10ˢ15°6	9ˢ10°3	4ˢ29°0		0ˢ17°[illegible]	0ˢ 7°7	2ˢ21°3	2ˢ 2°0	8ˢ 6°3	6ˢ26°4
2ᵈ	3 11,37	0 0,9	0 0,1	0 1,0	1 21,1	3 11,4	3 11,4	3 11,4		1 20,[illegible]	1 20,3	1 20,3	1 20,3	1 20,3	1 20,3
12ʰ	1 20,69	0,5		0,5	0 25,5	1 20,7	1 20 7	1 20 7		0 25,16	25,2	25,2	25 2	25,2	25,2
9ᵐ,3	0,64				0,3	0,6	0,6	0,6		0,32	0,3	0 3	0 3	0,3	0,3
	2 3,84	9 27,0	4 0,7	5 4,1	11 0,5	3 18,3	2 13,0	9 22,7		3 3,2[illegible]	2 23,5	5 1[illegible]	4 17,8	10 22 1	9 12,2
1	— 0,28								1	— 0,13					
2	— 0,07								2	— 0,0[illegible]					
4	— 0,91				5 + [illegible]				4	+ 0,[illegible]					
					6 [illegible]				5	+ 0,1[illegible]					
	2 2,58				7 + 0,01				6	+ 0,01			7 + 2,[illegible]		
S−G	4 9,25				— IX — 0,11								8 + 0,11		
Amplitude	9 23,33				+ 2,30					3 3,25			9 + 0,00		
									S−G	4 9,25			— IX — 0,11		
			$x = -8°{,}84$		$y = +1°{,}40$				Amplitude	[illegible]			+ 2,0[illegible]		

$$8{,}84 + 0{,}280 \angle t = -9{,}01 + 0{,}453 \angle t$$
$$+0{,}17 = +0{,}173 \angle t$$
$$\angle t = +0{,}983$$

First approximation 12 [illegible]

Second approximation 13 8 ,3

If we repeat the computation with this value we still do not get equality of the elongations. The amplitude of II becomes 9 2[illegible] that for III 10 26°[illegible] Furthermore we find

$$-8°{,}535 + 0°{,}327 \angle t = 8°{,}56 + 0°{,}4645 \angle t$$
$$+0°{,}025 = +0{,}1365 \angle t$$
$$\angle t = +0^h{,}182 = +10^m{,}9$$

13 8

Third approximation 13^h 19^m2 Civil time at Paris,
= 1 19 ·2 Mean
= 1 9 85 ,, Greenwich

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, N⁰. 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 2^{nd} 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 of 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 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.

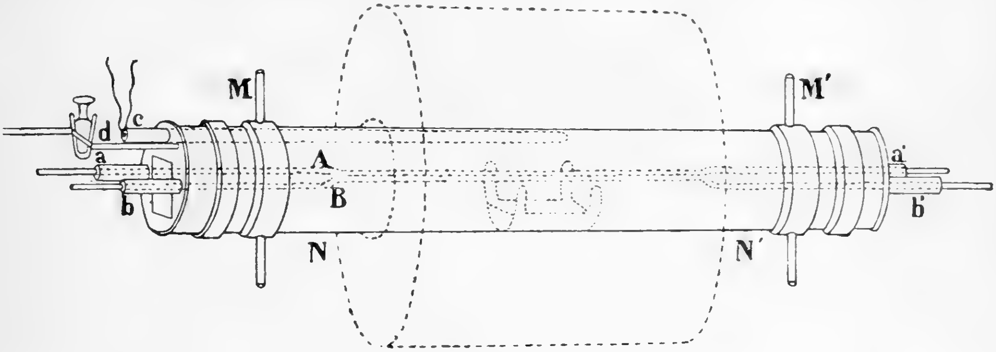

Fig. 1.

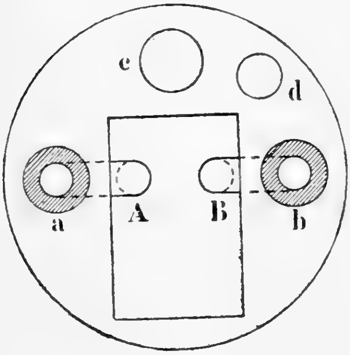

Fig. 2.

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.

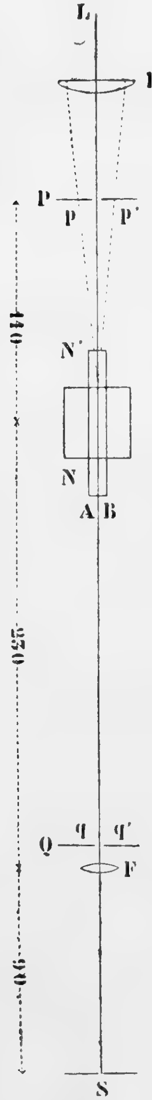

Fig. 3.

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.

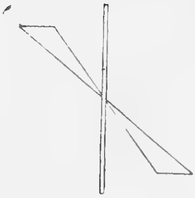

Fig. 4.

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.

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 $\varkappa$.

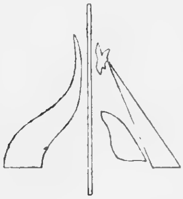

Fig. 5.

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 δ=1 cm., d=110 cms., l=27 cms. this gives: ϱ=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:

$$\varrho = \frac{n}{n'} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

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:

$$\varrho = \frac{R\Delta + 1}{R\dfrac{d\Delta}{ds}};$$

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

$$\varrho = \frac{1}{R\frac{d\Delta}{ds}} \quad \ldots \ldots \ldots \ldots \quad (2)$$

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 DEWAR¹) 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.

W. H. Julius. ARBITRARY DISTRIBUTION OF THE LIGHT IN DISPERSION BANDS. PL. I.


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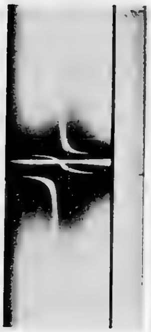
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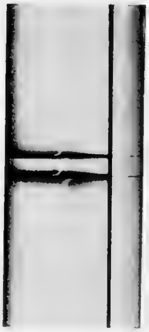
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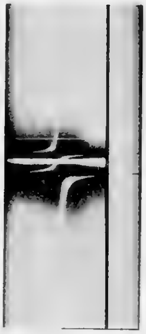
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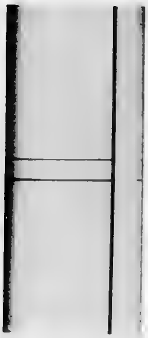
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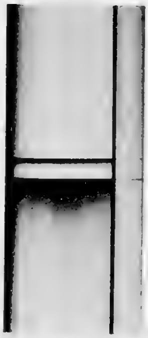
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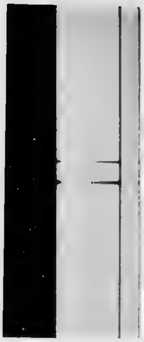
Heliotype, Van Leer, Amsterdam.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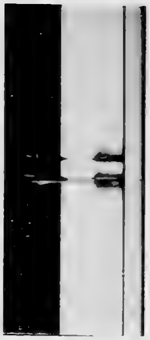
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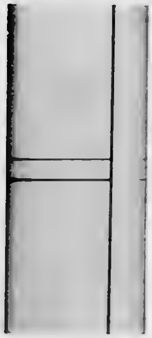
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Heliotype, Van Leer, Amsterdam.

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*: $C_{27}H_{45}O_2C.CH:CHC_6H_5$.

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 ⇆ 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 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. N^{os} 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. N^{os}. 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

$$\left.\begin{array}{l} \dfrac{u'_2}{1+at'_2}+\dfrac{u''_2}{1+at''_2}+\dfrac{u_3}{1+at_3}+\dfrac{u_4}{1+at_4}=\Sigma\dfrac{u}{1+at} \\[2ex] H_0\left[v_0+\beta_2+u_1+u'_2+u''_2+u'''_2+\dfrac{u}{1+15a}\right]=A, \end{array}\right\} \quad . \quad (2)$$

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	974 975	20.17 17.86	9.1 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	974 975	20.17 17.86	9.1 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,

$u_1 = 0.0105$ cm³	
$u_2' = 0.0126$ »	$t'_2 = -162°$
$u_2'' = 0.0140$ »	$t''_2 = 0°$
$u_3 = 0.6990$ »	$t_3 = 14°.5$
$u_4 = 0.2320$ »	$t_4 = 14°.9$
$u_2''' = 0.1141$ »	

$H_T = 81.53$ m.m.

$V_0 = 82.265$ cm³

$\beta_1 = -0.0041$ » , $\beta_2 = +0.0021$ cm³

$H_0 = 1091.88$ mm.

$u = 0.7991$ cm³

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 α, 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:

$3^u 20'$	— 252°.926
$3^u 58'$	— 252°.929

the two others with another resistance:

$2^u 35'$	— 252°.875
$3^u 7'$	— 252°.866 [2])

Determinations of one and the same temperature on different days

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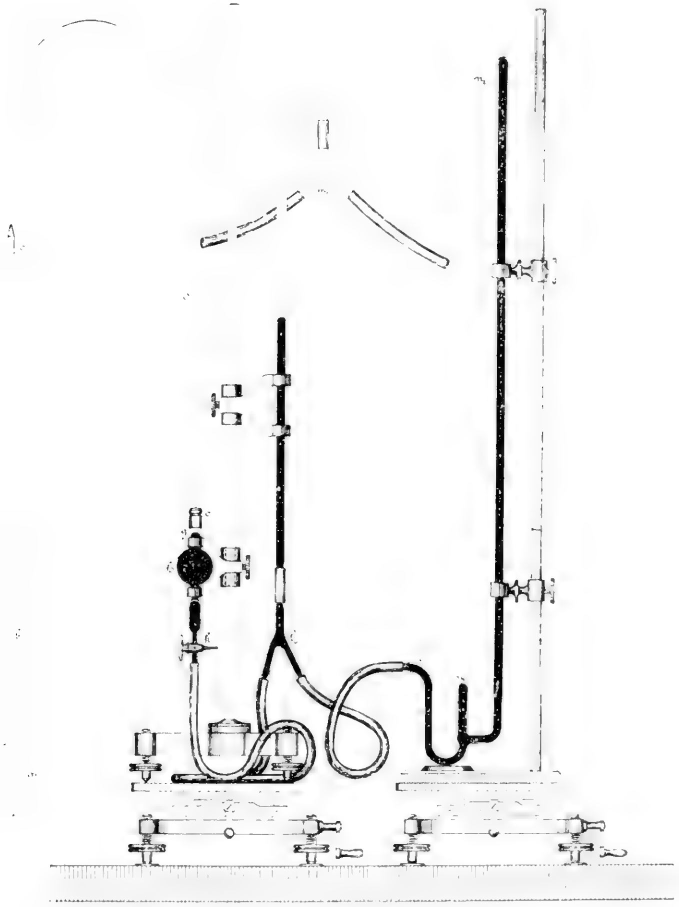
[1]) From the values of α found by Chappuis at different pressures and from Berthelot's calculations follows by extrapolation from Chappuis' value for $p = 1000$ m M. $\alpha = 0.00366262$ for $p = 1090$ m.M., from Travers' value of α for 700 m.M. with the same data $\alpha = 0.00366288$ for $p = 1090$ 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.

H. KAMERLINGH ONNES and C. BRAAK. "On the measurement of very low temperatures. XIII. Determinations with the hydrogen thermometer."

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

June 30th, '06	$5^u 50'$	— 217°.327	mean — 217°.345.
	$6^u 5'$	— 217°.362	
	$6^u 25'$	— 217°.347	

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 $\frac{1}{50}^{\circ}$ 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

$$H_o = 1056.04 \text{ mm.}$$

was found, and the pressure on June 8th '04 was

$$H_o = 1055.43 \text{ mm.}$$

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 sub-epithelial 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 °/₀ of the weight of the anthers, with *Ornithogalum umbellatum* to 86 °/₀, with *Diervilla floribunda* to 87 °/₀, with *Aesculus Hippocastanum* to 88 °/₀, with *Pyrus japonica* to 80 °/₀, with different cultivated tulips 59—68 °/₀. 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 °/₀, with *Canna hybrida grandiflora* to 56 °/₀, with *Lathyrus latifolius* to 24 °/₀.

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 accumnlation 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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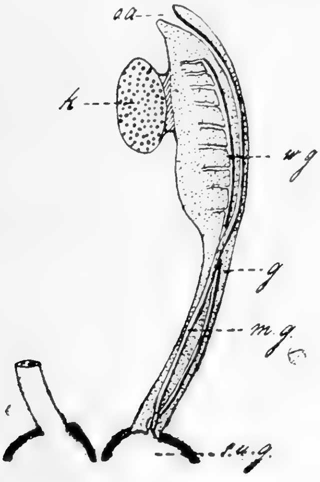
[1] Ch. Darwin. Origin of species. Sixth Edition. 1872. Chap. IV, p. 73 and The effects of Cross and Selffertilisation. Edition 1876. Chap. X, p. 402.

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.



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.

Fig. 1.

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].

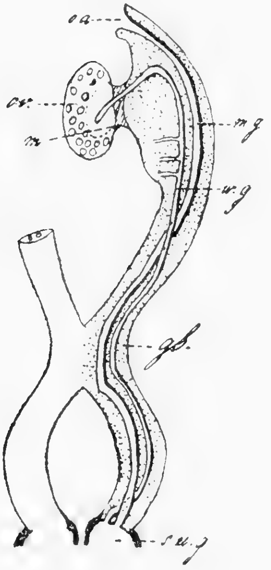


Fig. 2.

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.

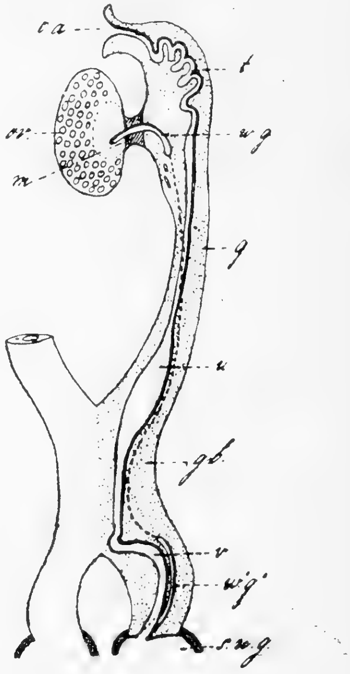


Fig. 3.

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.

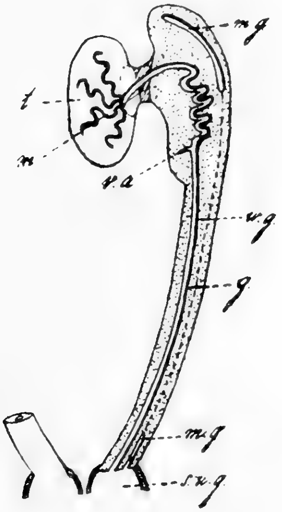

Fig. 4.

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.

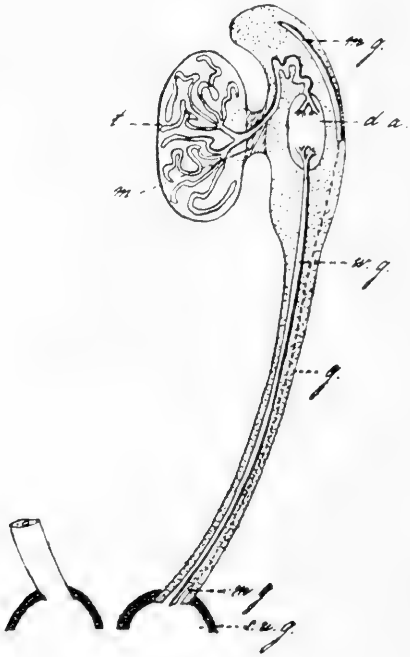

Fig. 5.

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-genital-organe 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

$$a'_4 = +4.32513 \qquad e'_4 = +0.023276$$
$$b'_4 = +0.409153 \qquad f'_4 = -0.0025269$$
$$c'_4 = +0.0015563$$

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. (CI), (CII), (CIII) representing the observations down to — 253°, whereas in (CIV) 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 $W—R_{CI}$, $W—R_{CII}$, $W—R_{CIII}$, $W—R_{CIV}$.

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 (CI), (CII), (CIII), and only those down to — 217° for (CIV), for

(CI)	± 3.0
(CII)	± 2.9
(CIII)	± 3.0
(CIV)	± 2.3

If — 182° is excluded, they become:

(CI)	± 2.7
(CII)	± 2.6
(CIV)	± 1.8

The mean errors of (CI), (CII), (CIII) must be compared with those of (BI) and (BIII), those of (CIV) with those of (BIV).

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 $\lambda-1$

$$\begin{aligned} I = {} & \sum_{p=0}^{\lambda-1} (\varrho_p\, N + \varrho_{p-1}\, M)\, x^p \\ & + \sum_{p=0}^{\lambda-1} [\{h_p + (p+1)\,\varrho_{p+1}\}\, n + \{h_{p-1} + p\varrho_p\}\, m]\, x^p \\ J = {} & \sum_{p=0}^{\lambda-1} (r_{p+1}\, G_p'' + s_{p+1}\, G_p' + t_{p+1}\, G_p) \\ & + x \sum_{p=0}^{\lambda-2} (r_{p+2}\, G_p'' + s_{p+2}\, G_p' + t_{p+2}\, G_p) \\ & + \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ & + x^{\lambda-2} \sum_{p=0}^{1} (r_{p+\lambda-1}\, G_p'' + s_{p+\lambda-1}\, G_p' + t_{p+\lambda-1}\, G_p) \\ & + x^{\lambda-1} \sum_{p=0} (r_{p+\lambda}\, G_p'' + s_{p+\lambda}\, G_p' + t_{p+\lambda}\, G_p). \end{aligned}$$

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

$$(x-\alpha)\,(x-\beta)\,\frac{d^2y}{dx^2} + [t_1\,(x-\alpha)\,(x-\beta) + 2x - \alpha - \beta]\,\frac{dy}{dx} + (t_0+t_1x)\,y = 0$$

where α, β, t_0 and t_1 are arbitrary constants.

When $\lambda = 3$ the most general equation may be written

$$\begin{aligned} (x-\alpha)\,(x-\beta)\,(\varrho_1x+\varrho_0)\,\frac{d^2y}{dx^2} + (t_2x^3+s_2x^2+s_1x+s_0)\,\frac{dy}{dx} + {} & \\ + (t_2x^2+t_1x+t_0)\,y = 0 & \end{aligned}$$

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

$$\sum_{\nu} \frac{xe^{x\nu}}{e^{xn}-1} = \sum_{d/n} \mu(d) \frac{x}{e^{xd}-1},$$

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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

$$\sum_{\nu}\left\{\frac{1}{n}+\sum_{k=1}^{k=\infty}x^k n^{k-1} f'_k\left(\frac{\boldsymbol{v}}{n}\right)\right\}=\sum_{d/n}\frac{\mu(d)}{d}\left\{1-\tfrac{1}{2}xd+\frac{B_1}{2\,!}x^2d^2-\frac{B_2}{4\,!}x^4d^4+\ldots\right\}.$$

By equating the corresponding terms on the two sides we get

$$\sum_{\nu} f'_{2m}\left(\frac{\boldsymbol{v}}{n}\right)=(-1)^{m-1}\frac{B_m}{2m\,!}\sum_{d/n}\mu(d)d'^{-2m+1}$$

as a first generalisation of the relation

$$\sum_{\nu}\boldsymbol{v}^0=\sum_{d/n}\mu(d)d'.$$

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,

$$\frac{\sum_{\nu} f'_{2m}\left(\frac{\boldsymbol{v}}{n}\right)}{\sum_{\nu'} f'_{2m}\left(\frac{\boldsymbol{v}'}{n'}\right)}=\left(\frac{n'}{n}\right)^{2m-1}.$$

In the same way an expression for the sum of the k^{th} powers of the integers $\boldsymbol{v}$ 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

$$\frac{1}{k\,!}\sum_{\nu}\boldsymbol{v}^k=\sum_{d/n}\mu(d)d^k f_k(d').$$

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

$$\sum_{\nu}\cos 2\pi x\boldsymbol{v}=\tfrac{1}{2}\sin 2\pi xn\sum_{d/n}\mu\,(d)\cot \pi xd,$$

$$\sum_{\nu}\sin 2\pi x\boldsymbol{v}=\quad\sin^2 \pi xn\sum_{d/n}\mu\,(d)\cot \pi xd.$$

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

$$2\sum \cos 2\pi\varrho_n = \mu(n),$$

and also

$$2\sum_{n \leq g} \cos 2\pi\varrho_n = \sum_{n \leq g} \mu(n).$$

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 $\sum\limits_{n \leq g} \cos 2\pi\varrho_n$ will annul each other, hence the equation

$$2\sum_{n \leq g} \cos 2\pi\varrho_n = \sum_{n \leq g} \mu(n)$$

is quite consistent with the supposition of VON STERNECK, that as g takes larger and larger values the absolute value of $\sum\limits_{n \leq g} \mu(n)$ 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,

$$\prod_{\nu} 2 \cos \frac{\pi \nu}{n} = \prod_{d/n} (-1)^{\frac{d'-1}{2}\mu(d)} = (-1)^{\frac{1}{2}\varphi(n)}.$$

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

$$\prod_{\nu} 2 \sin \frac{2\pi \nu}{n} = (-1)^{\frac{1}{2}\varphi(n)} \prod_{\varkappa} 2 \sin \frac{2\pi\varkappa}{n} = (-1)^{\frac{1}{2}\varphi(n)} \prod_{\varkappa} 2 \sin \frac{\pi\varkappa}{m},$$

and therefore

$$\prod_{\nu} 2 \cos \frac{\pi\nu}{n} = (-1)^{\frac{1}{2}\varphi(n)} \frac{\prod\limits_{\varkappa} 2 \sin \frac{\pi\varkappa}{m}}{\prod\limits_{\nu} 2 \sin \frac{\pi\nu}{n}} = (-1)^{\frac{1}{2}\varphi(n)} e^{\gamma\left(\frac{n}{2}\right) - \gamma(n)}$$

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

$$\prod_{\nu} 2 \sin \frac{2\pi\nu}{n} = (-1)^{\frac{1}{2}\varphi(u)} \prod_{\varkappa} \left(2 \sin \frac{2\pi\varkappa}{n}\right)^2 = (-1)^{\frac{1}{2}\varphi(n)} \prod_{\varkappa} \left(2 \sin \frac{\pi\varkappa}{m}\right)^2.$$

and therefore

$$\prod_{\nu} 2 \cos \frac{\pi\nu}{n} = (-1)^{\frac{1}{2}\varphi(n)} \frac{\prod\limits_{\varkappa} \left(2 \sin \frac{\pi\varkappa}{m}\right)}{\prod\limits_{\nu} 2 \sin \frac{\pi\nu}{n}} = (-1)^{\frac{1}{2}\varphi(n)} e^{2\gamma\left(\frac{n}{2}\right) - \gamma(n)}.$$

From the foregoing we may conclude as follows. If we put

$$\prod_{\nu} 2 \cos \frac{\pi\nu}{n} = (-1)^{\frac{1}{2}\varphi(n)} e^{\lambda(n)},$$

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 $13^h\, 52^m 1$ 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:

$$\alpha = 4^h\ 7^m\ 34^s84 \qquad \delta = +\ 42^\circ\ 30'\ 59''9$$

für die Aufnahmezeit: 1906 Aug. 28, $13^h\ 52^m1$ 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: $12^h\ 46^m0$ M.Z. Kgst.

$$\alpha_{1906.0} = 4^h\ 32^m\ 10^s02 \qquad \delta_{1906.0} = +\ 47^\circ\ 34'\ 54''6$$

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: $13^h\ 52^m1$ Kgst.:

$$\alpha_{1906.0} = 4^h\ 7^m\ 35^s00 \qquad \delta_{1906.0} = +\ 42^\circ\ 30'\ 58''3$$

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: $9^h\ 1^m0$ Kgst.

$$\alpha_{1906.0} = 4^h\ 34^m\ 48^s94 \qquad \delta_{1906.0} = +\ 49^\circ\ 54'\ 59''2$$

Sterne: A.G. Bonn 3759, 3768, 3777 ..... Der Komet war

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[1]) *Astron. Nachr.*, No. 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 Ω, 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 $\Delta \Omega = 0$ and also for $\Delta M = +50''$ $\Delta i = 0$ $\Delta \Omega = -10''$. Probably a somewhat larger value of $\Delta \Omega$ had been more convenient. The following table gives the variations of α and δ in the two cases.

TABLE VI.

N⁰.	$\Delta i = +10''$		$\Delta \Omega = -10''$	
	$\Delta \alpha$	$\Delta \delta$	$\Delta \alpha$	$\Delta \delta$
	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 Ω, 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
$\frac{\partial \delta}{\partial i}$	$+1.000$	$+1.195$	$+1.288$
$\frac{\partial \alpha}{\partial \Omega}$	-0.0040	-0.0067	-0.0080
$\frac{\partial \delta}{\partial \Omega}$	-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 $\frac{\Delta\Omega}{10}$ as unknown quantity.

Equations of condition.

a. From the Right ascensions:

$$\begin{array}{llllll}
0.22202\ \Delta M & +\ 9.21681_n\ \Delta i & +\ 9.64568_n\ \frac{\Delta\Omega}{10} & = 0.79873_n \\
0.25966\ \ \ ,, & +\ 9.03853_n\ \ ,, & +\ 9.83118_n\ \ ,, & = 0.71776_n \\
0.28811\ \ \ ,, & +\ 9.03023_n\ \ ,, & +\ 9.88800_n\ \ ,, & = 0.90136_n
\end{array}$$

b. From the Declinations:

$$\begin{array}{llllll}
9.42488\ \Delta M & +\ 0.00000\ \ \Delta i & +\ 0.10037_n\ \frac{\Delta\Omega}{10} & = 1.13386 \\
8.59106\ \ \ ,, & +\ 0.07737\ \ ,, & +\ 9.91908_n\ \ ,, & = 1.17898 \\
8.32222_n\ \ ,, & +\ 0.10992\ \ ,, & +\ 9.74819_n\ \ ,, & = 1.08099
\end{array}$$

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:

$$\begin{array}{llllll}
+\ 9.9278\ \ \Delta M & -\ 0.39596\ \Delta i & -\ 3.8260\ \frac{\Delta\Omega}{10} & = -\ 31.495 \\
-\ 0.39596\ \ \ ,, & +\ 4.1375\ \ \ ,, & -\ 2.7434\ \ \ ,, & = +\ 49.637 \\
-\ 3.8260\ \ \ ,, & -\ 2.7434\ \ \ ,, & +\ 3.8423\ \ \ ,, & = -\ 23.951
\end{array}$$

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:

$$\begin{array}{ll}
\Delta M & = -\ \ 2''\,7042 \\
\Delta i & = +\ 11.74
\end{array}$$

and the remaining errors:

$$\begin{array}{llll}
1. & \Delta\alpha = +\ 0^s014 & \Delta\delta = +\ 2''59 \\
2. & = +\ 0.097 & \ +\ 1.18 \\
3. & = -\ 0.151 & \ -\ 3.13
\end{array}$$

2. *Solution for* $\Delta i = 0$.

In this case we find:

$$\Delta M = -\ 9''0461$$
$$\Delta ☊ = -\ 2'32''41$$

and for the remaining errors:

	$\Delta\alpha$	$\Delta\delta$
1.	$+\ 0^s185$	$-\ 3''18$
2.	$+\ 0.089$	$+\ 2.80$
3.	$-\ 0.226$	$+\ 3.32$

3. *Solution with* 3 *unknown quantities:*

The results are:

$$\Delta M = -\ 5''3045$$
$$\Delta i = +\ 7.32$$
$$\Delta ☊ = -\ 1'\ 2.90$$

and according to the equations of condition there remain the following differences Obs.—Comp.

	$\Delta\alpha$	$\Delta\delta$
1.	$+\ 0^s088$	$-\ 0''23$
2.	$+\ 0.095$	$+\ 1.34$
3	$-\ 0.181$	$-\ 1.01$

As we see the solution with $\Delta ☊ = 0$ 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.

$$M_0 = 1266456''838$$
$$= 351°47'36''838$$
$$\mu = 517''447665$$
$$log\ a = 0.5574268$$
$$T = 1906 \text{ March } 14.09401$$
$$\varphi = 24°20'25''55$$
$$e = 0.4121574$$
$$\left.\begin{array}{l} i = 20°49'\ 0''62 \\ \pi = 346\ \ 2\ 31.63 \\ ☊ = 331\ 44\ 37.85 \end{array}\right\} 1906.0$$

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

$$n = 3(rst + 1) - 2(r + s + t) - (\alpha' r + \beta' s + \gamma' t) - \delta(r + s + t).$$

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 $\varkappa$ fixed points of intersection of C_r and C_s, then A_{rst} diminishes the order of L by $\varepsilon r + \zeta s + \varkappa t$; this holds for a point A_{st} too, but then we must regard ζ and $\varkappa$ 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:

$$\begin{aligned}(2r+2s-3)(2r+2t-3) - (4r^2 - 6r + 3 - \beta' - \gamma' - \delta) - \\ - (2\alpha' + 3\beta' + 3\gamma' + 9\delta) = \\ = 4(st + tr + rs) - 6(r+s+t) + 6 - 2(\alpha' + \beta' + \gamma' + 4\delta).\end{aligned}$$

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	— 4,94	— 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).

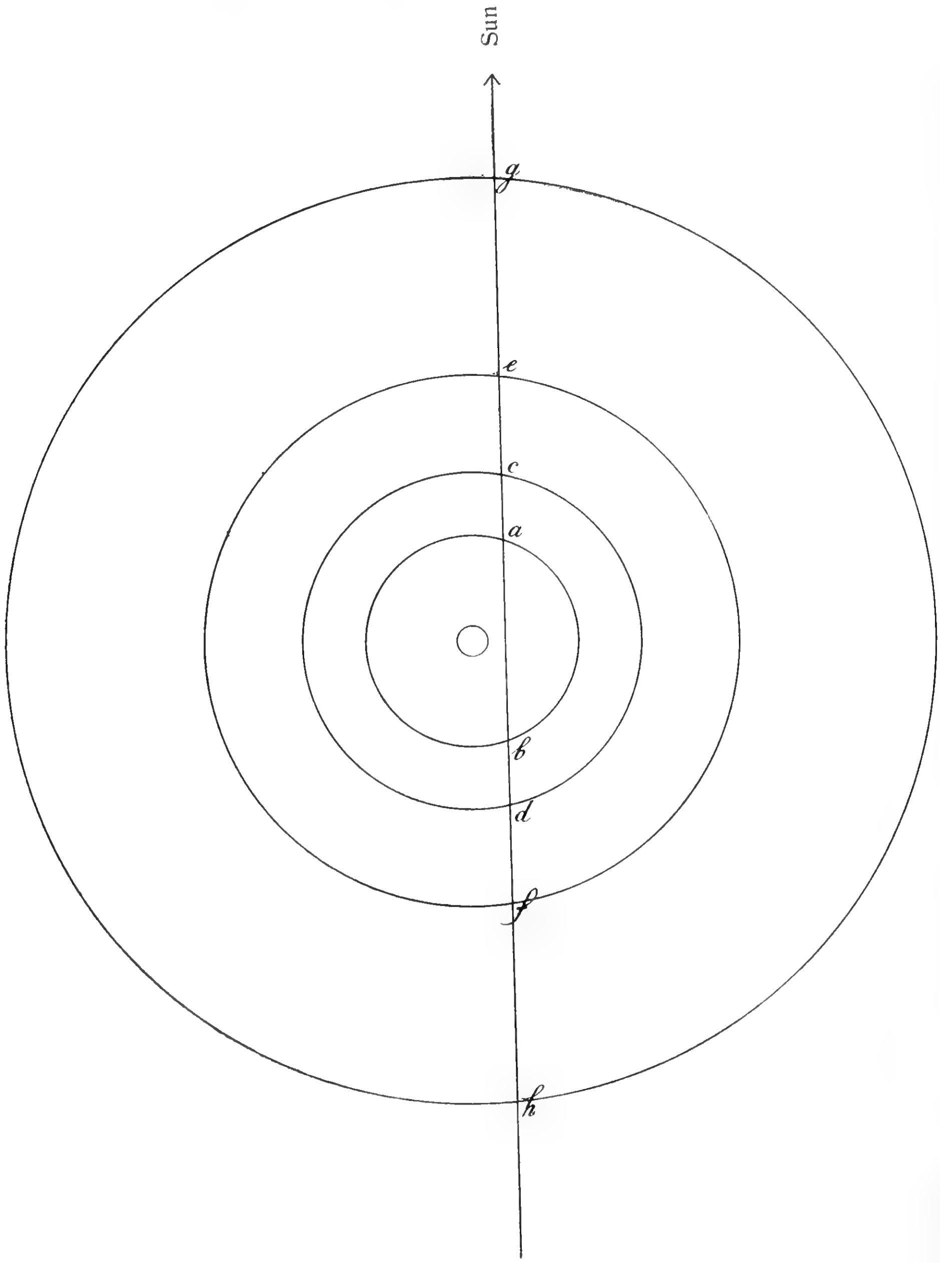
From occultations to eclipses there is but one step.

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^{h}37^m pour observer l'immersion du premier satellite, qui a eu lieu à 11^{h}42^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^{h}52^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^{h}56^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^{h}58^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^{m}40^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 $11^{h}47^{m}$ et le premier contact vers $11^{h}37^{m}$. Le premier satellite pénétra dans le disque de la planète à $11^{h}42^{m}$, 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 $23^{u}45^{m}$ civil time Paris = $11^{u}36^{m}$ 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 $11^{u}31^{m}$. 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 $11^{h}49^{m}$ M. T. Greenwich; Mr. COMAS already saw an oblong shadow at $11^{h}43^{m}20^{s}$ 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

Irradiation = 0″,264 ± 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 reappearance¹). 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^{m}45^{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	± 25^s	± 20^s	± 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 ± 2^s,6
similarly ,, II — 3 ,8 ,, ,, ,, ,, ,, ± 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.	$1^h 36^m 16^s$	M. T. Gr., R.	$2^h 8^m 17^s$,	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 $+ 23^m 30^s$, 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

$$1^h 44^m 14^s - 39^m 57^s,5 = 1^h 14^m 16^s,5,$$

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 $= 0°,2504 = 15' 2''4$, 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 Eclipsed satellite	 Eclipsing satellite	$x=x'$	Eclipsed satellite y	Eclipsing satellite y'	$y-y'$	Visible at
1	1 April 4^{h} 8^{m}	I$_{f}$	II$_{n}$	+5^{r}70	—0^{r}30	—0^{r}25^{5}	—0^{r}04^{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	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	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	I$_{e.e.}$	IV$_{n}$	+5, 99	—0, 32	—0, 38	+0,06	Wi., We., Lick, Fl,
19	12 » 23 33	III$_{f}$	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	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	I$_{e.e.}$	II$_{n}$	+5, 97	—0, 32	—0, 26	—0,06	Perth, To., Wi., We.

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					
28	19 April 5^{h}15^m	IV$_f$	III$_{w.e.}$	-15^r28	$+0^r80$	$+0^r85$	-0^r05	Kasan, Taschk., Madras.
29	19 » 22 57	IV$_f$	II$_n$	$-$ 8,69	$+$ 0,48	$+$ 0,43	$+$ 0,05	HK., Perth, Tokio, Wi., We.
30	20 » 3 14	III$_f$	II$_n$ $_{w.e.}$	$-$ 9,54	$+$ 0,55	$+$ 0,45	$+$ 0,10	Taschk., Madras, HK., Perth, To.
31	21 » 1 45	III$_f$	I$_n$	$+$ 2,27	$-$ 0,12	$-$ 0,13	$+$ 0,01	Madras, HK., P., Tokio.
32	21 » 1 46	IV$_f$	I$_n$	$+$ 2,26	$-$ 0,05	$-$ 0,12	$+$ 0,07	Madras, HK., P., Tokio.
33	21 » 1 52	IV$_f$	III$_f$	$+$ 2,33	$-$ 0,05	$-$ 0,12	$+$ 0,07	Madras, HK., P., Tokio.
34	21 » 3 23	II$_f$	I$_n$	$+$ 0,845	$-$0,088	$-$ 0,044	$-$ 0,044	Taschk., Madr., HK., P., Tokio.
35	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.
36	22 » 9 41	IV$_f$	III$_{(o.e.)}$	$+$ 14,84	$-$ 0,66	$-$ 0,83	$+$ 0,17	Grw., Pulk, Kasan, La Pl., Rio.
37	22 » 11 27	I$_{(e.e.)}$	II$_n$	$+$ 6,01	$-$ 0,32	$-$ 0,26	$-$ 0,06	Grw., Pulk., (Kasan), La Pl., Rio.
38	24 » 2 41	I$_f$	III$_n$	$+$ 5,02	$-$ 0,255	$-$ 0,28	$+$ 0,025	Taschk., Madr., HK., P., To.
39	26 » 0 41	I$_{e.e.}$	II$_n$	$+$ 6,03	$-$ 0,33	$-$ 0,25	$-$ 0,08	HK., P., To., Wi.
40	27 » 7 5	III$_f$	II$_f$	$-$ 9,62	$+$ 0,54	$+$ 0,45	$+$ 0,09	Bresl., Pulk., Kasan, Taschk.
41	28 » 4 28^5	I$_f$	III$_n$	$+$ 1,57	$-$ 0,08	$-$ 0,09	$+$ 0,01	Kasan, Taschk., Madr., HK.
42	28 » 5 36	II$_f$	I$_n$	$+$ 0,58	$-$ 0,03	$-$ 0,065	$+$ 0,035	Kasan, Taschk., Madras.
43	28 » 13 29	IV$_f$	III$_n$	$+$ 6,41	$-$ 0,36	$-$ 0,36	0,00	Grw., Tac., AA., Harv., La Pl., Rio.
43*	28 » 16 18	II	III	II $+$ 7,31 III $+$ 7,80	$-$ 0,38	$-$ 0,49	$+$ 0,06	

$x-x'$ diminishes gradually in absolute value, reaches its minimum 0,49 at the time assigned and then increases again. So there is no eclipse.

No.	Mean time at Greenwich	Eclipsed satellite	Eclipsing satellite	$x=x'$	Eclipsed satellite y	Eclipsing satellite y'	$y-y'$	Visible at
44	29 » 3 45	I$_f$	IV$_n$	$+$ 0,27	$-$ 0,02	$-$ 0,08	$+$ 0,08	Taschk., Madr., HK.
45	29 » 13 57	I$_{e.e.}$	II$_n$	$+$ 6,05	$-$ 0,33	$-$ 0,26	$-$ 0,07	Tac., AA., Harv., La Pl., Rio.
46	1 May 17 5	II$_f$	III$_n$	$-$ 0,74	$-$ 0,01	$-$ 0,62	$+$ 0,61	Lick, Fl., Tac., AA., Harv., La Pl.
47	1 » 18 43	II$_f$	I$_n$	$+$ 0,44	$-$ 0,07	$-$ 0,02	$-$ 0,05	Lick, Fl., Tac., AA.
48	3 » 3 16	I$_{e.e.}$	II$_n$	$+$ 6,06	$-$ 0,32^5	$-$ 0,24	$-$ 0,08^5	Taschk., Madr., HK., P., Tokio.
49	4 » 11 7	III$_f$	II$_{w.e.}$	$-$ 9,61	$+$ 0,54	$+$ 0,45	$+$ 0,09	Grw., Pulkowa.
50	5 » 7 48	II$_f$	I$_n$	$+$ 0,31	$-$ 0,07	$-$ 0,02	$-$ 0,05	Grw., Pulk., Kasan, Taschk.
51	5 » 8 17	III$_f$	I$_n$	$-$ 0,10	$-$ 0,09	$-$ 0,01	$-$ 0,08	Grw., Pulk., Kasan, (Taschk.).
52	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.	$+6''64+6''85$	$-$ 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.

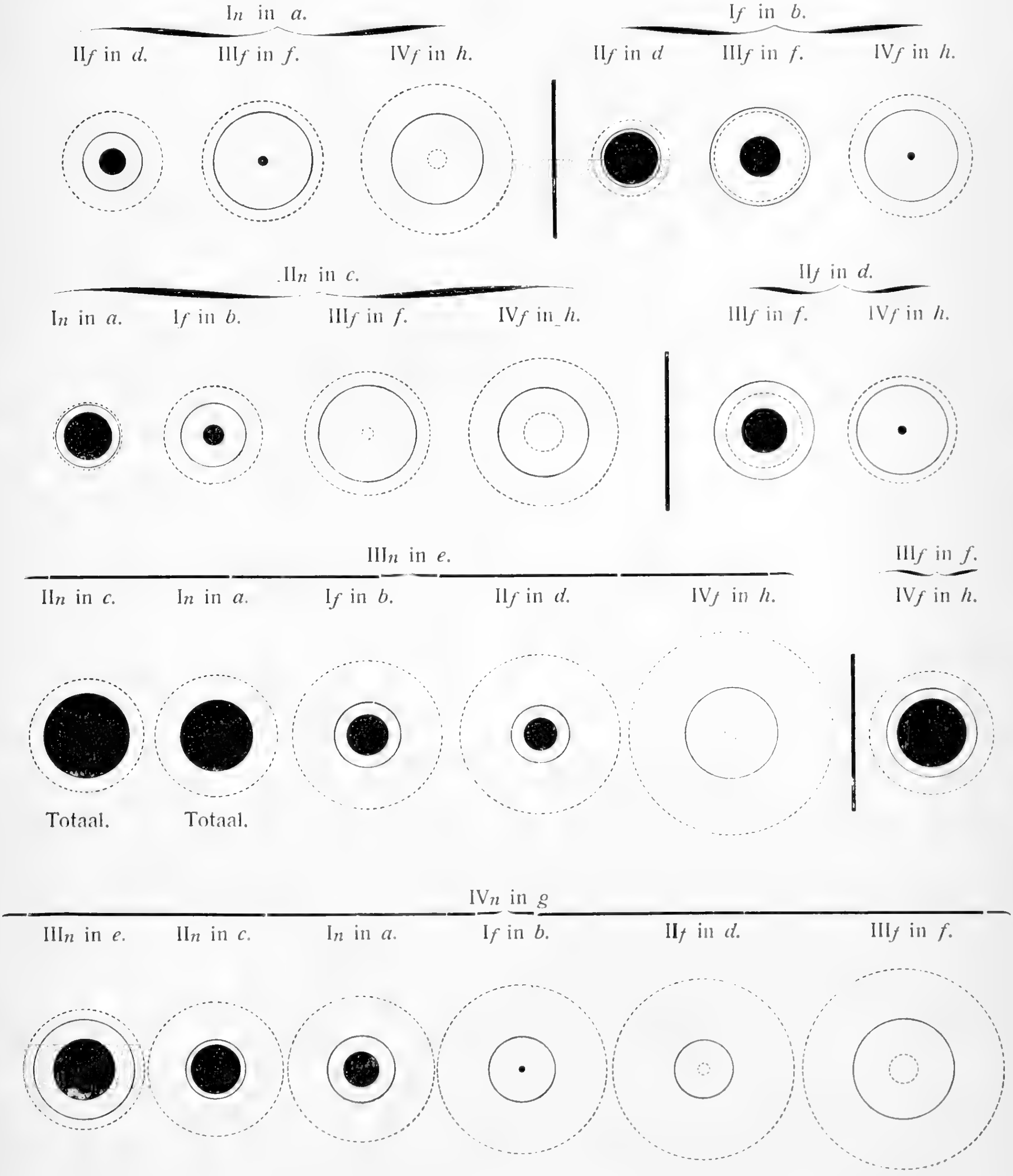
No.	Mean time at Greenwich	n = near f = far		$x = x'$	Eclipsed satellite y	Eclipsing satellite y'	$y-y'$	Visible at
		Eclipsed satellite	Eclipsing satellite					
53	6 » 16^{h}38^m	$I_{e.e.}$	II_n	+ 6^{r}03	— 0^{r}215	— 0^{r}24	+ 0^{r}02^5	Lick., Fl., Tac., AA., Harvard.
54	7 » 6 27	IV_n	I_n	— 3,[illegible]7	+ 0,20	+ 0,18	+ 0,02	Bresl. Pulk., Kasan, Taschk., Madr.
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., Madr.
57	8 » 20 54	II_f	I_n	+ 0,18	— 0,06	— 0,00	— 0,06	Wi., Wellington.
58	8 » 23 25	I_n	HI_n	— 2,04	+ 0,12	+ 0,13	— 0,01	Perth, Tokio, Windsor.
59	9 » 5 29	$I_{w.e.}$	III_n	— 5,36	+ 0,32	+ 0,34	— 0,02	Kasan, Taschk., Madras.
60	10 » 6 0	I_n (e.e.)	II_n	+ 5,99	— 0 32	— 0,38	+ 0,06	Kasan, Taschk., Madras.
61	10 » 16 41	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	$II_{w.e.}$	— 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 (e.e.)	IV_n	+ 15 17	— 0,87	— 0,75	— 0 12	Grw., Pulk., Rio.
71	14 » 13 46	$I_{(w.e.)}$	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 (w.e.)	IV_n	— 14,82	+ 0,80	+ 0,70	+ 0,10	Grw., Pulk., La Pl., Rio.
78	17 » 16 9	I_n	II_n	+ 1,22	— 0,08^5	— 0,02	— 0,06^5	Lick, Fl., Tac., AA., Harvard.
79	18 » 3 12	$I_{(w.e.)}$	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.

Plate II.

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″ heliocentric.



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 $v=0$.

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).

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

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